Abstract: Pressure is an important thermodynamic parameter, allowing the increase of matter density by reducing interatomic distances that result in a change of interatomic interactions. In this context, the long range in which pressure can be changed (over six orders of magnitude with respect to room pressure) may induce structural changes at a much larger extent than those found by changing temperature or chemical composition. In this article, we review the pressure-induced phase transitions of most sesquioxides, i.e., $A_2O_3$ compounds. Sesquioxides constitute a big subfamily of $ABO_3$ compounds, due to their large diversity of chemical compositions. They are very important for Earth and Materials Sciences, thanks to their presence in our planet’s crust and mantle, and their wide variety of technological applications. Recent discoveries, hot spots, controversial questions, and future directions of research are highlighted.

Keywords: sesquioxides; high pressure; phase transitions

1. Introduction

The family of sesquioxides (SOs), i.e., compounds with $A_2O_3$ stoichiometry, is very important from an applied point of view, since SOs play a vital role in the processing of ceramics as additives, grain growth inhibitors and phase stabilizers. They also have potential applications in nuclear engineering and as hosts for optical materials for rare-earth (RE) phosphors. Besides, SOs with corundum-like structure, like corundum ($\alpha$-$Al_2O_3$), hematite ($\alpha$-$Fe_2O_3$) and eskolaite ($\alpha$-$Cr_2O_3$), are relevant to Earth and planetology Sciences, because they are minerals present in the Earth’s crust or in meteorites. Therefore, knowledge and understanding of phase transitions (PTs) occurring at high pressure (HP) in SOs is very important for Physics, Chemistry and Earth and Materials Sciences.

SOs are mainly formed by materials featuring an $A$ cation of valence 3+, so that the two $A$ cations compensate the total negative valence (6−) of three O atoms acting with valence 2−. Among the cations featuring 3+ valence, we find all group-13 and group-15 elements, some transition metal (TM) elements and all RE elements. Additionally, we can also find SOs where cations show an average 3+ valence. In this context, SOs with cations showing both 2+ and 4+ valences (both valences present in the $A_2O_3$ compound), are named mixed-valence (MV) SOs. The different compositions of these compounds provide a very rich environment ranging from molecular or zero-dimensional (0D), one-dimensional (1D) and two-dimensional (2D) solids to the conventional (bulk) three-dimensional (3D) solids; all of them showing radically different properties and behaviors under compression.

After more than 50 years of exploration of pressure-induced PTs in SOs, we present in this work a review of the PTs of SOs at HP, including those occurring at high temperatures (HTs), at low
temperatures like room temperature (RT), and even at room pressure (RP). We have structured the present paper in five main sections that are devoted to RE-SOs, group-13-SOs, group-15-SOs, TM-SOs, and MV-SOs.

Finally, before attempting to present our results, we must comment that several reviews of the PTs in SOs at HP have been already published. We can cite the review on oxides of Liu and Basset in 1986 [1], of Adachi and Imanaka in 1998 [2], of Smyth et al. in 2000 [3], of Zinkevich in 2007 [4] and of Manjón and Errandonea in 2009 [5]. The present review goes beyond previous studies of SOs by expanding the number of families studied, by discussing the most recent results published in the last decade, and by suggesting pressure-based studies still to be performed.

2. High-Pressure Phase Transitions in Sesquioxides

2.1. Rare-Earth Sesquioxides

RE-SOs are highly interesting and versatile for different types of applications, since the atomic radius can be finely tuned along the lanthanide family, thus enabling a wide range of technological applications, including light emitters (lasers and improved phosphors), catalysts, and high-dielectric constant (high-k) gates.

RE-SOs, and in particular lanthanide SOs (Ln2O3, Ln = La to Lu, including Y and Sc), usually crystallize at room conditions in either the A-, B-, or C-type structures, depending on the RE atomic size. Large cations from La to Nd usually crystallize in the trigonal A-type structure (s.g. $P\bar{3}m1$), medium-size cations from Sm to Gd tend to show a monoclinic B-type structure (s.g. $C2/m$), and small cations from Tb to Lu, including Sc and Y, tend to adopt a cubic C-type structure (s.g. $la\bar{5}$). At HTs, two additional phases, hexagonal H (s.g. $P6_3/mmc$) and cubic X (s.g. $Im\bar{3}m$) structures, have also been found in Ln2O3 [6]. Zinkevich has reviewed temperature-induced PTs in RE-SOs and found that a $C\rightarrow B\rightarrow A$ sequence of PTs usually occurs upon an increase in temperature [4]. Since the density and cation coordination of the A-, B- and C-type structures increase in the sequence C-B-A, C→B, B→A, and even direct C→A transitions are expected on increasing pressure (upstroke), while inverse PTs are expected on decreasing pressure (downstroke) [7,8]. Curiously, it has been found that the cationic distances in the three structures of the RE-SOs at room conditions are similar to those in the bcc, fcc and hcp structures of the RE metals, thus suggesting that a relationship must exist between them [9,10].

The effect of HP on Ln2O3 has been extensively studied by many research groups, mainly by X-ray diffraction (XRD), Raman scattering (RS) and photoluminescence measurements. The HP behavior of C-type compounds has been studied in Lu2O3 [11–14], Yb2O3 [15–18], Tm2O3 [19,20], Er2O3 [11,21,22], Ho2O3 [23–26], Dy2O3 [27,28], Gd2O3 [11,29–36], Eu2O3 [11,37–43], Sm2O3 [11,32,44,45], Sc2O3 [46–48], Y2O3 [11,32,49–60], and recently on Tb2O3 [61]. Examples of pressure-driven C→B, B→A, direct C→A, and even C→A+B transitions have been shown to occur in a number of RE-SOs. As example, Lu2O3 was found to show either a C→B PT around 12 GPa without B→A PT up to 47 GPa [12,13], or a C→A+B PT above 25 GPa, with a recovery of a single B phase on downstroke from 47 GPa [14]. Similarly, Yb2O3 was found to exhibit a C→B PT above 13 GPa, and no further PT was found up to 20 GPa [15], but an A phase was found above 19.6 GPa that transforms into the B phase below 12 GPa [16]. The A phase in coexistence with the B phase was confirmed by RS measurements up to 45 GPa [17]. The C→B→A sequence of PTs was also found in Y2O3, the most studied RE- SO at HP, around 12 and 19 GPa [49], and has been confirmed in many studies [60]. In this context, it must be stressed that the pressure-induced PT sequence in Y2O3 has been shown to be affected by the nature of the sample, since different sequences of PTs have been observed in nanocrystals [33]. It must be stressed that direct C→A PT, with A→B PT on downstroke from 44 GPa, has been observed in Sm2O3 [44]. This sequence of PTs has also been observed in Gd2O3 [31]. Other PTs in RE-SOs have been found at HP and HT. In particular, an orthorhombic Gd2S3-type structure (s.g. $Pnma$) has been found in C-type Y2O3 above 8 GPa [57].
The HP behavior of B-type compounds has been also studied in Y$_2$O$_3$ [62], Eu$_2$O$_3$ [63], and Sm$_2$O$_3$ [64,65]. A reversible pressure-induced B→A PT has been observed in all B-type compounds. Additionally, the Gd$_3$S$_3$-type structure has been found in B-type Sc$_2$O$_3$ above 19 GPa upon laser heating [47]. Table 1 summarizes the experimental PT pressures observed in C- and B-type RE-SOs.

Table 1. Experimental data of the phase transition pressures (in GPa) for Ln$_2$O$_3$ and related sesquioxides having a C- or B-type phase at room conditions. The measurement technique (Tech.) and the pressure-transmitting medium (PTM) are also provided. Comp. stands for compound, MEW stands for the 16:3:1 mixture of methanol:ethanol:water and Polyethy. stands for polyethylene glycol.

| Comp. | $P_{C→A}$ | $P_{C→B}$ | $P_{B→A}$ | Tech. | PTM | Reference |
|-------|-----------|-----------|-----------|-------|-----|-----------|
| Sc$_2$O$_3$ | 36 | 25–28 | | XRD | MEW | [46] |
| Lu$_2$O$_3$ | 14 | 12.7–18.2 | 17.0–21.4 | XRD | Neon | [48] |
| Yb$_2$O$_3$ | 13 | 14 | 11.9 | XRD | Silicon Oil | [15] |
| | 30–47 | | | XRD | ME | [14,16] |
| | 17.0 | | | XRD | N$_2$ | [11] |
| | 20.6 | | | RS | ME | [18] |
| Tm$_2$O$_3$ | 7 | 12 | | XRD | MEW | [19] |
| Er$_2$O$_3$ | 9.9–16.3 | | | XRD | Silicon Oil | [66] |
| | 14 | | | XRD | N$_2$ | [11] |
| | 17.8–20.0 | 13.6 | 17.8–23.5 | XRD | He | [22] |
| | 6.6–12.7 | 22.5–42.0 | | XRD | Silicon Oil | |
| Y$_2$O$_3$ | 13.0 | 15.0–25.6 | 14.3–17.5 | | | [57] |
| | 17.0 | 23.5–44.0 | | XRD | Neon | [62] |
| | 13 | 24.5 | | | No PTM | [54] |
| Ho$_2$O$_3$ | 8.9–16.3 | 14.8–26.4 | | XRD | Silicon Oil | [24] |
| | 9.5 | | | XRD | MEW | [19] |
| | 9.5–16.0 | | | XRD | MEW | [23] |
| | 8.8 | | | XRD | MEW | [20] |
| Dy$_2$O$_3$ | 7.7–18.8 | 10.9–26.6 | | XRD | Silicon Oil | [28] |
| Tb$_2$O$_3$ | 7 | 12 | | XRD | MEW | [61] |
| Gd$_2$O$_3$ | 7.0–15.0 | 6.8 | | XRD | MEW | [31] |
| | 8.9–14.8 | 2.5 | 8.9 | XRD | Ar | [33] |
| | 7.0 | | | XRD | N$_2$, Ar, He | [11] |
| | 8.6–12.5 | 5.1 | | XRD | Silicon Oil | [34] |
| | 12.0 | | | XRD | MEW | [19] |
| Eu$_2$O$_3$ | 4.7 | | | XRD | Silicon Oil | [63] |
| | 5.0–13.1 | | | XRD | Silicon Oil | [40] |
| | 6.0 | | | XRD | N$_2$ | [11] |
| | 5.7–12.9 | | | XRD | MEW | [41,42] |
| Sm$_2$O$_3$ | 3.2–3.9 | | | XRD | Polyethy. | [64] |
| | 7.5–12.5 | 4.7 | | XRD | Silicon Oil | [44] |
| | 4.0 | | | XRD | N$_2$, Ar | [11] |
| | 4.2 | | | XRD | Silicon Oil | [45] |

The HP behavior of A-type compounds has been studied in Nd$_2$O$_3$ [67,68], Ce$_2$O$_3$ [69], and La$_2$O$_3$ [11]. A-type Nd$_2$O$_3$ has been observed to suffer a reversible PT above 27 GPa towards a monoclinic s.g. $P2_1/m$ phase [67]. However, other work has suggested a 1st-order isostructural PT
above 10 GPa [68]. This behavior is in contrast with that of Ce₂O₃, which seems to be stable in the A-type phase up to 70 GPa. Curiously, A-type Ce₂O₃ shows anomalies in the compressibility of the lattice parameters around 20 GPa, which could be related to an isostructural PT similar to that of Nd₂O₃. Finally, A-type La₂O₃ seems not to be stable above 4 GPa, following a PT to a hexagonal superlattice and eventually to a distorted monoclinic structure with a group–subgroup relationship with the hexagonal one [11].

It must be mentioned that RE-SOs and their pressure-induced PTs have also been investigated theoretically, and the simulations of the bandgap, volume, bulk modulus and its pressure derivative for the C, B and A phases, as well as their PT pressures, have been reported and found in rather good agreement with experiment [70–83]. Theoretical studies have found that the C→A and C→B PTs result in a decrease in the unit cell volume per formula unit at the transition pressure of the order of 10% ± 2%, in good agreement with experiments [81]. On the other hand, the B→A PT results in a decrease in the unit cell volume per formula unit at the transition pressure of the order of less than 2%, in good agreement with experiments [76]. Figures 1–3 show a comparison of experimental data (from Table 1) and theoretical data for the C→A, C→B and B→A PT pressures in bulk RE-SOs as a function of the atomic number of the lanthanide, Z_Ln, and of the ionic radius of the RE cation. In general, a good agreement between theoretical and experimental data can be found for all PTs. As regards the C→A PT, the pressure of the transition increases along the lanthanide series with the increase in atomic number, i.e., with the decrease in the ionic radius. It must be noted that no work has reported the C→A PT for Sc₂O₃, and that the reported C→A PT in materials with a small ionic radius, like Lu₂O₃ and Yb₂O₃, are doubtful. Regarding the C→B PT, the pressure of the transition also increases along the lanthanide series with the increase in atomic number or the decrease in the ionic radius. Unfortunately, no theoretical data exist for the C→B PT along the whole RE-SOs series; consequently, theoretical data for the C→A PTs are plotted for comparison with experimental data of the C→B PTs. It must be noted that the C→B PT is not observed in Sm₂O₃ and Eu₂O₃, since these two SOs undergo a direct C→A PT. Finally, as regards the B→A PT, the pressure of the transition once again increases along the lanthanide series with the increase in atomic number or the decrease in the ionic radius. As observed, no experimental data for the B→A PT has been reported in Sc₂O₃, Lu₂O₃ and Tm₂O₃. This will require new experiments up to 40 GPa in Lu₂O₃ and Tm₂O₃ and above 80 GPa in Sc₂O₃.

![Figure 1](image1.png)

**Figure 1.** Experimental (solid symbols) and theoretical (empty symbols) data for the C→A phase transition pressures in Ln₂O₃ and related sesquioxides as a function of (a) the atomic number, Z_Ln, and (b) the ionic radius. Experimental data are from Table 1, while theoretical data are from reference [81]. Ionic radii of Shannon for cation 6-fold coordination were considered.
In summary, there are many HP studies in cubic C-type RE-SOs that allow us to conclude that this structure undergoes a pressure-induced irreversible 1st-order PT either to a hexagonal A-type structure or to an intermediate monoclinic B-type structure. It is also observed that the A-type structure of RE-SOs usually reverts to the B-type structure on decreasing pressure, but the B-type structure remains metastable at room conditions and does not revert to the C-type structure unless it is conveniently heated. The irreversibility of the C→A and C→B PTs means that there is a considerable kinetic energy barrier between the C-type and the A- and B-type structures, due to the reconstructive nature of these PTs. On the other hand, the reversibility of the B→A PT is consequence of the weak 1st-order nature of this PT, as expected, because A- and B-type structures obey a group-subgroup relationship. In this context, HP studies of B-type RE-SOs show a pressure-induced reversible weak 1st-order PT to the A-type structure. It must be noted that some PTs for RE-SOs with a small RE ionic radius have yet to be reported. Besides, a pressure-induced PT to the Gd2S3 structure has been found from some C- and B-type RE-SOs at HT. Finally, we must comment that HP studies on trigonal A-type RE-SOs are quite scarce and do not allow us to conclude which is the typical HP phase of A-type RE-SOs. Consequently, more work has to be done in A-type RE-SOs, either studying C- or B-type RE-SOs at higher pressures or studying in better detail RE-SOs crystallizing in the A phase at room conditions, in order to understand the behavior of the trigonal structure and its pressure-induced PTs.
2.2. Group-13 Sesquioxides

Group-13-SOs are highly interesting compounds, due to their chemical and physical properties, which enable their application as catalyst, lasers and light emitting materials [84]. HP studies in group-13-SOs have been conducted on the five compounds. \( \text{Al}_2\text{O}_3 \), also known as alumina, is by far the most studied compound [85–99], followed by \( \text{In}_2\text{O}_3 \) [100–109], \( \text{Ga}_2\text{O}_3 \) [107,110–114], and \( \text{B}_2\text{O}_3 \) [115–121]. Finally, \( \text{Tl}_2\text{O}_3 \) has been the least studied compound [122].

The interest in alumina comes from its high stability, making it interesting for HP science applications, especially as windows in shockwave experiments [123]. However, its main application occurs when alumina is doped with a small amount of \( \text{Cr}^{3+} \). \( \text{Al}_2\text{O}_3: \text{Cr}^{3+} \), also known as ruby, presents fluorescence lines that are pressure-dependent and is used as a pressure standard in static HP experiments using anvil cells [124]. Corundum (\( \alpha\text{-Al}_2\text{O}_3 \)) is a mineral of alumina that is found in abundance in the earth mantle incorporated into enstatite (\( \text{MgSiO}_3 \)) [99]. Given that both minerals might adopt similar structures at ultra-HPs, their study is interesting from a geophysical point of view. In fact, the most stable phase of alumina at room conditions is the corundum structure (s.g. \( R3c \)), where coordination of all Al atoms is six-fold and of O atoms is four-fold [94]. The unit cell has two formula units, with O atoms forming a slightly distorted, hexagonal, close-packed structure [88,125]. The same structure is also found in other SO minerals, such as hematite (\( \text{Fe}_2\text{O}_3 \)), eskolaite (\( \text{Cr}_2\text{O}_3 \)), karelianite (\( \text{V}_2\text{O}_3 \)), and also \( \text{Tl}_2\text{O}_3 \) and \( \text{Ga}_2\text{O}_3 \) [125]. In this structure, cations occupy positions \((0, 0, z)\) and oxygens occupy positions \((x, 0, \frac{1}{2})\) and, if both \( z \) and \( x \) coordinates were \( 1/3 \), the corundum-type structure would have a perfect hexagonal close-packed packing [125].

\( \beta\text{-Al}_2\text{O}_3 \) is another very interesting polymorph of alumina from a technological application point of view. This material is a non-stoichiometric compound \((\text{Na}_2\text{O}_x \cdot \text{Al}_2\text{O}_3, 5 \leq x \leq 11)\) and not a simple variation of alumina [126,127]. Due to its layered crystalline structure, \( \beta\text{-Al}_2\text{O}_3 \) has a high ionic conductivity and has been studied for solid state battery applications [126,127]. We have not found any HP study of this material.

Theoretical studies of corundum predicted a pressure-induced PT to the Rh\( \text{O}_2\text{-II} \) structure (s.g. \( Pbcn \)) between 78 and 91 GPa [87,92,96,98] and a second PT to an orthorhombic perovskite (Pv) structure (s.g. \( Pbnnm \)) at 223 ± 15 GPa [87,92,96,98,128]. Other theoretical studies predicted that the post-perovskite (PPv) \( \text{CaIrO}_3 \)-type structure (s.g. \( Cmcm \)) would be more stable than the Pv structure at pressures higher than 150 GPa [85,99,129]. However, RT measurements performed up to 175 GPa under hydrostatic and non-hydrostatic conditions showed no PT [88,89]. The PT to the Rh\( \text{O}_2\text{-II} \) structure was only observed at HP (>95 GPa) and HT (>1200 K) [86,97] once the energy supplied by temperature allows the overcoming of the kinetic barrier of this 1st-order PT [86,89,96,97,128]. The Rh\( \text{O}_2\text{-II} \) structure is directly related to corundum structure; nevertheless, it presents a great distortion in the \( \text{AlO}_6 \) octahedron [97]. Lin et al. reported that the Rh\( \text{O}_2\text{-II} \)-type \( \text{Al}_2\text{O}_3 \) (\( \text{Cr}^{3+} \) doped) remains stable up to 130 GPa and 2000 K [97]. However, studies using shock waves have shown that a decrease by one order of magnitude in resistivity occurs at 130 GPa [123] that it is coincident with an increase in the density of \( \text{Al}_2\text{O}_3 \) [130], thus indicating a possible PT. This hypothesis was supported by the discovery of a PPv \( \text{CaIrO}_3 \)-type polymorph of \( \text{Fe}_2\text{O}_3 \) [131] and \( \text{MgSiO}_3 \) [132]. In 2005, Oganov and Ono were finally able to synthesize the PPv \( \text{CaIrO}_3 \)-type phase of \( \text{Al}_2\text{O}_3 \) at ~ 170 GPa and 2500 K [94,129]. They showed that the Rh\( \text{O}_2\text{-II} \) → \( \text{CaIrO}_3 \)-type PT is a 1st-order PT with ~ 5% of volume decrease [94,129]. The possibility of obtaining this structure at HP and HT was important to understand the physical properties of the elements present in the D\(^*\) layer of the earth mantle [129]. This layer is basically composed of a solid solution of \( \text{MgSiO}_3 \), \( \text{Fe}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3 \). Since, under the HP and HT conditions of the Earth mantle, all these materials are isostructural, their solubility may be facilitated [94].

When synthesized as nanoparticles smaller than 20 nm, alumina tends to crystallize into a cubic structure known as a phase \( \gamma \) (s.g. \( Fd\bar{3}m \)) [133]. HP experiments at room temperature observed an amorphization of \( \gamma\text{-Al}_2\text{O}_3 \) around 5 GPa [133]. On the other hand, it was also observed that the \( \gamma\text{-Al}_2\text{O}_3 \) \( \rightarrow R\bar{3}c \) PT, which occurs at RP near 1473 K, decreases to ~ 1023 K when \( \gamma\text{-Al}_2\text{O}_3 \) is pressurized at
1 GPa [134]. In addition, HP-HT experiments have revealed other phases of alumina, like polymorphs of RE-SOs B- and C-type, as well as polymorphs λ and μ [135,136]; however, no HP studies on these phases have been reported to our knowledge.

The search for new high hardness materials, such as Al2O3, has attracted the attention of many research groups for SOs, including indium oxide (In2O3) and gallium oxide (Ga2O3) [106]. In2O3 is a semiconductor with high potential for many transparent oxide applications, including touch and photovoltaic devices, thermoelectric and gas sensors [137]. At room conditions, In2O3 crystallizes in the cubic bixbyite structure (s.g. Iași), also known as the C-type RE-SO structure (c-In2O3) [106]. In this structure there are two types of In atoms (they are surrounded by oxygen in the octahedral and trigonal prismatic coordination) located at positions 8b and 24d and one type of O located at position 48c [138]. In the 1960s, a PT from c-In2O3 to a metastable corundum-like rhombohedral phase (rh-In2O3; s.g. R3c) was reported at HP and HT (6.5 GPa and 1000 °C) [106,139,140]. This PT was also observed through shockwave compression experiments between 15 and 25 GPa [141]. Some HP-XRD studies of both bulk and nanoparticle samples claimed that the c-In2O3 → rh-In2O3 PT occurs at RT when the sample is exposed to pressures between 12 and 25 GPa [103,104]. This result is controversial since other studies using HP-XRD and HP-RS measurements did not clearly observe this PT up to 30 GPa [100,101]. On the other hand, García-Domene et al. reported that bulk c-In2O3 actually undergoes a PT to an R2O3-II-type structure (o1-In2O3; s.g. Pbcn) orthorhombic phase at pressures above 31 GPa at RT [101]. This structure was also obtained at 7 GPa after laser heating at 1500 °C [106]. This result is consistent with the prediction of theoretical calculations that the Rh2O3-II-type phase is the most stable In2O3 structure between 8 GPa and 36 GPa [101]. On top of that, looking for a possible CaIrO3-type PPV phase in In2O3, Yusa et al. observed another PT from Rh2O3-II-type to α-Ga2O3-type structure (s.g. Pnma) above 40 GPa and 2000 K [107]. A reduction of 7%–8% in volume was observed, unlike the reduction of 2% expected for a Rh2O3-II-type → CaIrO3-type transition [107].

Releasing the pressure after obtaining the Rh2O3-II-type structure in In2O3, García-Domene et al. demonstrated that, at 12 GPa, o1-In2O3 undergoes a PT to a previously unknown phase [101]. The combination of experimental and theoretical results helped to conclude that, upon decreasing the pressure to 12.1 GPa, the In2O3 recrystallizes in a distorted bixbyite-like structure (o3-In2O3; s.g. Pbcn), isomorphic to Rh2O3-III [101,108]. Decreasing the pressure below 1 GPa, o3-In2O3 undergoes another PT to the metastable rh-In2O3 structure. The metastable rh-In2O3 phase at room conditions remains stable up to 15 GPa and above this pressure shows a reversible PT to o3-In2O3, which is stable up to 25 GPa [101]. The observation of the Pbcn phase took place only when decreasing pressure using original bulk c-In2O3 samples was related to kinetic barriers in the c-In2O3 → o3-In2O3 PT, that cannot be overcome at RT during upstroke [101]. Similar studies in c-In2O3 nanoparticles performed up to 44 GPa did not clearly show these PTs [100,104,105]. Qi et al. reported that, when compressing 6 nm c-In2O3 nanoparticles, an irreversible PT to the rh-In2O3 phase occurs between 20–25 GPa [104]. Nowadays, it is now possible to synthesize In2O3 nanoparticles at room conditions with the rh-In2O3 metastable phase at relatively low temperatures (250 to 500 °C) [142–144]. Sans et al. studied rh-In2O3 nanoparticles (10–30 nm) up to 30 GPa using XRD and RS measurements [109]. XRD measurements did not show any PT up to 30 GPa, but RS measurements showed peaks of the o3-In2O3 phase above 20 GPa [109]. One reason for this discrepancy was attributed to the sensitivity of RS measurements to local structural changes, which is responsible for the observation of PTs at lower pressures in RS compared to XRD measurements [109]. Another reason might be related to the use of less hydrostatic pressure-transmitting medium in RS (MEW) than in XRD (Ar) measurements [109].

Regarding Ga2O3, its most stable structure at room conditions is the monoclinic phase (s.g. C2/m), known as β-Ga2O3 [145,146]. However, depending on the pressure, temperature and atmosphere conditions, it is possible to find Ga2O3 in the α, β, γ, σ and ε phases [111,147]. Compared to Al2O3 and In2O3, HP studies on Ga2O3 are scarcer. In 1965, Remeika and Marezio reported the synthesis of α-Ga2O3 (s.g. R3c), which is isostructural to α-Al2O3, by pressurizing β-Ga2O3 to 4.4 GPa, after heating to 1000 °C and quenching to room conditions [147]. Lipinska-Kalita et al. reported that, upon
pressing nanoparticles (~15 nm) of β-Ga2O3 homogeneously dispersed in a host silicon oxide-based glass matrix, it is possible to observe a PT to α-Ga2O3 at 6 GPa [111]. In that study, the β-Ga2O3 → α-Ga2O3 PT is not completed up to 15 GPa and it is not clear whether the PT is induced by glass matrix densification or is an intrinsic behavior of the β-Ga2O3 nanoparticles [111]. This work led Machon et al. to study the behavior of β-Ga2O3 microparticles by XRD and RS measurements with different pressure-transmitting media [113]. They observed a PT to the α phase above 20 GPa, unlike what was observed in reference [111]. A highly disordered α-Ga2O3 was recovered at RP after a fast decompression from 25 GPa and a mixture of α and β phases were recovered when decompression was performed slowly [113]. The β-Ga2O3 → α-Ga2O3 PT can be considered to be of 1st-order and involves a change in O2+ ions packing from cubic to hexagonal, accompanied by a change in Ga3+ coordination from four to six [111,113,148].

The β-Ga2O3 → α-Ga2O3 PT was not clearly observed in an experiment performed up to 65 GPa without pressure-transmitting medium [106]. Instead, XRD measurements at 65 GPa showed only a diffraction pattern similar to a material with low crystallinity or amorphous. After laser heating (~2300 K), a recrystallization to an orthorhombic phase Rh2O3-II-type (s.g. Pbcm) was observed [106]. This phase remained stable up to 108 GPa and 2500 K. During decompression, the Rh2O3-II-type → α-Ga2O3 PT was observed between 32 and 21 GPa, being the α phase metastable at RP [106]. These results differ from other published by Lipinska-Kalite et al. up to 70 GPa with (N2) and without pressure-transmitting medium [110]. In that study, a β-Ga2O3 → α-Ga2O3 PT was clearly observed, which starts at 6.5–7.0 GPa (3 GPa) and completes at 40 GPa (30 GPa) when measured with (without) pressure-transmitting medium [110]. Through XRD measurements, Lipinska-Kalita et al. observed no evidence of pressure-induced amorphization or deterioration of the diffractogram up to 70 GPa [110]. The β-Ga2O3 → α-Ga2O3 PT was also observed at 16 GPa in shockwave experiments [149]. Wang et al. conducted HP studies on β-Ga2O3 nanoparticles (14 nm) at RT and found the PT to α-Ga2O3 above 13.6 GPa [114]. Above this pressure, the α phase remains stable up to 64.9 GPa and stays metastable upon returning to RP [114].

Boron sesquioxide (B2O3) is one of the most important oxides in applications involving vitreous systems. In glass form, B2O3 has a low melting point (750 K) and a structure similar to vitreous SiO2 and H2O [117]. When pressing the glassy material, it is possible to observe a structural rearrangement around 3 GPa that was considered a low- to high-density vitreous PT [118]. Furthermore, starting from the glassy material, it is possible to obtain B2O3 crystals at HP and HT. At room conditions, the most stable structure of B2O3 is a trigonal structure (s.g. P3121) known as B2O3-I, where B is in the center of triangles of O atoms [115–117,119,121]. Despite its stability at room conditions, working with this material is not simple due to its strong hygroscopic behavior, capable of decomposing the sample in a few minutes [121]. Above 3.5 GPa and 800 K, B2O3-I undergoes a PT to an orthorhombic structure, known as B2O3-II (s.g. Ccm21), composed of distorted BO4 tetrahedra [116,120]. The B2O3-I → B2O3-II transition leads to an increase of B and O coordination from 3 to 4, and from 2 to an intermediate between 2 and 3, respectively, and a volume change of ~27% [117,120,150].

The last group-13-SO is thalium oxide (Tl2O3). This material is very interesting from a technological point of view as it has potential for interesting applications such as solar cell electrode, optical communication and HT superconductors [151–154]. Its most stable phase at room conditions is c-Tl2O3, a bixbyite body-centered cubic phase isostructural to c-In2O3. A corundum-like structure (s.g. R3̅c) was also observed at HP (6.5 GPa) and HT (500–600 °C) [140]. So far, only one paper reports the properties of the c-Tl2O3 at HP, probably due to the toxicity of this material [122]. Theoretical calculations predict a c-Tl2O3 → Rh3O2-II-type (s.g. Pbcm) PT at 5.8 GPa and a second Rh2O3-II-type → α-Gd2S2-type (s.g. Pmna) PT at 24.2 GPa [122]. However, ADXRD measurements at RT, performed using MEW as pressure-transmitting medium, showed only an irreversible pressure-induced amorphization at 25.2 GPa, which was a consequence of kinetic barriers that cannot be overcome at RT [122]. In addition, theoretical calculations predicted a mechanical instability of c-Tl2O3 above 23.5 GPa [122]. Future work involving HP and HT is needed to better understand the behavior of Tl2O3 at HP.
To finish this section, we summarize in Table 2 the phase transition pressures observed in group-13-SOs.

Table 2. Experimental data of the phase transition pressures (in GPa) for group-13 sesquioxides. The letters A, B, C, D, E, F, G, H, and I refer to the structures $R\bar{3}c$, $Rh_2O_3$ – II-type, $CaIrO_3$-type, $Ia\bar{5}$, $\alpha$ – $Ga_2S_3$-type, $Pbca$, $C2/m$, $P3_121$, and $Cmm2_1$, respectively. Between parentheses are the transition temperatures (when necessary). SW stands for shockwave experiments and NP for nanoparticles.

| Structure | $P_{A\rightarrow B}$ | $P_{A\rightarrow C}$ | $P_{D\rightarrow A}$ | $P_{D\rightarrow B}$ | $P_{B\rightarrow E}$ | $P_{B\rightarrow F}$ | Reference |
|-----------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|-----------|
| $Al_2O_3$ | 95 (1200 K)          | 96 (>2000 K)         | 150 (>1500 K)        | 170 (2500 K)         | [86]                 | [97]                 |           |
| $In_2O_3$ | 6.5 (1273 K)         | 15–25 (SW)           | 31                   | 7 (>1700 K)          | [140]                | [141]                |           |
| $Gd_2O_3$ | 4.4 (1273 K)         | 20–29                | 16 (SW)              | 16.4–39.2 (NP)       | [147]                | [149]                | [113]     |
| $B_2O_3$  | 3.5 (800 K)          |                      |                      |                      | [116,120]            |                      |           |
| $Ti_2O_3$ | 6.5 (>720 K)         |                      |                      |                      | [140]                |                      |           |

2.3. Transition-Metal Sesquioxides

TM-SOs belong to a highly heterogeneous family of compounds, as their fundamental (electronic, magnetic) properties strongly depend on the number, and therefore on the spin state, of $d$ electrons in the $A^{3+}$ cation. TM-SOs include, among others, the ubiquitous ferric oxide ($Fe_2O_3$), the commonly-used green pigment $Cr_2O_3$, or the relatively rare $Ti_2O_3$ oxide, found in the famous Allende meteorite as the mineral tistarite [155]. Thus, each of these compounds has its own particularities and, regarding the HP structural properties, its specific behavior upon compression.

Among all the TMs, excluding the f-block lanthanide and actinide series and including group-3 and group-12 elements, in this section we will only consider $A_2O_3$ compounds with at least one $d$ electron. Thus, $Sc_2O_3$, $Y_2O_3$ and $La_2O_3$ are not included here, since they have been discussed together with the RE-SOs in Section 2.1. Among the rest of possible TM-SOs, only the following compounds have been found to be stable at room conditions: $Ti_2O_3$, $V_2O_3$, $Cr_2O_3$, $Mn_2O_3$, $Fe_2O_3$, $Co_2O_3$, $Ni_2O_3$, $Rh_2O_3$ and $Au_2O_3$. Other compounds, like $Hf_2O_3$ and $Zr_2O_3$, might be metastable at HP [156].

With the exception of $Mn_2O_3$, the most stable form of all TM-SOs at room conditions corresponds to the rhombohedral structure of the corundum. As can be seen in Figure 4a, the lattice parameters of the corundum-like structure adopted by most of TM-SOs are barely reduced by increasing the number of $d$ electrons in the $A^{3+}$ cation. This result simply reflects the slight reduction in the atomic radius of the cations with increasing atomic number. However, as can be seen in Figure 4b, the c/a ratio of these compounds displays a well-known anomaly around $Ti_2O_3$ and $V_2O_3$ that deserves further attention. In particular, $V_2O_3$ has highly remarkable properties and behaves, upon compression, in a highly
different fashion than other corundum-type TM-SOs [157]. In turn, Mn$_2$O$_3$ crystallizes in the so-called bixbyite structure (e.g. 206, $Ia\bar{3})$, which takes the name of the mineral form of Mn$_2$O$_3$. The absence of the corundum structure in Mn$_2$O$_3$ at room conditions has been attributed to the Jahn-Teller distortion associated with the $d^4$ Mn$^{3+}$ ion [158].

Most TM-SOs have also been found to exhibit other stable or metastable polymorphs at room conditions, as well as at HP. Next, we focus on the rich and varied HP behavior of the different phases of TM-SOs, with special emphasis on Fe$_2$O$_3$, Mn$_2$O$_3$ and V$_2$O$_3$.

Iron oxides are highly important materials in a large variety of disciplines, including materials science, geology, mineralogy, corrosion science, planetology and biomedicine. In the particular case of iron SO (iron (III) oxide or ferric oxide), there exist several polymorphs that are stable or metastable at room conditions: $\alpha$, $\beta$, $\gamma$, $\epsilon$ and $\zeta$. First, we will briefly describe these phases at room conditions and, afterwards, we will discuss their HP behavior.

The most common phase of Fe$_2$O$_3$ is the $\alpha$ phase, which has the corundum structure and is ubiquitously found in nature as the mineral hematite. $\alpha$-Fe$_2$O$_3$ is a wide-gap antiferromagnetic insulator, with a Morin transition around 250 K. It is weakly ferromagnetic from this temperature up to a Néel temperature around 950 K, above which it becomes paramagnetic. Besides temperature and doping, pressure is a highly convenient tool to modify the insulating/metallic state of this type of material. In particular, hematite can be considered as an archetypal Mott insulator [159] and is interesting from the point of view of metal-insulator PTs in highly correlated electron systems.

The mineral hematite is the main ore of iron and a very common phase in sedimentary rocks, where it occurs as a weathering or alteration product. It is, however, unlikely that Fe$_2$O$_3$ or any of its HP phases have much relevance in the Earth’s lower mantle, where Fe$^{3+}$ is mainly incorporated into other minerals, like bridgmanite or garnet, with the possible coexistence of reduced iron-rich metal (Fe$^0$) [160]. In contrast, it cannot be ruled out that Fe$_2$O$_3$ may be responsible for the presence of magnetic anomalies in the upper mantle arising from deep-subduction processes [161]. Thus, the HP behavior of hematite may still be highly relevant from a geophysical point of view, as it might play a key role in relation to the magnetic properties of recycled crust materials in subduction zones.

The $\gamma$ phase of Fe$_2$O$_3$ is also found in the Earth’s crust as the relatively common mineral maghemite, which is formed by weathering or low-temperature oxidation of magnetite and related spinel minerals. Maghemite, which is also a very common corrosion product, is metastable and transforms upon
heating into the \( \alpha \) phase. \( \gamma\text{-Fe}_2\text{O}_3 \) has the same cubic spinel ferrite structure (s.g. 227, \( Fd\bar{3}m \)) as magnetite (\( \text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4 \)), with 1/3 of Fe atoms tetrahedrally coordinated with oxygen (A sites), and 2/3 octahedrally coordinated with oxygen (B sites). Thus, maghemite can be considered as a \( \text{Fe}^{2+}-\text{deficient} \), with all A sites filled with \( \text{Fe}^{3+} \) and only 5/6 of the total available B sites filled with \( \text{Fe}^{3+} \); i.e., with 1/6 of vacant (V) B sites, so it can be noted as \( (\text{Fe}^{3+})_4(\text{Fe}^{3+}_{5/3}\text{V}_{1/3})\text{O}_4 \). \( \gamma\text{-Fe}_2\text{O}_3 \) exhibits soft ferromagnetism at RT, with a Curie temperature around 950 K [162]. Most remarkably, ultrafine particles of \( \gamma\text{-Fe}_2\text{O}_3 \) exhibit super-paramagnetism, which is related to the thermally induced random flip of the magnetization in ferromagnetic nanoparticles. This phase is being intensively investigated in order to construct an appropriate theoretical framework for this phenomenon, which might set a limit on the storage density of hard disk drives.

A rare orthorhombic polymorph of \( \text{Fe}_2\text{O}_3 \), named \( \epsilon\text{-Fe}_2\text{O}_3 \) (s.g. 33, \( Pna2_1 \)), has also been found to be stable at room conditions. This phase seems to exist only in nanosized form and was first reported back in 1934 [163]. A few years later, it was synthesized and characterized by Schrader et al. [164]. The crystal arrangement of \( \epsilon\text{-Fe}_2\text{O}_3 \) is considered as intermediate between the structures of the \( \alpha \) and \( \gamma \) phases, with three octahedral \( \text{FeO}_6 \) units (two of which are distorted) and a \( \text{FeO}_4 \) tetrahedral unit. It is worth noting that this phase has recently been found in nature as the Al-bearing nanomineral luogufengite, which is an oxidation product of Fe-rich basaltic glass at HT [165]. It has also been found in ancient black-glazed wares from Jianyang county, China, produced during the Song dynasty (960–1279 AD) [166]. Recent studies have also shown that this polymorph is a non-collinear ferrimagnet [167]. Owing to its remarkable magnetic properties, such as giant coercive field, ferromagnetic resonance and magnetoelastic coupling [168], this phase is highly promising to develop a broad range of novel applications. Besides, the giant coercive field of luogufengite might explain the observed high-remanent magnetization in some igneous and metamorphic rocks [169].

In contrast to \( \epsilon\text{-Fe}_2\text{O}_3 \), \( \beta\text{-Fe}_2\text{O}_3 \) and the recently discovered “\( \zeta\text{-Fe}_2\text{O}_3 \)” phase [170] have not been found to occur in nature so far. These two rare polymorphs are metastable phases that have been obtained by synthetic methods and which only exist in nanocrystalline form. The beta phase exhibits the bixbyite structure, with trivalent Fe ions occupying two non-equivalent octahedral sites. It exhibits paramagnetic behavior at room conditions, with a Neél temperature just above 100 K. Antiferromagnetic ordering is observed below this temperature. Upon heating, \( \beta\text{-Fe}_2\text{O}_3 \) undergoes a PT to either the \( \alpha \) or \( \gamma \) phases. In turn, “\( \zeta\text{-Fe}_2\text{O}_3 \)” displays a monoclinic structure (s.g. 15, \( I2/n \)) and was obtained by applying HP (>30 GPa) to \( \beta\text{-Fe}_2\text{O}_3 \) [169]. Surprisingly, this new phase (with a Neél temperature around 70 K) is metastable after releasing pressure, being able to withstand pressures up to ~70 GPa.

In spite of much effort to elucidate the structural, magnetic and electronic properties of \( \alpha\text{-Fe}_2\text{O}_3 \) (hematite) at HT and HP [159,170–176], the HP behavior of the most important phase of \( \text{Fe}_2\text{O}_3 \) is still under debate. Only recently was the complete T-P phase diagram of \( \alpha\text{-Fe}_2\text{O}_3 \) established [176]. According to that work, \( \alpha\text{-Fe}_2\text{O}_3 \) transforms at RT to a HP phase above ~50 GPa, with an ~8.4% volume discontinuity. It is worth noting that in this work the HP phase was called “\( \zeta \)-phase” and was indexed as triclinic \( (P\bar{T}) \) [175]. This phase is not equivalent to the monoclinic s.g. \( I2/a \) phase stable at room conditions, also named “\( \zeta\text{-Fe}_2\text{O}_3 \)”, which was produced by Tucek et al. [169]. It must be noted that the \( P\bar{T} \) phase was previously indexed as monoclinic (\( P2_1/n \)) in reference [175]. The fact that this HP phase is relabeled as “double perovskite” in reference [170] and treated as s.g. \( P2_1/n \) only adds confusion to the nomenclature of the different phases of such an important compound as \( \text{Fe}_2\text{O}_3 \).

As already mentioned, the single-crystal diffraction patterns of the \( P\bar{T} \) HP phase were initially indexed in a monoclinic unit cell [173], but were subsequently refined into a triclinic s.g. \( P\bar{T} \) structure [175]. However, previous works had assigned the HP phase (~50 GPa) of hematite to either a distorted corundum phase (\( \text{Rh}_2\text{O}_3\text{-II}-\text{type structure, s.g. } P\overline{6}cm \)) [159,170,172,177] or to a \( \text{Pv} \) structure (s.g. \( Pbmm \)) [129,178]. According to reference [175], the \( P\bar{T} \) structure of \( \text{Fe}_2\text{O}_3 \) is closer to a distorted (and not “double”), as in reference [176] \( \text{Pv} \) structure. However, a more recent study up to ~79 GPa has put into question the very existence of the distorted \( \text{Pv} \) phase [174], in agreement with
previous results [179]. The data and analysis of reference [159] indicate that the 1st-order PT around 50 GPa is accompanied by an insulator-to-metal transition with collapse of the magnetic properties. The structural PT would thus be very progressive [160,170], starting from the corundum-type structure and leading to a distorted Rh$_2$O$_3$-II-type structure. In contrast, Bykova et al. suggested that the Rh$_2$O$_3$-II-type structure only occurs below 50 GPa at HT and would be reconstructive, with a volume change of ~1.3% [173]. According to this work, the distorted Pv phase shows a PT at RT around ~67 GPa to a possibly metastable orthorhombic structure (s.g. Cmcm (s.g. Aba2)) [175]. In fact, the Aba2 to PPv PT was observed at HT (above 1600 K). After quenching the samples to RT, the PPv polymorph was found to be stable up to 100 GPa and down to 26 GPa; however, hematite was recovered below this pressure. In turn, the metastable Aba2 phase seems to be preserved at 78 GPa, up to 1550 K. This polymorph, also observed by Greenberg et al. [176] at RT, can be considered as a metastable HP phase at low temperature. It adopts a similar packing to the Rh$_2$O$_3$-II-type structure observed at low pressures, but, instead of octahedra, it consists of FeO$_3$ prisms. Recent results obtained by Sanson et al. are compatible with the existence of the Aba2 polymorph [174]. However, these authors seem to rule out not only the P2$_1$/n HP phase, but also the Pbam one.

Regarding the PPv structure, Ono et al. had previously reported a PT from hematite to the PPv structure above 30 GPa at HT [131]. Moreover, a new phase was found above 50 GPa to an unknown phase that was tentatively assigned to an orthorhombic or a monoclinic lattice. In relation to the magnetic and electronic properties of this phase, Shim et al. showed that the magnetic ordering of PPv-type Fe$_2$O$_3$ is recovered after laser heating at 73 GPa [179]. According to these authors, the appearance of the PPv phase gives rise to the transformation of Fe$^{3+}$ ions from a low-spin to a high-spin state, with Fe$_2$O$_3$ undergoing a semiconducting-to-metal PT. This effect might be relevant to understand the electromagnetic coupling between the Earth’s mantle and the core. Previous research had already investigated with Mössbauer spectroscopy the high-spin to low-spin PT in α-Fe$_2$O$_3$, at HP associated to the structural PT [180,181].

Indeed, one of the main interests of studying hematite at HP, besides its crystal structure and phase diagram, has to do with its electronic properties and the nature of the HP-PT [171]. What drives the HP-PT in hematite? Is it the crystal structure, or the electronic structure? Note that one could expect that electronic PTs, such as the insulator-metal Mott PT observed at 50 GPa [159] or the high-spin to low-spin PT, are isostructural. According to this argument, the PT observed in hematite at ~50 GPa, accompanied by a large volume change, should drive the change in electronic properties. Badro et al. reached this conclusion and indicated that the electronic PT is isostructural and occurs after the crystal structure PT [171]. However, Sanson et al. have recently reached the opposite conclusion, i.e., that the structural PT is driven by the electronic transition [174]. These authors analyzed the local structure and observed no FeO$_6$ octahedra distortion at HP, in disagreement with previous works [170]. A careful analysis recently performed by Greenberg et al. suggests that the pressure-induced insulator-to-metal PT in hematite arises from site-selective delocalization of electrons [176]. According to this study, such site-selective Mott transition ought to be characterized by delocalization (i.e., metallization) of Fe 3$d$ electrons on only half of the sites in the unit cell. This work suggests that the interplay between crystal structure and electronic correlations may yield a complex behavior that could be also relevant to understand the HP behavior of other TM-S Os.

With regard to the rest of Fe$_2$O$_3$ phases stable at room conditions (γ, β and ε), the amount of published works regarding their HP behavior is sizably lower in comparison to hematite. The phase diagram of γ-Fe$_2$O$_3$ (maghemite) is relatively simple, since this phase readily transforms to α-Fe$_2$O$_3$ around 35 GPa [182]. Therefore, much of the effort regarding this phase has been in relation to the comparison of the compression behavior between bulk and nanocrystalline samples (see reference [183] and references therein). Further details about polymorphic PTs of nanosized Fe$_2$O$_3$, including doping, temperature and HP, can be found in reference [184]. In the case of maghemite, Jiang et al. found that nanocrystalline γ-Fe$_2$O$_3$ transforms to hematite at ~27 GPa, below the PT pressure for bulk material [182]. As shown by Zhu et al., the γ-to-α PT might be initiated at the same pressure, around
16 GPa, both in bulk and nanocrystalline forms [183]. According to these authors, vacancies might play an important role in the structural PT. More recently, a combination of XRD and Mössbauer spectroscopy up to 30 GPa on vacancy-ordered maghemite has shown that the γ-to-α PT would be initiated at 13–16 GPa, giving rise to a particular texture in the transformed α-Fe₂O₃ material [185].

Finally, in relation to the Fe₂O₃ polymorphs, we must mention the recent HP study of ε-Fe₂O₃ by Sans et al. [186]. These authors found that this rare nanocrystalline phase, which is a promising magnetic material for a range of technological applications, is stable up to 27 GPa. Above this pressure, evidence for a PT, in which the tetrahedrally coordinated iron ions change towards quasi-octahedral coordination, was observed. Given that this phase has very high magnetic coercivity, it remains to be investigated whether its mineral form may play any relevant role in the magnetic remanence of mantle xenoliths, and in the magnetism of subducting slabs at depths corresponding to the mantle transition zone [161].

Manganese SO (Mn₂O₃) is unique among 3d-TM-SOs because its most stable phase at room conditions (α-Mn₂O₃) does not adopt the corundum structure. Instead, it crystallizes in the so-called cubic bixbyite structure that takes the name from the mineral form of this compound. In bixbyite, Mn³⁺ occupies five different crystallographic sites, each of them surrounded by a highly distorted octahedron of O atoms. Such distortion originates from the Jahn-Teller effect, due to the lowering of overall energy as a consequence of a distortion-induced loss of degeneracy in the 3d-orbitals of the sixfold-coordinated Mn³⁺ ions. As discussed by several authors, the Jahn-Teller distortion might explain the fact that Mn₂O₃ does not adopt the corundum structure at room conditions [158]. Also, it has been predicted that HP might suppress the Jahn-Teller effect, which would make Mn₂O₃ transform to a corundum-type polymorph and, afterwards, follow the usual sequence of pressure-induced PTs observed in the rest of TM-SOs [140]. α-Mn₂O₃ has been shown to be antiferromagnetic, with a Néel temperature of around 79 K [187] and has recently attracted considerable interest due to its potential use in chemical catalysis and magnetic devices, and also for energy conversion and storage applications.

Interestingly, the bixbyite structure actually occurs in doped samples and/or at temperatures slightly above RT. Indeed, it has been shown that Mn₂O₃ undergoes a subtle cubic-to-orthorhombic (Pcab) PT around RT and that the bixbyite structure is stabilized by the presence of impurities [188]. The low-temperature phase Pcab is just an orthorhombically distorted bixbyite structure. There exists another polymorph of Mn₂O₃ stable at room conditions, namely γ-Mn₂O₃. It is a tetragonal spinel-like polymorph (s.g. I₄₁/amd), related to Mn₂O₄. This phase, which is ferrimagnetic below 39 K, can be viewed as the equivalent of maghemite in the case of the Fe₂O₃ system.

Several studies have investigated the HP phases of Mn₂O₃ [140,189–194]. It is now clear that α-Mn₂O₃ transforms at RT to a CaIrO₃-type PPv-like structure above 16 GPa [190–194] with a large volume collapse of ~12%. Thus, no Pv polymorph is observed between the bixbyite and PPv structures at RT. As pointed out by Santillán et al. [190], this might be due to the similarity between the two structures (cubic bixbyite and PPv). Yamanaka et al. also reported a monoclinic HP phase of Mn₂O₃ that has not been confirmed by any other study [189]. More recently, synthesis performed with a multianvil apparatus and subsequent study of the recovered material has shown that, at HTs (between ~850 and 1150 K) the Pv structure, also called γ-Mn₂O₃, can be synthesized and recovered at room conditions [193]. This polymorph is formed by a Pv octahedral framework with strongly tilted MnO₆ octahedra. Its crystal structure was determined within the 4aₚ supercell, s.g. F'T (s.g. P'T in the standard setting, see reference [193]), where Mn cations are preferentially found in different sites depending on their valence state (Mn²⁺, Mn³⁺, Mn⁴⁺). This phase has been shown to be a narrow direct bandgap semiconductor (0.45 eV) with remarkable hardness [195], and to exhibit a 3:1 charge ordering between two different sites, and a unique orbital texture involving a remarkable alternation of orbitals states [196].

A corundum-type polymorph of Mn₂O₃ (ε-Mn₂O₃) was also recovered at room conditions after applying intermediate pressures (15 GPa) and HT (> 1200 K) [193]. This phase, which is about 1% denser than the bixbyite polymorph, seems to confirm the existence of the undistorted, corundum-type
structure in the exotic Mn$_2$O$_3$. It should be noted that, in contrast to this phase and the $\zeta$ phase, the more usual HP PPv polymorph is not quenchable at room conditions. The multianvil apparatus experiments also show that reduction of Mn$_2$O$_3$ to Mn$_3$O$_4$ is observed below 12 GPa at HT (>1200 K) [193]. No HP studies of $\epsilon$ and $\gamma$ phases are available to our knowledge.

Among TM-SOs, vanadium oxide (V$_2$O$_3$) is one of the most interesting materials both from fundamental and applied points of view, due to its remarkable electronic and magnetic properties. This compound has a very rich phase diagram at RP and is often considered a paradigmatic example of metal to Mott-insulator transition in strongly correlated materials. Depending on temperature and doping with small amounts of Cr or Ti, V$_2$O$_3$ exhibits different phases including a paramagnetic metallic state, a paramagnetic insulating state or a low-temperature antiferromagnetic insulating state [197,198]. V$_2$O$_3$ adopts a corundum-type structure at atmospheric conditions and is found in nature as the rare mineral karelianite, first found in glacial boulders from the North Karelia region, in Finland. A metastable polymorph of V$_2$O$_3$ with bixbyite structure was obtained by synthetic methods [199]. This phase transforms into the stable corundum phase above 800 K, and is found to exhibit a paramagnetic to canted antiferromagnetic transitions at about 50 K.

The application of HP strongly modifies the phase diagram of corundum-type V$_2$O$_3$. Several studies have investigated the Mott-insulator transition in V$_2$O$_3$ and Cr-doped V$_2$O$_3$ at HP with a range of different experimental techniques [200–205]. Here, we would like to first focus on the link between the structural and electronic properties of V$_2$O$_3$. In particular, McWhan and Remeika [200] studied V$_2$O$_3$ and (V$_{0.96}$Cr$_{0.04}$)$_2$O$_3$ samples and found that the metallic state typically found in undoped V$_2$O$_3$ is recovered by compressing the Cr-doped sample. These authors also showed that the $c/a$ ratio of the trigonal lattice is related to the insulating/metallic state as a function of Cr-doping level and as a function of pressure. In particular, they found that the $a$ parameter of their Cr-doped sample, which was larger than that of undoped V$_2$O$_3$ at RP, dropped to the value of V$_2$O$_3$ at 4 GPa. In contrast, the $c$ parameter was found to barely increase at HP in both samples, implying a remarkable increase in the $c/a$ ratio in the Cr-doped sample as the metallic state was approached. In fact, they found a sharp increase in $c/a$ ratio just at the insulator–metal transition. These authors also showed that undoped V$_2$O$_3$ becomes even more metallic at HP, with a suppression of the antiferromagnetic-insulating phase above 0.3 GPa.

More recently, Lupi et al. [198] studied with submicron resolution the Mott-insulator transition in Cr-doped V$_2$O$_3$. These authors found that, with decreasing temperature (which yields the antiferromagnetic insulator phase), microscopic domains become metallic and coexist with an insulating matrix. This seems to explain why the paramagnetic metallic phase is a poor metal. They attributed the observed phase separation to a thermodynamic instability around the Mott-insulator transition, showing that such instability is reduced at HP. Therefore, they concluded that the Mott-insulator transition is a more genuine Mott transition in compressed samples, which also exhibited an abrupt increase in the $c/a$ ratio around the insulator-to-metal transition (i.e., around 0.3 GPa). This result confirms the close relationship between the structural properties of V$_2$O$_3$, the nature of the Mott-insulator transition and the role of HP in the modification of the electronic properties of this interesting compound.

In contrast to other TM-SOs, the compression of V$_2$O$_3$ is highly anisotropic (the $a$ axis is nearly three times more compressible than the $c$ axis) [206] and the unusual behavior of the $c/a$ ratio is closely related to the Mott-insulator transition. It was also shown that the atomic positions in V$_2$O$_3$ tend to those of the ideal hcp lattice at HP, with large changes in interionic distances and bond angles upon compression [206]. Zhang et al. observed a pressure-induced PT to an unknown phase around 30 GPa [207]. Ovsyannikov et al. found two different PTs above 21 GPa and 50 GPa, respectively, and attributed the first HP phase to an Rh$_2$O$_3$-II-type orthorhombic structure [157]. With regard to the second HP phase, they conclude that it seems not to be related to the Th$_2$S$_3$- and $\alpha$-Gd$_2$S$_3$-type structures predicted by Zhang et al. in V$_2$O$_3$, of around 30–50 GPa [208]. In conclusion, more work is needed to unveil the HP behavior of both the corundum and bixbyite polymorphs of V$_2$O$_3$. 

\textit{Crystals 2019, 9, 630}
Besides the compounds discussed above, other TM-SOs have been synthesized and/or exist in nature that crystallize in the corundum-structure at room conditions: the 3d-SOs Ti$_2$O$_3$, Cr$_2$O$_3$, and Co$_2$O$_3$, and the 4d-SO Rh$_2$O$_3$. There are also a few reports about the possible synthesis and characterization at room conditions of hexagonal Ni$_2$O$_3$ [209,210] and 5d-SO Au$_2$O$_3$ [211]. However, more work would be required to unambiguously demonstrate the stability of these two latter compounds at room conditions. Note that no natural occurrence of SOs with Ni or Co ions, both of which are more stable as divalent cations, has been found so far. On the other hand, no HP study is known for Au$_2$O$_3$.

The amount of HP investigations on the above mentioned materials is variable. Minomura and Drickammer [212] reported HP resistance measurements on several compounds at RT. They found a resistance maximum around 11 GPa in Ni$_2$O$_3$ that could be indicative of a PT. Unfortunately, no additional HP investigations can be found in the literature on this material. In the case of Co$_2$O$_3$, Chenavas et al. reported a low spin to high spin transition in quenched material, subject to 8 GPa and 850 °C, from a synthesis process involving different chemical reactions [213]. Therefore, the fundamental properties of both Ni$_2$O$_3$ and Co$_2$O$_3$ at HP have yet to be fully investigated.

Chromia (Cr$_2$O$_3$) is another important TM-SO, both from technological and fundamental points of view. This material with corundum structure occurs in nature as the uncommon mineral eskolaite. However, it is probably better known for its high stability and hardness, which makes it a commonly used green pigment and abrasive material. Cr$_2$O$_3$ is a typical antiferromagnetic insulator with a Neél temperature $T_N$ ~307 K, but it is remarkable as it shows an intriguing linear magnetoelectric effect that has attracted some research attention in relation to spintronic applications. Although the existence of HP polymorphs of Cr$_2$O$_3$ have not yet been well-established [214,215], it is clear that HP affects the magnetic properties of this compound. For instance, as recently shown by Kota et al., hydrostatic pressure may increase the $T_N$ of corundum-type Cr$_2$O$_3$, which could provide an enhancement of the magnetoelectric operating temperature in compressed samples [215]. However, there is an ongoing controversy in the literature in relation to the sign of $dT_N/dP$ (see reference [215] and references therein).

With regard to its crystal structure at HP, no PT was found either by Finger and Hazen up to 5 GPa [206], or by Kantor et al. up to ~70 GPa [216]. In contrast, Shim et al. observed several changes around 15–30 GPa on pure synthetic Cr$_2$O$_3$ under cold compression that were compatible with a PT to a monoclinic $V_2$O$_3$-type (I2/a) structure [217]. According to these authors, a second PT could occur above 30 GPa at HT. The new HP-HT phase might be explained by either orthorhombic, Pn, or Rh$_2$O$_3$-II-type structures. In fact, the orthorhombic Rh$_2$O$_3$-II-type phase had been previously predicted to exist at ~15 GPa by first-principles calculations [218]. However, the recent results by Golosova et al. up to 35 GPa, also on synthetic Cr$_2$O$_3$ seem to rule out both PTs [219]. While these authors report a somewhat lower ($1/T_N$)$d(T_N/dP)$ value in relation to reference [215] (0.0091 GPa$^{-1}$ vs. 0.016 GPa$^{-1}$), their structural data point towards a slight anisotropy in the pressure behavior of the c/a axis at around 20 GPa, which could be of magnetic origin. Additional work is thus required to fully understand the HP behavior of chromia.

In the case of Ti$_2$O$_3$, which can be found in nature as the rare tistarite mineral, HP-XRD studies were first conducted by McWhan and Remeika [200] with the aim of comparing the results obtained for this compound with those of V$_2$O$_3$. Later on, Nishio-Hamane et al. reported a PT from corundum-type Ti$_2$O$_3$ to an orthorhombic Th$_2$S$_3$-type (s.g. $Pnma$) structure above 19 GPa and 1850 K, being the new polymorph metastably recovered at room conditions [220]. The same structure had been previously predicted at ultra HP for the case of Al$_2$O$_3$ [221]; hence, the synthesis of the Th$_2$S$_3$-type polymorph in Ti$_2$O$_3$ has been a remarkable finding, shedding new light on the fundamental properties of the TM-SOs family. In Ti$_2$O$_3$, the Th$_2$S$_3$-type structure was found to be ~10% denser than the corundum-type phase. Subsequently, Ovsyannikov et al. [222] synthesized polycrystalline Ti$_2$O$_3$ samples with Th$_2$S$_3$-type structure with the aim of studying its structural stability up to 73 GPa and 2200 K. The HP behavior of the structural, optical and electronic properties of this unusual, golden-colored polymorph of Ti$_2$O$_3$ were later thoroughly investigated [223,224], together with the T-P phase diagram of Ti$_2$O$_3$ [224].
With regard to 4d-SOs, there are a few reports on the existence of such compounds at room conditions, the most relevant of which is Rh$_2$O$_3$. Two low-pressure polymorphs of this material are known, namely Rh$_2$O$_3$-I and Rh$_2$O$_3$-III. While the stable phase at room conditions, Rh$_2$O$_3$-I, adopts a corundum-type structure, the Rh$_2$O$_3$-III polymorph crystallizes in an orthorhombic Pbca structure and is only stable at RP and HT (>750 °C) [225]. In addition, an HP phase, known as Rh$_2$O$_3$-II, was synthesized by Shannon and Prewitt at 6.5 GPa and 1200 °C [226]. This phase was found to adopt an orthorhombic Pbma structure, similar to that of corundum as it contains RhO$_6$ octahedra that share their faces. In Rh$_2$O$_3$-II, however, only two edges of each octahedra are shared with other octahedra. In spite of the use of HP to synthesize Rh$_2$O$_3$-II, only a limited number of HP studies on this phase can be found in the literature. Zhuo and Sohlberg investigated theoretically the stability of this phase in comparison to Rh$_2$O$_3$-I and Rh$_2$O$_3$-III, which allowed them to predict the phase diagram of Rh$_2$O$_3$ [227]. According to their results, Rh$_2$O$_3$-II is stable below ~5 GPa and HT (>700 K), while the Rh$_2$O$_3$-III form is the main phase above 5 GPa, regardless of temperature. Unfortunately, no experimental HP studies dealing with the structural properties of any of the Rh$_2$O$_3$ phases have been published so far. Experimental work on this material, and, in particular, on the Rh$_2$O$_3$-III polymorph, due to its connection to the HP phases of other SOs, as described above, is still necessary.

Possible stable forms of other 4d-SOs, like Mo$_2$O$_3$ and W$_2$O$_3$, have been reported in relation to the growth of thin films or coatings (see bibliography in reference [228]). Recent DFT calculations predict that corundum-type Mo$_2$O$_3$ might be stabilized at 15 GPa, while a much higher pressure (60 GPa) is obtained by these authors for W$_2$O$_3$ [228]. Similar conclusions have been reached by other authors in relation to Hf$_2$O$_3$ and Zr$_2$O$_3$ using crystal prediction methods [157,229]. These two SOs might be metastable at HP. So far, however, there is no experimental evidence for the existence and stability of these SOs at HP. Much experimental and theoretical effort is still required to understand the stability and behavior of these two SOs upon compression, which could lead to the discovery of new HP phases with remarkable properties.

To finish this section, we summarize in Table 3 the phase transition pressures and HP phases observed in the best studied TM-SOs.

Table 3. Summary of the high pressure (HP) phases and phase transition (PT) pressures, P$_T$ (in GPa) reported for the best studied transition-metal sesquioxides (TM-SO) materials: Fe$_2$O$_3$, Mn$_2$O$_3$, V$_2$O$_3$ and Ti$_2$O$_3$. The fourth column shows the resulting phase obtained at HP starting from the phase displayed in the first column (DPv: distorted perovskite; PPv: post-perovskite; LH: laser heating).

| Compound                  | P$_T$ (GPa) | Temperature | HP Phase                  | Reference |
|---------------------------|-------------|-------------|---------------------------|-----------|
| α-Fe$_2$O$_3$ (hematite, R$_3$c) | 54          | RT          | DPv, P$T$                 | [175]     |
| α-Fe$_2$O$_3$ (hematite, R$_3$c) | 67          | RT          | A$_{2}a$                  |           |
| α-Fe$_2$O$_3$ (hematite, R$_3$c) | 40          | LH          | Rh$_2$O$_3$-II, P$_{bcn}$ | [173]     |
| α-Fe$_2$O$_3$ (hematite, R$_3$c) | 68          | LH          | P$_{nv}, C_{mcm}$         |           |
| β-Fe$_2$O$_3$ (la$\bar{5}$) | 30          | RT          | “$\epsilon$-Fe$_2$O$_3$” | [169]     |
| γ-Fe$_2$O$_3$ (maghemite, Fd$\bar{3}$m) | 35          | RT          | α-Fe$_2$O$_3$             | [182]     |
| ε-Fe$_2$O$_3$ (luogufengite, P$n$2$_1$) | 27          | RT          | $\epsilon'$-Fe$_2$O$_3$   | [186]     |
| α-Mn$_2$O$_3$ (bixbyite, la$\bar{5}$) | 16–25       | RT          | PPv, C$_{mcm}$            | [190]     |
| α-Mn$_2$O$_3$ (bixbyite, la$\bar{5}$) | 18          | 800 K       | P$_v$, P$T$               | [193]     |
| α-Mn$_2$O$_3$ (bixbyite, la$\bar{5}$) | 13          | 1100 K      | ε-Mn$_2$O$_3$, R$_3$c     |           |
| V$_2$O$_3$ (karelianite, R$_3$c) | 21–27       | LH          | Rh$_2$O$_3$-II, P$_{bcn}$ | [157]     |
| V$_2$O$_3$ (karelianite, R$_3$c) | 50          | LH          | PPv, C$_{mcm}$ (?)        |           |
| Ti$_2$O$_3$ (tistartite, R$_3$c) | 19          | 1850 K      | Th$_2$S$_3$-type, P$n$2$_1$ | [220]     |

2.4. Group-15 Sesquioxides

Group-15-SOs are relevant in a multitude of technological [230–232] and medical [233–235] applications, but the main interest in the study of the properties of these compounds resides in the
physical-chemical interactions of their chemical bonds. The progressive increase in the strength of the stereoactive cationic lone electron pair (LEP) going up along the group 15 column, i.e., as the cation becomes lighter, dominates the formation and compressibility of the resulting crystallographic structures. In other words, the influence of the cation LEP determines the different existing polymorphs of group-15-SOS and it is possible to observe several trendlines of their behavior at HP. According to the literature, the group-15-SO polymorphs can be obtained from a defective fluorite structure where oxygen vacancy arrays are applied along different crystallographic directions [236,237]. These arrays define most of the polymorphs found at room conditions in these SOs. Nevertheless, the crystalline phases formed are quite different from the rest of SOs, mainly due to the above-mentioned influence of the LEP.

Structural phases belonging to the cubic family are observed in group-15-SOs since the most usual structures of arsenic and antimony SO crystallizes in the s.g. $Fd\bar{3}m$. They are obtained by applying an array model along the (111) direction to a defective fluorite structure. They have been experimentally found in $c$-$As_2O_3$ (whose mineral form is called arsenolite) and $\alpha$-$Sb_2O_3$ (whose mineral form is called senarmontite). These SOs are also noted as $As_4O_6$ and $Sb_4O_6$, respectively, because this notation reflects the molecular arrangement of these two molecular or zero-dimensional solids. The molecular units $X_3O_6$ ($X=As,Sb$) are disposed in a closed-compact adamantane-type molecular cages, joined together by van der Waals (vdW), and chalcogen bonding among the closest arsensics belonging to different molecular units. In this case, the cations belonging to the same molecular unit form pseudo-tetrahedral units following the same disposition as their counterpart, the white phosphorus ($P_4$). The molecular cages are stabilized by the cationic LEP oriented towards the outside of the cage, which confers great stability to the molecular unit. The HP behavior of both $Sb_4O_6$ and $As_4O_6$ dimorphs is quite different. They undergo different PTs [238–242], and both compounds show a pressure-induced amorphization driven by mechanical instability [238–240]. The origin of this instability is associated with the steric repulsion caused by the increase in the interaction between different molecular units when pressure increases [238]. It has been shown in a HP study using different pressure-transmitting media that the instability is enhanced by the loss of the hydrostatic conditions [241]. However, up to 15 GPa, both compounds behave differently. Whereas two 2nd-order isostructural PTs were observed in $Sb_3O_6$ at 3.5 and 12 GPa, respectively [242], no pressure-induced PT was reported in $As_4O_6$ [239,240]. The PTs exhibited by $Sb_3O_6$ at 3.5 and 12 GPa were suggested to be due to the loss of its molecular character and related to changes in the hybridization of Sb $5s$ and O $2p$ electrons, i.e., they are related to the decrease in LEP stereactivity at HP [242].

At 15 GPa, $Sb_3O_6$ tends to form a new HP structure that can be defined by a distortion of the structural lattice due to the loss of the molecular character [238]. This HP phase crystallizes in a tetragonal structure (s.g. $P4_21c$) similar to that of $\beta$-$Bi_2O_3$ [243] that will be described later. At HP (9–11 GPa) and HT (573–773 K), cubic $Sb_4O_6$ undergoes a 1st-order PT towards a new polymorph called $\gamma$-$Sb_2O_3$ [244]. This new phase crystallizes in an orthorhombic structure s.g. $P2_1z_21z$, where the trigonal pyramid form given by the coordination of the Sb atom surrounded by O atoms in the cubic phase is changed by a tetrahedral unit in the orthorhombic phase, where the LEP acts as a pseudo-ligand. The tetrahedral units are arranged, forming chains or rods along the $a$-axis that show strong similarities with the $\beta$-$Sb_2O_3$ polymorph (s.g. $Pccn$), whose ($Sb_2O_3$)$_\infty$ rods are aligned along the $c$-axis. Due to its rod-like structure, orthorhombic $\beta$-$Sb_2O_3$ is a quasi-molecular or acicular solid with two independent rods in the unit cell. In this structure, each Sb atom is bonded to three oxygen atoms, with their LEP oriented towards the void formed by the rod arrangement. Thus, this SO can be described by rods and linear voids oriented along the $c$-axis, being isostructural to the $\epsilon$-$Bi_2O_3$ phase [245]. No HP study of $\epsilon$-$Bi_2O_3$ is known so far.

HP studies of $\beta$-$Sb_2O_3$ revealed a 1st-order PT around 15 GPa [246,247]. Nevertheless, the nature of its HP phase is still under debate. Zou et al. tentatively assigned it to a monoclinic structure with s.g. $P2_1/c$. $\beta$-$Sb_2O_3$ also shows strong similarities with the tetragonal phase of bismuth SO (named $\beta$-$Bi_2O_3$), which crystallizes in s.g. $P4_21c$ [243]. In fact, $\beta$-$Bi_2O_3$ is a metastable polymorph obtained by heating...
the most stable phase of the bismuth SO (α-Bi$_2$O$_3$) to 650 °C [248]. This material can be considered a defective fluorite structure, where an (100) array of vacant sites is applied [236]. This polymorph contains a linear channel, as well as β-Sb$_2$O$_3$, with the cation LEP oriented towards the center of the empty channel. β-Bi$_2$O$_3$ is very interesting from a physical–chemical point of view because it is a clear example of an isostructural 2nd-order PT. This structure is characterized by a Bi atom located at an 8e Wyckoff site and two O atoms located at 8e and 4d Wyckoff sites, with the Bi atom coordinated to six O atoms, forming a distorted pyramid. Above 2 GPa, several Wyckoff coordinates of β-Bi$_2$O$_3$ symmetrize, remaining fixed up to 12 GPa [243]. Thus, the six different Bi-O interatomic distances observed at RP in the polyhedral unit only become three different Bi-O bond lengths, thus reducing the eccentricity of the Bi atom drastically, up to 2 GPa. This PT is even more explicit when analyzing the compressibility of the unit cell volume below and above 2 GPa. Finally, a progressive broadening of the peaks leads to a pressure-induced amorphization above 12 GPa that is completed at 20 GPa [243].

 α-Bi$_2$O$_3$ crystallizes in a monoclinic s.g. $P2_1/c$ structure, where Bi atoms are located in two inequivalent crystallographic 4e sites and O atoms are located in three inequivalent 4e Wyckoff positions. One of the Bi atoms is penta-coordinated and the other is hexa-coordinated. This polymorph remains in the same structure up to 20 GPa, where a pressure-induced amorphization occurs [249]. The amorphization was explained by a frustrated PT towards the HPC-Bi$_2$O$_3$ polymorph, since the HPC-phase is thermodynamically more stable than the α-phase above 6 GPa, according to DFT calculations. This ongoing PT is likely inhibited by the kinetic barriers between both phases. The correlation between the amorphous phase and the HPC polymorph was revealed, thanks to the analysis of the diffraction pattern as a function of the interionic distances, using the process described in reference [250]. Results indicated average interatomic Bi-O distances closer to those of the HPC-Bi$_2$O$_3$ than to any other polymorph. HPC-Bi$_2$O$_3$ crystallizes in the hexagonal s.g. $P6_3/mc$ structure, and it is the HP phase of the HP-Bi$_2$O$_3$ phase, above 2 GPa [251]. In turn, HP-Bi$_2$O$_3$ with s.g. $P31c$ was obtained from α-Bi$_2$O$_3$ at HP and HT (6 GPa and 880 °C) [252]. The strong polymorphism exhibited by Bi$_2$O$_3$ does not require the application of HP. It must be noted that α-Bi$_2$O$_3$ at HT (above 400 °C) shows a PT to R-Bi$_2$O$_3$ (s.g. $P2_1/n$) [252], which, despite belonging to the same s.g. as α-Bi$_2$O$_3$, has a completely different structure. No HP study of R-Bi$_2$O$_3$ is known.

In the same s.g. $P2_1/n$, related to the α- and R-Bi$_2$O$_3$ phases, one can find two additional As$_2$O$_3$ polymorphs, whose names are claudetite-I [253] and claudetite-II [254]. The naturally stable phase, claudetite-I, has been only characterized by HP-RS measurements to our knowledge, revealing a possible PT between 7–13 GPa and a lack of pressure-induced amorphization up to 40 GPa [255]. Claudetite-II is a synthesized quasi-layered material, similar to As$_4$O$_6$, where the molecular unit is an open shell forming AsO$_E$ pseudo-tetrahedra (where $E$ denotes the cation LEP) [256]. In this case, the LEPs of neighboring cations are oriented towards opposite neighboring layers. This particular structure shows several pressure-induced 2nd-order PTs around 2 and 6 GPa [257], given by two abrupt breakdowns of inversion centers that lead to doubling and hexaplicating the original unit cell, respectively. Additionally, a PT around 10.5 GPa leads to the non-centrosymmetric HP phase β-As$_2$O$_3$ (s.g. $P2_1$).

Another group-15-SO crystallizing in the monoclinic s.g. $P2_1/n$ structure is the phosphorous SO (P$_2$O$_3$), which keeps the molecular character of cubic arsenic and antimony SOs, i.e., P$_4$O$_6$ [258]. Nevertheless, the symmetric distribution of the different P$_4$O$_6$ molecular cages is distorted in the case of monoclinic P$_2$O$_3$. The HP study of P$_2$O$_3$ exhibits strong difficulties, since it is only stable at low-temperatures, below RT. Thus, the HP behavior of this compound is still unknown.

To finish, we summarize in Table 4 the 1st- and 2nd-order PTs observed in group-15-SOs.
Table 4. Experimental and theoretical (DFT) data of the PT pressures (in GPa) for group-15-SOs. PIA stands for pressure-induced amorphization and MEW for methanol-ethanol mixture.

| s.g. | Compound          | 2nd-Order PT | 1st-Order PT | PIA  | Technique       | Reference |
|------|------------------|--------------|--------------|------|-----------------|-----------|
| Fd3m | As₄O₆            | -            | -            | 18.7 | DFT             | [240]     |
|      |                  | -            | -            | 15   | XRD (MEW)      | [239]     |
|      |                  | -            | -            |      | XRD (He)       | [241]     |
|      | Sb₄O₆            | 3.5          | 10           |      | XRD, DS, DFT   | [242]     |
|      |                  | -            | 25           | 30   | XRD (Ne)       | [238]     |
| P2₁/c| mII-As₂O₃ (claudeite II) | 2          | 6            | 11   | -               | [256]     |
|      | α-Bi₂O₃          | -            | -            | 20   | XRD, RS, DFT   | [249]     |
|      | ml-As₂O₃ (claudeite I) | -          | -            | -    | RS              | [253]     |
| Pccn | β-Sb₂O₃          | 7            | 15           | 33   | XRD, RS (Ne)   | [246]     |
|      |                  | -            | 13.5         | -    | XRD, RS (MEW)  | [247]     |
| P4₂₁c| β-Bi₂O₃          | 2            | -            | 12   | XRD, RS, DFT   | [243]     |

2.5. Mixed-Valence Sesquioxides

As mentioned in the introduction, there are A₂O₃ compounds where the A has two different valences, which constitute the subfamily MV-SOs. MV-SOs are highly interesting because they feature cations with different valences and consequently can be differently coordinated, thus resulting in a distortion in the structures of normal SOs. Examples of this kind of SOs are Sn₂O₃ and Pb₂O₃, where Sn and Pb cations show both 2+ and 4+ valences. While Pb₂O₃ has been known for almost a century [259] and crystallizes in the monoclinic s.g. P2₁/a [260], Sn₂O₃ has just recently been predicted [261] and experimentally found to crystallize in the triclinic s.g. Pñana [262,263]. No HP studies on these two interesting but complex compounds have been reported to our knowledge.

3. Conclusions and Future Prospects

A great deal of work has been done on sesquioxides under compression and many pressure-induced phase transitions have been elucidated. In particular, the pressure-induced phase transitions of rare-earth sesquioxides and group-13 sesquioxides are quite well known, except for Tl₂O₃. The knowledge of pressure-induced phase transitions in transition-metal sesquioxides is not so well known, and those of group-15 sesquioxides have been recently studied, but still require more work. Finally, pressure-induced phase transitions in mixed-valence sesquioxides are completely unknown. It must be stressed that most of the high-pressure work done on sesquioxides corresponds to cubic, tetragonal, hexagonal, rhombohedral, and orthorhombic phases, while most of the high-pressure work still to be done on sesquioxides corresponds to complex monoclinic and triclinic phases. The study of these complex phases was rather difficult in the past, and is a challenge that must be accomplished in the 21st century with current and future experimental and theoretical techniques.

It must be noticed that the crystalline structures of the different subfamilies of sesquioxides and their pressure-induced phase transitions have some features in common. The archetypic structure of rare-earth sesquioxides is the C-type structure, which is isostructural to the bixbyite structure of several transition metal sesquioxides (Mn₂O₃) and group-13 sesquioxides (In₂O₃ and Tl₂O₃). On the other hand, the archetypic structure of group-13 and transition-metal sesquioxides is the corundum structure (Al₂O₃). In this context, it is remarkable that the pressure-induced transitions of C-type rare-earth sesquioxides, including Sc₂O₃ and Y₂O₃, are markedly different to those of C-type group-13 and transition-metal sesquioxides. In fact, these last compounds seem to have pressure-induced transitions
that are closer to those of corundum-type structures of group-13 and transition-metal sesquioxides. On the other hand, the crystalline structures and pressure-induced phase transitions of group-15 sesquioxides are completely different to those of other sesquioxides, due to the stereochemically active lone electron pair of group-15 cations, which lead to more open-framework structures than those present in other subfamilies. Consequently, we can speculate that a similar behavior is expected to be observed in future experiments of mixed-valence sesquioxides under compression, since this subfamily is also characterized by having some cations with lone electron pairs.

Finally, it should be mentioned that we are not aware of studies of negative pressures in sesquioxides. In principle, it is possible to reach absolute negative pressures (of the order of a few GPa) [264] where novel structures might appear [265]. In fact, negative pressures have been found in several solids, such CaWO$_4$ nanocrystals [266] and ice polymorphs [267]. Therefore, the application of negative pressures to materials is a route that can also be explored in sesquioxides, since it would lead to the expansion of the crystalline lattice, leading to the possible instability of the stable phase at room conditions in certain compounds, thus opening a new avenue to obtain novel and exotic metastable phases.

**Author Contributions:** F.J.M. contributed to the conceptualization and writing of the introduction, Sections 2.1 and 2.5 and conclusions; A.L.J.P. contributed to the writing of Section 2.2; J.I. contributed to the writing of Section 2.3 and J.A.S.T. contributed to the writing of Section 2.4 and the revision of the manuscript.

**Funding:** This research was funded by Spanish Ministerio de Ciencia, Innovación y Universidades under grants MAT2016-75586-C4-1/2-P, FIS2017-83295-P, PGC2018-094417-B-I00, and RED2018-102612-T (MALTA-Consolider-Team network) and by Generalitat Valenciana under grant PROMETEO/2018/125 (EFIMAT). J. A. S. also acknowledges Ramón y Cajal Fellowship for financial support (RYC-2015-17482).

**Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

**References**

1. Liu, L.-G.; Bassett, W.A. *Elements, Oxides, Silicates, High-Pressure Phases with Implications for the Earth’s Interior;* Oxford Monographs on Oxology and Geophysics; Oxford University Press: Oxford, UK, 1986; Volume 4.
2. Adachi, G.-Y.; Imanaka, N. The Binary Rare Earth Oxides. *Chem. Rev.* 1998, 98, 1479–1514. [CrossRef] [PubMed]
3. Smyth, J.R.; Jacobsen, S.D.; Hazen, R.M. Comparative Crystal Chemistry of Dense Oxide Minerals. In *Reviews in Mineralogy and Geochemistry;* Mineralogical Society of America: Chantilly, VA, USA, 2000; Volume 41.
4. Zinkevich, M. Thermodynamics of rare earth sesquioxides. *Prog. Mat. Sci.* 2007, 52, 597–647. [CrossRef]
5. Manjón, F.J.; Errandonea, D. Pressure-induced structural phase transitions in materials science. *Phys. Stat. Sol. B* 2009, 246, 9–31. [CrossRef]
6. Foex, M.; Traverse, J.P. Remarques sur les transformations cristallines presentees a haute temperature par les sesquioxydes de terres rares. *Rev. Int. Hautes Temp. Refract.* 1966, 3, 429–453.
7. Hoekstra, H.R.; Gingerich, K.A. High-Pressure B-Type Polymorphs of Some Rare-Earth Sesquioxides. *Science* 1964, 144, 1163–1164. [CrossRef]
8. Sawyer, J.O.; Hyde, B.G.; Eyring, L. Pressure and Polymorphism in the Rare Earth Sesquioxides. *Inorg. Chem.* 1965, 4, 426–427. [CrossRef]
9. Vegas, A.; Isea, R. Distribution of the M-M Distances in the Rare Earth Oxides. *Acta Cryst. B* 1998, 54, 732–740. [CrossRef]
10. Vegas, A. *Structural Models of Inorganic Crystals;* Editorial Universitat Politècnica de Valencia: Valencia, Spain, 2018.
11. McClure, J.P. High Pressure Phase Transitions in the Lanthanide Sesquioxides. Ph.D. Thesis, University of Nevada, Las Vegas, NV, USA, 2009.
12. Jiang, S.; Liu, J.; Lin, C.L.; Bai, L.G.; Xiao, W.S.; Zhang, Y.F.; Zhang, D.C.; Li, X.D.; Li, Y.C.; Tang, L.Y. Pressure-induced phase transition in cubic Lu$_2$O$_3$. *J. Appl. Phys.* 2010, 108, 083541. [CrossRef]
13. Lin, C.-M.; Wu, K.-T.; Hung, T.-L.; Sheu, H.-S.; Tsai, M.-H.; Lee, J.-F.; Lee, J.-J. Phase transitions in Lu$_2$O$_3$ under high pressure. *Solid State Commun.* 2010, 150, 1564–1569. [CrossRef]
14. Yusa, H.; Kikegawa, T. Photon Factory Activity Report #28 Part B 223; Kishimoto, S., Ed.; High Energy Accelerator Research Organization (KEK): Ibaraki, Japan, 2010.
15. Meyer, C.; Sanchez, J.P.; Thomasson, J.; Itié, J.P. Mossbauer and energy-dispersive x-ray-diffraction studies of the pressure-induced crystallographic phase transition in C-type Yb$_2$O$_3$. Phys. Rev. B 1995, 51, 12187–12193. [CrossRef]
16. Yusa, H.; Kikegawa, T.; Tsuchiya, T. Photon Factory Activity Report #27 Part B 195; lwano, K., Ed.; High Energy Accelerator Research Organization (KEK): Ibaraki, Japan, 2009.
17. Lonappan, D. High Pressure Phase Transformation Studies on Rare Earth Sesquioxides. Ph.D. Thesis, Indira Gandhi Centre for Atomic Research, Tamil Nadu, India, 2012.
18. Pandey, S.D.; Samanta, K.; Singh, J.; Sharma, N.D.; Bandyopadhyay, A.K. Anharmonic behavior and structural phase transition in Yb$_2$O$_3$. AIP Adv. 2013, 3, 122123. [CrossRef]
19. Sahu, P.C.; Lonappan, D.; Chandra Shekar, N.V. High Pressure Structural Studies on Rare-Earth Sesquioxides. J. Phys. Conf. Ser. 2012, 377, 012015. [CrossRef]
20. Irshad, K.A.; Anees, P.; Sahoo, S.; Sanjay Kumar, N.R.; Srihari, V.; Kalavathi, S.; Chandra Shekar, N.V. Pressure induced structural phase transition in rare earth sesquioxide Tm$_2$O$_3$: Experiment and ab initio calculations. J. Appl. Phys. 2018, 124, 155901. [CrossRef]
21. Yan, D.; Wu, P.; Zhang, S.P.; Liang, L.; Yang, F.; Pei, Y.L.; Chen, S. Assignments of the Raman modes of monoclinic erbium oxide. J. Appl. Phys. 2013, 114, 193502. [CrossRef]
22. Ren, X.T.; Yan, X.Z.; Yu, Z.H.; Li, W.T.; Wang, L. Photoluminescence and phase transition in Er$_2$O$_3$ under high pressure. J. Alloy. Compd. 2017, 725, 941–945. [CrossRef]
23. Lonappan, D.; Chandra Shekar, N.V.; Ravindran, T.R.; Sahu, P.C. High-pressure phase transition in Ho$_2$O$_3$. Mater. Chem. Phys. 2010, 120, 65–67. [CrossRef]
24. Jiang, S.; Liu, J.; Li, X.D.; Bai, L.G.; Xiao, W.S.; Zhang, Y.F.; Lin, C.L.; Li, Y.C.; Tang, L.Y. Phase transformation of Ho$_2$O$_3$ at high pressure. J. Appl. Phys. 2011, 110, 013526. [CrossRef]
25. Pandey, S.D.; Samanta, K.; Singh, J.; Sharma, N.D.; Bandyopadhyay, A.K. Raman scattering of rare earth sesquioxide Ho$_2$O$_3$: A pressure and temperature dependent study. J. Appl. Phys. 2014, 116, 133504. [CrossRef]
26. Yan, X.Z.; Ren, X.T.; He, D.W.; Chen, B.; Yang, W.G. Mechanical behaviors and phase transition of Ho$_2$O$_3$ nanocrystals under high pressure. J. Appl. Phys. 2014, 116, 033507. [CrossRef]
27. Sharma, N.D.; Singh, J.; Dogra, S.; Varandani, D.; Poswal, H.K.; Sharma, S.M.; Bandyopadhyay, A.K. Pressure-induced anomalous phase transformation in nano-crystalline dysprosium sesquioxide. J. Raman Spectrosc. 2011, 42, 438–444. [CrossRef]
28. Jiang, S.; Liu, J.; Lin, C.L.; Bai, L.G.; Zhang, Y.F.; Li, X.D.; Li, Y.C.; Tang, L.Y.; Wang, H. Structural transformations in cubic Dy$_2$O$_3$ at high pressures. Solid State Commun. 2013, 169, 37–41. [CrossRef]
29. Chen, H.Y.; He, C.Y.; Gao, C.X.; Ma, Y.M.; Zhang, J.H.; Wang, X.J.; Gao, S.Y.; Li, D.M.; Kan, S.H.; Zou, G.T. The structural transition of Gd$_2$O$_3$ nanoparticles induced by high pressure. J. Phys. Condens. Matter 2007, 19, 425229. [CrossRef]
30. Chen, H.Y.; He, C.Y.; Gao, C.X.; Ma, Y.M.; Zhang, J.H.; Gao, S.Y.; Li, H.L.; Nie, Y.G.; Li, D.M.; Kan, S.H.; et al. Structural Transition of Gd$_2$O$_3$: Eu Induced by High Pressure. Chin. Phys. Lett. 2007, 24, 158–160. [CrossRef]
31. Zhang, F.X.; Lang, M.; Wang, J.W.; Becker, U.; Ewing, R.C. Structural phase transitions of cubic Gd$_2$O$_3$ at high pressures. Phys. Rev. B 2008, 78, 064114. [CrossRef]
32. Dilawar, N.; Varandani, D.; Mehrotra, S.; Poswal, H.K.; Sharma, S.M.; Bandyopadhyay, A.K. Anomalous high pressure behaviour in nanosized rare earth sesquioxides. Nanotechnology 2008, 19, 115703. [CrossRef] [PubMed]
33. Bai, L.G.; Liu, J.; Li, X.D.; Jiang, S.; Xiao, W.S.; Li, Y.C.; Tang, L.Y.; Zhang, Y.F.; Zhang, D.C. Pressure-induced phase transformations in cubic Gd$_2$O$_3$. J. Appl. Phys. 2009, 106, 073507. [CrossRef]
34. Zou, X.; Gong, C.; Liu, B.B.; Li, Q.J.; Li, Z.P.; Liu, B.; Liu, J.; Chen, Z.Q.; Zou, B.; et al. X-ray diffraction of cubic Gd$_2$O$_3$Er under high pressure. Phys. Stat. Sol. B 2011, 248, 1123–1127. [CrossRef]
35. Zhang, C.C.; Zhang, Z.M.; Dai, R.C.; Wang, Z.P.; Ding, Z.J. High Pressure Luminescence and Raman Studies on the Phase Transition of Gd$_2$O$_3$:Eu$^{3+}$ Nanorods. J. Nanosci. Nanotechnol. 2011, 11, 9887–9891. [CrossRef] [PubMed]
36. Yang, X.; Li, Q.J.; Liu, Z.D.; Bai, X.; Song, H.W.; Yao, M.G.; Liu, B.; Liu, R.; Gong, C.; Lu, S.C.; et al. Pressure-Induced Amorphization in GdO$_2$/Er$^{3+}$ Nanorods. *J. Phys. Chem. C* 2013, *117*, 8503–8508. [CrossRef]

37. Chen, G.; Haire, R.G.; Peterson, J.R. Effect of pressure on cubic (C-type) EuO$_2$ studied via Eu$^{3+}$ luminescence. *High Press. Res.* 1991, *6*, 371–377. [CrossRef]

38. Chen, G.; Stump, N.A.; Haire, R.G.; Peterson, J.R. Study of the phase behavior of EuO$_2$ under pressure via luminescence of Eu$^{3+}$. *J. Alloy. Compd.* 1992, *181*, 503–509. [CrossRef]

39. Dilawar, N.; Varandani, D.; Pandey, V.P.; Kumar, M.; Shivaprasad, S.M.; Sharma, P.K.; Bandyopadhyay, A.K. Structural Transition in Nanostructured EuO$_2$ Under High Pressures. *J. Nanosci. Nanotechnol.* 2006, *6*, 105–113. [PubMed]

40. Jiang, S.; Bai, L.G.; Liu, J.; Xiao, W.S.; Li, X.D.; Li, Y.C.; Tang, L.Y.; Zhang, Y.F.; Zhang, D.C.; Zheng, L.R. The Phase Transition of EuO$_2$ under High Pressures. *Chin. Phys. Lett.* 2006, *23*, 076101. [CrossRef]

41. Irshad, K.A.; Chandra Shekar, N.V.; Srihari, V.; Pandey, K.K.; Kalavathi, S. High pressure structural phase transitions in Ho: EuO$_2$. *J. Alloy. Compd.* 2017, *701*, 542–548. [CrossRef]

42. Irshad, K.A.; Chandra Shekar, N.V. Anomalous lattice compressibility of hexagonal EuO$_2$. *Mat. Chem. Phys.* 2017, *195*, 88–93. [CrossRef]

43. Yu, Z.H.; Wang, Q.L.; Ma, Y.Z.; Wang, L. X-ray diffraction and spectroscopy study of nano-EuO$_2$ structural transformation under high pressure. *J. Alloy. Compd.* 2017, *701*, 542–548. [CrossRef]

44. Guo, Q.X.; Zhao, Y.S.; Jiang, C.; Mao, W.L.; Wang, Z.W. Phase transformation in Sm$_2$O$_3$ at high pressure: In situ synchrotron X-ray diffraction study and ab initio DFT calculation. *Solid State Commun.* 2008, *145*, 250–254. [CrossRef]

45. Jiang, S.; Liu, J.; Lin, C.L.; Li, X.D.; Li, Y.C. High-pressure x-ray diffraction and Raman spectroscopy of phase transitions in Sm$_2$O$_3$. *J. Appl. Phys.* 2013, *113*, 113502. [CrossRef]

46. Liu, D.; Lei, W.W.; Li, Y.W.; Ma, Y.M.; Hao, J.; Chen, X.H.; Jin, Y.X.; Liu, D.; Yu, S.D.; Cui, Q.L.; et al. High-Pressure Structural Transitions of Sc$_2$O$_3$ by X-ray Diffraction, Raman Spectra, and Ab Initio Calculations. *Inorg. Chem.* 2009, *48*, 8251–8256. [CrossRef]

47. Yusa, H.; Tsuchiya, T.; Sata, N.; Ohishi, Y. High-Pressure Phase Transition to the Gd$^{3+}$ Structural and vibrational properties of single crystals of Scandia, Sc$_2$O$_3$ under high pressure. *J. Appl. Phys.* 2019, *125*, 113501. [CrossRef]

48. Ovsyannikov, S.V.; Bykova, E.; Bykov, M.; Wenz, M.D.; Pakhomova, A.S.; Glazyrin, K.; Liermann, H.-P.; Dubrovinsky, L. Structural and vibrational properties of single crystals of Scandia, Sc$_2$O$_3$ under high pressure. *J. Appl. Phys.* 2015, *118*, 169501. [CrossRef]

49. Husson, E.; Proust, C.; Gillet, P.; Itié, J.P. Phase transitions in yttrium oxide at high pressure studied by Raman spectroscopy. *Mater. Res. Bull.* 1999, *34*, 2085–2092. [CrossRef]

50. Bai, X.; Song, H.W.; Liu, B.B.; Hou, Y.Y.; Pan, G.H.; Ren, X.G. Effects of High Pressure on the Luminescence Properties of Nanocrystalline and Bulk Y$_2$O$_3$:Eu$^{3+}$. *J. Nanosci. Nanotechnol.* 2008, *8*, 1404–1409. [CrossRef] [PubMed]

51. Jovanic, B.R.; Dramicanin, M.; Viana, B.; Panic, B.; Radenkovic, B. High-pressure optical studies of Y$_2$O$_3$:Eu$^{3+}$ nanoparticles. *Radiat. Eff. Defects Solids* 2008, *163*, 925–931. [CrossRef]

52. Wang, L.; Pan, Y.X.; Ding, Y.; Yang, W.G.; Mao, W.L.; Sinogeikin, S.V.; Meng, Y.; Shen, G.Y.; Mao, H.-K. High-pressure induced phase transitions of Y$_2$O$_3$ and Y$_2$O$_3$:Eu$^{3+}$. *Appl. Phys. Lett.* 2009, *94*, 061921. [CrossRef]

53. Wang, L.; Yang, W.; Ding, Y.; Ren, Y.; Xiao, S.G.; Liu, B.B.; Sinogeikin, S.V.; Meng, Y.; Gosztola, D.J.; Shen, G.Y.; et al. Size-Dependent Amorphization of Nanoscale Y$_2$O$_3$ at High Pressure. *Phys. Rev. Lett.* 2010, *105*, 095701. [CrossRef]

54. Halevy, I.; Carmon, R.; Winterrose, M.L.; Yeheskel, O.; Tiferet, E.; Ghose, S. Pressure-induced structural phase transitions in Y$_2$O$_3$ sesquioxide. *J. Phys. Cond. Mat.* 2010, *21*, 012003. [CrossRef]

55. Dai, R.C.; Zhang, Z.M.; Zhang, C.C.; Ding, Z.J. Photoluminescence and Raman Studies of Y$_2$O$_3$:Eu$^{3+}$ Nanotubes Under High Pressure. *J. Nanosci. Nanotechnol.* 2010, *10*, 7629–7633. [CrossRef]

56. Dai, R.C.; Wang, Z.P.; Zhang, Z.M.; Ding, Z.J. Photoluminescence study of SiO$_2$ coated Eu$^{3+}$:Y$_2$O$_3$ core-shells under high pressure. *J. Rare Earth* 2010, *28*, 241–245. [CrossRef]

57. Yusa, H.; Tsuchiya, T.; Sata, N.; Ohishi, Y. Dense Yttria Phase Eclipsing the A-Type Sesquioxide Structure: High-Pressure Experiments and ab initio Calculations. *Inorg. Chem.* 2010, *49*, 4478–4485. [CrossRef]
58. Bose, P.P.; Gupta, M.K.; Mittal, R.; Rols, S.; Achary, S.N.; Tyagi, A.K.; Chaplot, S.L. High Pressure Phase Transitions in Yttria, $Y_2O_3$. J. Phys. Conf. Ser. 2012, 377, 012036. [CrossRef]
59. Srivastava, A.M.; Renero-Lecuna, C.; Santamaría-Pérez, D.; Rodríguez, F.; Valiente, R. Pressure-induced $Pr_3^+$ luminescence in cubic $Y_2O_3$. J. Lumin. 2014, 146, 27–32. [CrossRef]
60. Jiang, S.; Liu, J.; Li, X.-D.; Li, Y.-C.; He, S.-M.; Zhang, J.-C. High-Pressure Phase Transitions of Cubic $Y_2O_3$ under High Pressures by In-situ Synchrotron X-Ray Diffraction. Chin. Phys. Lett. 2019, 36, 046103. [CrossRef]
61. Srivastava, A.M.; Renero-Lecuna, C.; Santamaría-Pérez, D.; Rodríguez, F.; Valiente, R. Pressure-induced $Pr_3^+$ luminescence in cubic $Y_2O_3$. J. Lumin. 2014, 146, 27–32. [CrossRef]
62. Zhang, Q.; Wu, X.; Qin, S. Pressure-induced phase transition of B-type $Y_2O_3$. Chin. Phys. B 2017, 26, 090703. [CrossRef]
63. Chen, G.; Peterson, J.R.; Brister, K.E. An Energy-Dispersive X-Ray Diffraction Study of Monoclinic Eu$_2O_3$ under Pressure. J. Solid State Chem. 1994, 111, 437–439. [CrossRef]
64. Atou, T.; Kusaba, K.; Tsuchida, Y.; Utsumi, W.; Yagi, T.; Syono, Y. Reversible B-type- A-type transition of $Sm_2O_3$ under high pressure. Mater. Res. Bull. 1989, 24, 1171–1176. [CrossRef]
65. Hongo, T.; Kondo, K.; Nakamura, K.G.; Atou, T. High pressure Raman spectroscopic study of structural phase transition in samarium oxide. J. Mater. Sci. 2007, 42, 2588–2585. [CrossRef]
66. Guo, Q.X.; Zhao, Y.S.; Jiang, C.; Mao, W.L.; Wang, Z.W.; Zhang, J.Z.; Wang, Y.J. Pressure-Induced Cubic to Monoclinic Phase Transformation in Erbium Sesquioxide Er$_2$O$_3$. Inorg. Chem. 2007, 46, 6164–6169. [CrossRef]
67. Pandey, K.K.; Garg, N.; Mishra, A.K.; Sharma, S.M. High pressure phase transition in Nd$_2$O$_3$. J. Phys. Conf. Ser. 2012, 377, 012006. [CrossRef]
68. Jiang, S.; Liu, J.; Bai, L.G.; Li, X.Y.; He, S.M.; Yan, S.; Liang, D.X. Anomalous compression behaviour of the cerium oxides Ce$_3$O$_5$ studied by x-ray diffraction and Raman spectroscopy. AIP Adv. 2018, 8, 025019. [CrossRef]
69. Lipp, M.J.; Jefferies, J.R.; Cynn, H.; Park Klepeis, J.H.; Evans, W.J.; Mortensen, D.R.; Seidler, G.T.; Xiao, Y.; Chow, P. Comparison of the high-pressure behavior of the cerium oxides Ce$_3$O$_5$. J. Phys. Conf. Ser. 2012, 377, 012053. [CrossRef] [PubMed]
70. Hironaka, N.; Ogata, S.; Kocer, C. Ab initio calculation of the crystal structure of the lanthanide Ln$_2$O$_3$ sesquioxides. J. Alloy. Compd. 2003, 351, 31–34. [CrossRef]
71. Marsella, L.; Fiorentini, V. Structure and stability of rare-earth and transition-metal oxides. Phys. Rev. B 2004, 69, 172103. [CrossRef]
72. Petit, L.; Svane, A.; Szotec, Z.; Temmerman, W.M. First-principles study of rare-earth oxides. Phys. Rev. B 2005, 72, 205118. [CrossRef]
73. Wu, B.; Zinkevich, M.; Chong, W.A.N.G.; Aldinger, F. Ab initio energetic study of oxide ceramics with rare-earth elements. Rare Met. 2006, 25, 549–555. [CrossRef]
74. Singh, N.; Saini, S.M.; Nautiyal, T.; Auluck, S. Electronic structure and optical properties of rare earth sesquioxides (R$_2$O$_3$, R = La, Pr, and Nd). J. Appl. Phys. 2006, 100, 083525. [CrossRef]
75. Mikami, M.; Nakamura, S. Electronic structure of rare-earth sesquioxides and oxysulfides. J. Alloy. Compd. 2006, 408–412, 687–692. [CrossRef]
76. Wu, B.; Zinkevich, M.; Aldinger, F.; Wen, D.Z.; Chen, L. Ab initio study on structure and phase transition of A- and B-type rare-earth sesquioxides Ln$_2$O$_3$ (Ln = La–Lu, Y, and Sc) based on density function theory. J. Solid State Chem. 2007, 180, 3280–3287. [CrossRef]
77. Rahm, M.; Skorodumova, N.V. Phase stability of the rare-earth sesquioxides under pressure. Phys. Rev. B 2009, 80, 104105. [CrossRef]
78. Jiang, H.; Gomez-Abal, R.I.; Rinke, P.; Scheffler, M. Localized and Itinerant States in Lanthanide Oxides United by GW0LDA+U. Phys. Rev. Lett. 2009, 102, 126403. [CrossRef] [PubMed]
79. Gillen, R.; Clark, S.J.; Robertson, J. Nature of the electronic band gap in lanthanide oxides. Phys. Rev. B 2013, 87, 125116. [CrossRef]
80. Richard, D.; Muñoz, E.L.; Rentería, M.; Errico, L.A.; Svane, A.; Christensen, N.E. Ab initio LSDA and LSDA+U study of pure and Cd-doped cubic lanthanide sesquioxides. Phys. Rev. B 2013, 88, 165206. [CrossRef]
81. Richard, D.; Errico, L.A.; Rentería, M. Structural properties and the pressure-induced C → A phase transition of lanthanide sesquioxides from DFT and DFT+U calculations. J. Alloy. Compd. 2016, 664, 580–589. [CrossRef]
82. Ogawa, T.; Otani, N.; Yokoi, T.; Fisher, C.A.J.; Kuwabara, A.; Moriwake, H.; Yoshiya, M.; Kitaoka, S.; Takata, M. Density functional study of phase stabilities and Raman spectra of \( \text{Yb}_2\text{O}_3 \), \( \text{Yb}_2\text{SiO}_5 \) and \( \text{Yb}_2\text{Si}_2\text{O}_7 \) under pressure. *Phys. Chem. Chem. Phys.* 2018, 20, 16518–16527. [CrossRef]

83. Pathak, A.K.; Vazhappilly, T. Ab Initio Study on Structure, Elastic, and Mechanical Properties of Lanthanide Sesquioxides. *Phys. Stat. Sol. B* 2018, 255, 1700668. [CrossRef]

84. Catlow, C.R.A.; Guo, Z.X.; Miskufova, M.; Shevlin, S.A.; Smith, A.G.H.; Sokol, A.A.; Walsh, A.; Wilson, D.J.; Woodley, S.M. Advances in computational studies of energy materials. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* 2010, 368, 3379–3456. [CrossRef]

85. Caracas, R.; Cohen, R.E. Prediction of a new phase transition in \( \text{Al}_2\text{O}_3 \) at high pressures. *Geophys. Res. Lett.* 2005, 32, 1–4. [CrossRef]

86. Funamori, N. High-Pressure Transformation of \( \text{Al}_2\text{O}_3 \). *Science* 1997, 278, 1109–1111. [CrossRef]

87. Cynn, H.; Isaak, D.G.; Cohen, R.E.; Nicol, M.F.; Anderson, O.L. A high-pressure phase transition of corundum predicted by the potential induced breathing model. *Am. Mineral.* 1990, 75, 439–442.

88. Jephcoat, A.P.; Hemley, R.J.; Mao, H.K. X-ray diffraction of ruby (\( \text{Al}_2\text{O}_3\cdot \text{Cr}^{3+} \)) to 175 GPa. *Phys. B C* 1988, 150, 115–121. [CrossRef]

89. Dewaele, A.; Torrent, M. Equation of state of \( \alpha\text{-Al}_2\text{O}_3 \). *Phys. Rev. B* 2013, 88, 064107. [CrossRef]

90. Costa, T.M.H.; Gallas, M.R.; Benvenutti, E.V.; da Jornada, J.A.H. Study of Nanocrystalline \( \gamma\text{-Al}_2\text{O}_3 \) Produced by High-Pressure Compaction. *J. Phys. Chem. B* 1999, 103, 4278–4284. [CrossRef]

91. Hart, H.V.; Drickamer, H.G. Effect of high pressure on the lattice parameters of \( \text{Al}_2\text{O}_3 \). *J. Chem. Phys.* 1965, 43, 2265–2266. [CrossRef]

92. Marton, F.C.; Cohen, R.E. Prediction of a high-pressure phase transition in \( \text{Al}_2\text{O}_3 \). *Am. Miner.* 1994, 79, 789–792.

93. Mashimo, T.; Tsumoto, K.; Nakamura, K.; Noguchi, Y.; Fukuoka, K.; Syono, Y. High-pressure phase transformation of corundum (\( \alpha\text{-Al}_2\text{O}_3 \)) observed under shock compression. *Geophys. Res. Lett.* 2000, 27, 2021–2024. [CrossRef]

94. Ono, S.; Ogano, A.R.; Koyama, T.; Shimizu, H. Stability and compressibility of the high-pressure phases of \( \text{Al}_2\text{O}_3 \) up to 200 GPa: Implications for the electrical conductivity of the base of the lower mantle. *Earth Planet. Sci. Lett.* 2006, 246, 326–335. [CrossRef]

95. Zhao, J.; Hearne, G.R.; Maaza, M.; Laher-Lacour, F.; Witcomb, M.J.; Le Bihan, T.; Mezouar, M. Compressibility of nanostructured alumina phases determined from synchrotron x-ray diffraction studies at high pressure. *J. Appl. Phys.* 2001, 90, 3280–3285. [CrossRef]

96. Thomson, K.T.; Wentzcovitch, R.M.; Bukowinski, M.S.T. Polymorphs of alumina predicted by first principles: Putting pressure on the ruby pressure scale. *Science* 1996, 274, 1880–1882. [CrossRef]

97. Lin, J.F.; Degtyareva, O.; Prewitt, C.T.; Dera, P.; Sata, N.; Gregoryanz, E.; Mao, H.K.; Hemley, R.J. Crystal structure of a high-pressure/high-temperature phase of alumina by in situ X-ray diffraction. *Nat. Mater.* 2004, 3, 389–393. [CrossRef]

98. Jahn, S.; Madden, P.A.; Wilson, M. Dynamic simulation of pressure-driven phase transformations in crystalline \( \text{Al}_2\text{O}_3 \). *Phys. Rev. B* 2004, 69, 020106. [CrossRef]

99. Tsuchiya, J.; Tsuchiya, T.; Wentzcovitch, R.M. Transition from the Rh\(_3\text{O}_3\)(II)-to-CaIrO\(_3\) structure and the high-pressure-temperature phase diagram of alumina. *Phys. Rev. B* 2005, 72, 020103. [CrossRef]

100. Garcia-Domene, B.; Ortiz, H.M.; Gomis, O.; Sans, J.A.; Manjón, F.J.; Muñoz, A.; Rodriguez-Hernández, P.; Achary, S.N.; Errandonea, D.; Martínez-García, D.; et al. High-pressure lattice dynamical study of bulk and nanocrystalline \( \text{In}_2\text{O}_3 \). *J. Appl. Phys.* 2012, 112, 123511. [CrossRef]

101. Garcia-Domene, B.; Sans, J.A.; Gomis, O.; Manjón, F.J.; Ortiz, H.M.; Errandonea, D.; Santamaría-Pérez, D.; Martínez-García, D.; Vilaplana, R.; Pereira, A.L.J.; et al. \text{Pbca}-type \( \text{In}_2\text{O}_3 \): The high-pressure post-corundum phase at room temperature. *J. Phys. Chem. C* 2014, 118, 20545–20552. [CrossRef]

102. Gurlo, A. Structural stability of high-pressure polymorphs in \( \text{In}_2\text{O}_3 \) nanocrystals: Evidence of stress-induced transition? *Angew. Chem. Int. Ed.* 2010, 49, 5610–5612. [CrossRef]

103. Liu, D.; Lei, W.W.; Zou, B.; Yu, S.D.; Hao, J.; Wang, K.; Liu, B.B.; Cui, Q.L.; Zou, G.T. High-pressure x-ray diffraction and Raman spectra study of indium oxide. *J. Appl. Phys.* 2008, 104, 083506. [CrossRef]

104. Qi, J.; Liu, J.F.; He, Y.; Chen, W.; Wang, C. Compression behavior and phase transition of cubic \( \text{In}_2\text{O}_3 \) nanocrystals. *J. Appl. Phys.* 2011, 109, 063520. [CrossRef]
105. Tang, S.; Li, Y.; Zhang, J.; Zhu, H.; Dong, Y.; Zhu, P.; Cui, Q. Effects of microstructures on the compression behavior and phase transition routine of In$_2$O$_3$ nanocubes under high pressures. *RSC Adv.* 2015, 5, 85105–85110. [CrossRef]

106. Yusa, H.; Tsuchiya, T.; Sata, N.; Ohishi, Y. Rh$_2$O$_3$(II)-type structures in Ga$_2$O$_3$ and In$_2$O$_3$ under high pressure: Experiment and theory. *Phys. Rev. B* 2008, 77, 064107. [CrossRef]

107. Yusa, H.; Tsuchiya, T.; Sata, N.; Ohishi, Y. α-Gd$_2$S$_3$-type structure in In$_2$O$_3$: Experiments and theoretical confirmation of a high-pressure polymorph in sesquioxide. *Phys. Rev. B* 2008, 78, 092107. [CrossRef]

108. Garcia-Domene, B.; Sans, J.A.; Manjón, F.J.; Ovsyannikov, S.V.; Dubrovinsky, L.S.; Martínez-García, D.; Comis, O.; Errandonea, D.; Moutaabbid, H.; Le Godec, Y.; et al. Synthesis and High-Pressure Study of Corundum-Type In$_2$O$_3$. *J. Phys. Chem. C* 2015, 119, 29076–29087. [CrossRef]

109. Sans, J.A.; Vilaplana, R.; Errandonea, D.; Cuenca-Gotor, V.P.; García-Domene, B.; Popescu, C.; Manjón, F.J.; Singhal, A.; Achary, S.N.; Martínez-Garcia, D.; et al. Structural and vibrational properties of corundum-type In$_2$O$_3$ nanocrystals under compression. *Nanotechnology* 2017, 28, 205701. [CrossRef] [PubMed]

110. Lipinska-Kalita, K.E.; Kalita, P.E.; Hemmers, O.A.; Hartmann, T. Equation of state of gallium oxide to 70 GPa: Comparison of quasihydrostatic and nonhydrostatic compression. *Phys. Rev. B* 2008, 77, 094123. [CrossRef]

111. Lipinska-Kalita, K.E.; Chen, B.; Kruger, M.B.; Ohki, Y.; Murowchick, J.; Gogol, E.P. High-pressure x-ray diffraction studies of the nanostructured transparent vitroceramic medium K$_2$O-SiO$_2$-Ga$_2$O$_3$. *Phys. Rev. B* 2003, 68, 035209. [CrossRef]

112. Luan, S.; Dong, L.; Jia, R. Analysis of the structural, anisotropic elastic and electronic properties of β-Ga$_2$O$_3$ with various pressures. *J. Cryst. Growth* 2019, 505, 74–81. [CrossRef]

113. Machon, D.; McMillan, P.F.; Xu, B.; Dong, J. High-pressure study of the β-to-α transition in Ga$_2$O$_3$. *Phys. Rev. B* 2006, 73, 094125. [CrossRef]

114. Wang, H.; He, Y.; Chen, W.; Zeng, Y.W.; Stahl, K.; Kikegawa, T.; Jiang, J.Z. High-pressure behavior of β-Ga$_2$O$_3$ nanocrystals. *J. Appl. Phys.* 2010, 107, 033520. [CrossRef]

115. Claussen, W.F.; Mackenzie, J.D. Crystallization of B$_2$O$_3$ at High Pressures. *J. Am. Chem. Soc.* 1959, 81, 1007. [CrossRef]

116. Prewitt, C.T.; Shannon, R.D. Crystal structure of a high-pressure form of B$_2$O$_3$. *Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem.* 1968, 24, 869–874. [CrossRef]

117. Brazhkin, V.V.; Katayama, Y.; Inamura, Y.; Kondrin, M.V.; Lyapin, A.G.; Popova, S.V.; Voloshin, R.N. Structural transformations in liquid, crystalline, and glassy B$_2$O$_3$ under high pressure. *JETP Lett.* 2003, 78, 393–397. [CrossRef]

118. Nicholas, J.; Sinogeikin, S.; Kieffer, J.; Bass, J. Spectroscopic evidence of polymorphism in vitreous B$_2$O$_3$. *Phys. Rev. Lett.* 2004, 92, 3–6. [CrossRef] [PubMed]

119. Lee, S.K.; Mibe, K.; Fei, Y.; Cody, G.D.; Mysen, B.O. Structure of B$_2$O$_3$ glass at high pressure: A 11B solid-state NMR study. *Phys. Rev. Lett.* 2005, 94, 27–30. [CrossRef] [PubMed]

120. Kulikova, L.F.; Dyuzheva, T.I.; Nikolaev, N.A.; Brazhkin, V.V. Single-crystal growth of the high-pressure phase B$_2$O$_3$ II. *Crystallogr. Rep.* 2012, 57, 332–335. [CrossRef]

121. Burianek, M.; Birkenstock, J.; Mair, P.; Kahlenberg, V.; Medenbach, O.; Shannon, R.D.; Fischer, R.X. High-pressure synthesis, long-term stability of single crystals of diboron trioxide, B$_2$O$_3$, and an empirical electronic polarizability of [3]B$^{3+}$. *Phys. Chem. Miner.* 2016, 43, 527–534. [CrossRef]

122. Comis, O.; Santamaria-Pérez, D.; Ruiz-Fuertes, J.; Sans, J.A.; Vilaplana, R.; Ortiz, H.M.; García-Domene, B.; Manjón, F.J.; Errandonea, D.; Rodriguez-Hernández, P.; et al. High-pressure structural and elastic properties of Th$_2$O$_3$. *J. Appl. Phys.* 2014, 116, 133521. [CrossRef]

123. Weir, S.T.; Mitchell, A.C.; Nellis, W.J. Electrical resistivity of single-crystal Al$_2$O$_3$ shock-compressed in the pressure range 91-220 GPa (0.91-2.20 Mbar). *J. Appl. Phys.* 1996, 80, 1522–1525. [CrossRef]

124. Syassen, K. Ruby under pressure. *High Press. Res.* 2008, 28, 75–126. [CrossRef]

125. Smyth, J.R.; Jacobsen, S.D.; Hazen, R.M. Comparative Crystal Chemistry of Dense Oxide Minerals. *Rev. Miner. Geochem.* 2000, 41, 157–186. [CrossRef]

126. Song, H.I.; Kim, E.S.; Yoon, K.H. Phase transformation and characteristics of beta-alumina. *Phys. B C* 1988, 150, 148–159. [CrossRef]
127. Engürlü, S.; Taslicukur Öztürk, Z.; Kuskonmaz, N. Investigation of the Production of β-Al2O3 Solid Electrolyte from Seydiseh Me-Al2O3. Süleyman Demirel Üniversitesi Fen Bilimleri Enstitüsü Derg. 2017, 21, 816. [CrossRef]

128. Duan, W.; Wentzcowitch, R.M.; Thomson, K.T. First-principles study of high-pressure alumina polymorphs. Phys. Rev. B 1998, 57, 10363–10369. [CrossRef]

129. Oganova, A.R.; Ono, S. The high-pressure phase of alumina and implications for Earth’s D” layer. Proc. Natl. Acad. Sci. USA 2005, 102, 10828–10831. [CrossRef]

130. Hama, J.; Suito, K. The evidence for the occurrence of two successive transitions in Al2O3 from the analysis of Hugoniot data. High Temp. High Press. 2002, 34, 323–334. [CrossRef]

131. Ono, S.; Kikegawa, T.; Ohishi, Y. High-pressure phase transition of hematite, Fe3O2. J. Phys. Chem. Solids 2004, 65, 1527–1530. [CrossRef]

132. Mishra, R.S.; Lesher, C.E.; Mukherjee, A.K. High-Pressure Sintering of Nanocrystalline γ-Al2O3. High Temp. High Press. 2002, 2989–2992. [CrossRef]

133. Vaidya, S.N.; Karunakaran, C.; Achary, S.N.; Tyagi, A.K. New polymorphs of alumina: Part II mu and lambda alumina. High Press. Res. 1999, 16, 147–160. [CrossRef]

134. Vaidya, S.N.; Karunakaran, C.; Achary, S.N.; Tyagi, A.K. New polymorphs of alumina: Part II mu and lambda alumina. High Press. Res. 1999, 16, 265–278. [CrossRef]

135. Bekheet, M.F.; Schwarz, M.R.; Lauterbach, S.; Kleebe, H.J.; Kroll, P.; Riedel, R.; Gurlo, A. Orthorhombic In2O3: A metastable polymorph of indium sesquioxide. Angew. Chem. Int. Ed. 2013, 52, 6531–6535. [CrossRef]

136. Vaidya, S.N.; Karunakaran, C.; Achary, S.N.; Tyagi, A.K. New polymorphs of alumina: Part II mu and lambda alumina. High Press. Res. 1999, 16, 265–278. [CrossRef]

137. Bekheet, M.F.; Schwarz, M.R.; Lauterbach, S.; Kleebe, H.J.; Kroll, P.; Riedel, R.; Gurlo, A. Orthorhombic In2O3: A metastable polymorph of indium sesquioxide. Angew. Chem. Int. Ed. 2013, 52, 6531–6535. [CrossRef]

138. Karazhanov, S.Z.; Ravindran, P.; Vajeeston, P.; Ulyashin, A.; Finstad, T.G.; Fjellvang, H. Phase stability, electronic structure, and optical properties of indium oxide polytypes. Phys. Rev. B 2007, 76, 075129. [CrossRef]

139. Shannon, R.D. New high pressure phases having the corundum structure. Solid State Commun. 1966, 4, 629–630. [CrossRef]

140. Prewitt, C.T.; Shannon, R.D.; Rogers, D.B.; Sleight, A.W. The C rare earth oxide-corundum transition and the high pressure-temperature phase diagram of gallia: A first-principles and x-ray diffraction study. Phys. Rev. B 2007, 76, 174108. [CrossRef]

141. Kishimura, H.; Matsumoto, H. Evaluation of the shock-induced phase transition in α-Al2O3. Jpn. J. Appl. Phys. 2018, 57, 125003. [CrossRef]

142. Phillips, R.J.; Shane, M.J.; Switzer, J.A. Electrochemical and photoelectrochemical deposition of thallium(III) oxide thin films. J. Mater. Res. 1989, 4, 923–929. [CrossRef]
153. Van Leeuwen, R.A.; Hung, C.J.; Kammler, D.R.; Switzer, J.A. Optical and electronic transport properties of electrodeposited thallium(III) oxide films. *J. Phys. Chem.* 1995, 99, 15247–15252. [CrossRef]

154. Bhattacharya, R.N.; Yan, S.L.; Xing, Z.; Xie, Y.; Wu, J.Z.; Feldmann, M.; Chen, J.; Xiong, Q.; Ren, Z.F.; Blaugher, R.D. Superconducting Thallium Oxide and Mercury Oxide Films. *MRS Online Proc. Libr. Arch.* 2000, 659. [CrossRef]

155. Ma, C.; Rossman, G.R. Tistarite, Ti2O3, a new refractory mineral from the Allende meteorite. *Am. Mineral.* 2009, 94, 841–844. [CrossRef]

156. Xue, K.H.; Blaise, P.; Fonseca, L.R.C.; Nishi, Y. Prediction of semimetallic tetragonal Hf2O3 and Zr2O3 from first principles. *Phys. Rev. Lett.* 2013, 110, 065502. [CrossRef]

157. Ovsyannikov, S.V.; Trots, D.M.; Kurnosov, A.V.; Morgenroth, W.; Liermann, H.P.; Dubrovinsky, L. Anomalous compression and new high-pressure phases of vanadium sesquioxide, V2O3. *J. Phys. Condens. Matter* 2013, 25, 385401. [CrossRef]

158. Goodenough, J.B.; Hamnett, A.; Huber, G.; Hullinger, F.; Leiß, M.; Ramasesha, S.K.; Werheit, H. *Physics of Non-Tetrahedrally Bonded Binary Compounds III/Physik der Nicht-Tetraedrisch Gebundenen Binären Verbindungen III*; Madelung, O., Ed.; Springer: Berlin, Germany, 1984.

159. Pasternak, M.P.; Rozenberg, G.K.; Machavariani, G.Y.; Naaman, O.; Taylor, R.D.; Jeanloz, R. Breakdown of the mott-hubbard state in FeO: A first-order insulator-metal transition with collapse of magnetism at 50 GPa. *Phys. Rev. Lett.* 1999, 82, 4663–4666. [CrossRef]

160. Frost, D.J.; Liebske, C.; Langenhorst, F.; McCammon, C.A.; Trønnes, R.G.; Rubie, D.C. Experimental evidence for the existence of iron-rich metal in the Earth’s lower mantle. *Nature* 2004, 428, 409–412. [CrossRef]

161. Kupenko, I.; Aprilis, G.; Vasiukov, D.M.; McCammon, C.; Chariton, S.; Cerantola, V.; Kantor, I.; Chumakov, A.I.; Dejoie, C.; Sciau, P.; Li, W.; Noda, K. An unusual superconducting Thallium Oxide and Mercury Oxide Films. *MRS Online Proc. Libr. Arch.* 2000, 659. [CrossRef]

162. Schrader, R.; Büttner, G. Eine neue Eisen(III)-oxidphase: *Z. Anorg. Allg. Chem.* 1963, 320, 220–234. [CrossRef]

163. Xu, H.; Lee, S.; Xu, H. Luogufengite: A new nano-mineral of Fe2O3 with giant coercive field. *Am. Mineral.* 2017, 102, 711–719. [CrossRef]

164. Dejoie, C.; Sciau, P.; Li, W.; Noë, L.; Mehta, A.; Chen, K.; Luo, H.; Kunz, M.; Tamura, N.; Liu, Z. Learning from the past: Rare ε-Fe2O3 in the ancient black-glazed Jian (Tenmoku) wares. *Sci. Rep.* 2015, 4, 4941. [CrossRef]

165. Xu, H.; Lee, S.; Xu, H. Luogufengite: A new nano-mineral of Fe2O3 with giant coercive field. *Am. Mineral.* 2017, 102, 711–719. [CrossRef]

166. Dejoie, C.; Sciau, P.; Li, W.; Noë, L.; Mehta, A.; Chen, K.; Luo, H.; Kunz, M.; Tamura, N.; Liu, Z. Learning from the past: Rare ε-Fe2O3 in the ancient black-glazed Jian (Tenmoku) wares. *Sci. Rep.* 2015, 4, 4941. [CrossRef]

167. Tronc, E.; Chanéac, C.; Jolivet, J.P. Structural and Magnetic Characterization of ε-Fe2O3. *J. Solid State Chem.* 1998, 139, 93–104. [CrossRef]

168. Tuček, J.; Zbořil, R.; Namai, A.; Ohkoshi, S. Fe2O3. *Z. Anorg. Allg. Chem.* 1995, 632, 220–234. [CrossRef]

169. Tuček, J.; Machala, L.; Ono, S.; Namai, A.; Yoshikiyo, M.; Imoto, K.; Tokoro, H.; Ohkoshi, S.; Zbořil, R. Zeta-Fe2O3—A new stable polymorph in iron(III) oxide family. *Sci. Rep.* 2015, 5, 15091. [CrossRef]

170. Rozenberg, G.K.; Dubrovinsky, L.S.; Pasternak, M.P.; Naaman, O.; Le Bihan, T.; Ahuja, R. High-pressure structural studies of hematite (Fe2O3). *Phys. Rev. B* 2002, 65, 064112. [CrossRef]

171. Badro, J.; Fiquet, G.; Struzhkin, V.V.; Somayazulu, M.; Mao, H.K.; Shen, G.; Le Bihan, T. Nature of the high-pressure transition in Fe2O3 hematite. *Phys. Rev. Lett.* 2002, 89, 205504. [CrossRef]

172. Ito, E.; Fukui, H.; Katsura, T.; Yamazaki, D.; Yoshino, T.; Aizawa, Y.; Kubo, A.; Yokoshi, S.; Kawabe, K.; Zhai, S.; et al. Determination of high-pressure phase equilibria of Fe2O3 using the Kawai-type apparatus equipped with sintered diamond anvils. *Am. Mineral.* 2009, 94, 205–209. [CrossRef]

173. Bykova, E.; Bykov, M.; Prakapenka, V.; Konopková, Z.; Liermann, H.-P.; Dubrovinskaia, N.; Dubrovinsky, L. Novel high pressure monoclinic Fe2O3 polymorph revealed by single-crystal synchrotron X-ray diffraction studies. *High Press. Res.* 2013, 33, 534–545. [CrossRef]

174. Sanson, A.; Kantor, I.; Cerantola, V.; Irifune, T.; Carnera, A.; Pascarelli, S. Local structure and spin transition in Fe2O3 hematite at high pressure. *Phys. Rev. B* 2016, 94, 014112. [CrossRef]
175. Bykova, E.; Dubrovinsky, L.; Dubrovinskaia, N.; Bykov, M.; McCammon, C.; Ovsyannikov, S.V.; Liermann, H.P.; Kupenko, I.; Chumakov, A.I.; Rüffer, R.; et al. Structural complexity of simple Fe$_3$O$_4$ at high pressures and temperatures. *Nat. Commun.* 2016, 7, 10661. [CrossRef]

176. Greenberg, E.; Leonov, I.; Layek, S.; Konopkova, Z.; Pasternak, M.P.; Dubrovinsky, L.; Jeanloz, R.; Abrikosov, I.A.; Rozenberg, G.K. Pressure-Induced Site-Selective Mott Insulator-Metal Transition in Fe$_3$O$_4$. *Phys. Rev. X* 2018, 8, 31059. [CrossRef]

177. Liu, H.; Caldwell, A.; Benedetti, L.R.; Panero, W.; Jeanloz, R. Static compression of α-Fe$_2$O$_3$: Linear incompressibility of lattice parameters and high-pressure transformations. *Phys. Chem. Miner.* 2003, 30, 582–588. [CrossRef]

178. Olsen, J.S.; Cousins, C.S.G.; Gerward, L.; Jhans, H.; Sheldon, B.J. A study of the crystal structure of Fe$_2$O$_3$ in the pressure range up to 65 GPa using synchrotron radiation. *Phys. Scr.* 1991, 43, 327–330. [CrossRef]

179. Shim, S.H.; Bengtson, A.; Morgan, D.; Sturhahn, W.; Catalli, K.; Zhao, J.; Lerche, M.; Prakapenka, V.B. High-pressure phase transition in Mn$_3$O$_4$. *J. Solid State Chem.* 1998, 50, 97–100. [CrossRef]

180. Syono, Y.; Ito, A.; Morimoto, S.; Suzuki, T.; Yagi, T.; Akimoto, S. Mössbauer study on the high pressure phase of Fe$_2$O$_3$. *Solid State Commun.* 1984, 50, 1183–1186. [CrossRef]

181. Nasu, S.; Kurimoto, K.; Nagatomo, S.; Endo, S.; Fujita, F.E. 57Fe Mössbauer study under high pressure; ε-Fe$_2$O$_3$ and Fe$_3$O$_4$. *Hyperfine Interact.* 1986, 29, 1583–1586. [CrossRef]

182. Jiang, J.Z.; Olsen, J.S.; Gerward, L.; Merup, S. Enhanced bulk modulus and reduced transition pressure in γ-Fe$_2$O$_3$ nanocrystals. *Eur. Phys. Lett.* 1998, 44, 620–626. [CrossRef]

183. Zhu, H.; Ma, Y.; Yang, H.; Ji, C.; Hou, D.; Guo, L. Pressure induced phase transition of nanocrystalline and bulk maghemite (γ-Fe$_2$O$_3$) to hematite (α-Fe$_2$O$_3$). *J. Phys. Chem. Solids* 2010, 71, 1183–1186. [CrossRef]

184. MacHala, L.; Tuček, J.; Zbořil, R. Polymorphous transformations of nanometric iron(III) oxide: A review. *J. Solid State Chem.* 2012, 187, 134–142. [CrossRef]

185. Hearne, G.; Pischedda, V. Pressure response of vacancy ordered maghemite (Fe$_{0.98}Fe_{0.02}O_3$) and implications for planetary magnetic records and deep interiors. *Proc. Natl. Acad. Sci. USA* 2009, 106, 5508–5512. [CrossRef]

186. Sans, J.A.; Monteseguro, V.; Garbarino, G.; Gich, M.; Cerantola, V.; Cuartero, V.; Monte, M.; Irifune, T.; Muñoz, A.; Popescu, C. Stability and nature of the volume collapse of ε-Fe$_2$O$_3$ and magnetic structures of the postperovskite-type Fe$_3$O$_4$. *Phys. Scr.* 2013, 87, 065005. [CrossRef]

187. Grant, R.W.; Geller, S.; Cape, J.A.; Espinosa, G.P. Magnetic and crystallographic transitions in the α-Mn$_2$O$_3$-Fe$_2$O$_3$ system. *Phys. Rev.* 1968, 175, 686–695. [CrossRef]

188. Geller, S. Structure of α-Mn$_2$O$_3$, (Mn$_{0.98}Fe_{0.02})_2$O$_3$ and (Mn$_{0.37}Fe_{0.63})_2$O$_3$ and relation to magnetic ordering. *Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem.* 1971, 27, 821–828. [CrossRef]

189. Yamanaka, T.; Nagai, T.; Okada, T.; Fukuda, T. Structure change of Mn$_2$O$_3$ under high pressure and pressure-induced transition. *Z. Kristallog.* 2005, 220, 938–945. [CrossRef]

190. Santillán, J.; Shim, S.H.; Shen, G.; Prakapenka, V.B. High-pressure phase transition in Mn$_2$O$_3$: Application for the crystal structure and preferred orientation of the CaIr$_3$O$_7$ type. *Geophys. Res. Lett.* 2006, 33, L15307. [CrossRef]

191. Shim, S.H.; LaBounty, D.; Duffy, T.S. Raman spectra of bixbyite, Mn$_3$O$_2$, up to 40 GPa. *Phys. Chem. Miner.* 2011, 38, 685–691. [CrossRef]

192. Mukherjee, G.D.; Vaidya, S.N.; Karunakaran, C. High Pressure and High Temperature Studies on Manganese Oxides. *Phase Trans.* 2002, 75, 557–566. [CrossRef]

193. Ovsyannikov, S.V.; Abakumov, A.M.; Tsirlin, A.A.; Schnelle, W.; Egoavil, R.; Verbeeck, J.; Van Tendeloo, G.; Glazyrin, K.V.; Hanfland, M.; Dubrovinsky, L. Perovskite-like Mn$_2$O$_3$: A path to new manganites. *Angew. Chem. Int. Ed.* 2013, 52, 1494–1498. [CrossRef]

194. Hong, F.; Yue, B.; Hirao, N.; Liu, Z.; Chen, B. Significant improvement in Mn$_3$O$_5$ transition metal oxide electrical conductivity via high pressure. *Sci. Rep.* 2017, 7, 44078. [CrossRef]

195. Ovsyannikov, S.V.; Karkin, A.E.; Morozova, N.V.; Shchennikov, V.V.; Bykova, E.; Abakumov, A.M.; Tsirlin, A.A.; Glazyrin, K.V.; Dubrovinsky, L. A hard oxide semiconductor with a direct and narrow bandgap and switchable p-n electrical conduction. *Adv. Mater.* 2014, 26, 8185–8191. [CrossRef]

196. Khalyavin, D.D.; Johnson, R.D.; Manuel, P.; Tsirlin, A.A.; Abakumov, A.M.; Kozlenko, D.P.; Sun, Y.; Dubrovinsky, L.; Ovsyannikov, S.V. Magneto-orbital texture in the perovskite modification of Mn$_3$O$_5$. *Phys. Rev. B* 2018, 98, 014426. [CrossRef]
197. McWhan, D.B.; Rice, T.M.; Remeika, J.P. Mott Transition in Cr-Doped V$_2$O$_3$. *Phys. Rev. Lett.* 1969, 23, 1384–1387. [CrossRef]

198. Lupi, S.; Balassarre, L.; Mansant, B.; Perucchi, A.; Barinov, A.; Dudin, P.; Papalazarou, E.; Rodolakis, F.; Ruff, J.P.; Itié, J.P.; et al. A microscopic view on the Mott transition in chromium-doped V$_2$O$_3$. *Nat. Commun.* 2010, 1, 105. [CrossRef]

199. Weber, D.; Stork, A.; Nakhal, S.; Wessel, C.; Reimann, C.; Hermes, W.; Müller, A.; Ressler, T.; Pöttgen, R.; Bredow, T.; et al. Bixbyte-Type V$_2$O$_3$—A Metastable Polymorph of Vanadium Sesquioxide. *Inorg. Chem.* 2011, 50, 6762–6766. [CrossRef] [PubMed]

200. McWhan, D.B.; Remeika, J.P. Metal-Insulator Transition in (V$_{1-x}$Cr$_x$)O$_3$. *Phys. Rev. B* 1970, 2, 3734–3750. [CrossRef]

201. Jayaraman, A.; McWhan, D.B.; Remeika, J.P.; Dernier, P.D. Critical Behavior of the Mott Transition in Cr-Doped V$_2$O$_3$. *Phys. Rev. B* 1970, 2, 3751–3756. [CrossRef]

202. Carter, S.A.; Rosenbaum, T.F.; Lu, M.; Jaeger, H.M.; Metcalf, P.; Honig, J.M.; Spalek, J. Magnetic and transport studies of pure V$_2$O$_3$ under pressure. *Phys. Rev. B* 1994, 49, 7898–7903. [CrossRef] [PubMed]

203. Limelette, P.; Georges, A.; Jérome, D.; Wzietek, P.; Metcalf, P.; Honig, J.M. Universality and critical behavior at the Mott transition. *Science* 2003, 302, 89–92. [CrossRef]

204. Rodolakis, F.; Hansmann, P.; Ruff, J.-P.; Toschi, A.; Haverkort, M.W.; Sangiovanni, G.; Tanaka, A.; Saha-Dasgupta, T.; Andersen, O.K.; Held, K.; et al. Inequivalent Routes across the Mott Transition in V$_2$O$_3$ Explored by X-Ray Absorption. *Phys. Rev. Lett.* 2010, 104, 047401. [CrossRef]

205. Alyabyeva, N.; Sakai, J.; Bavencoffe, M.; Wolfman, J.; Limelette, P.; Funakubo, H.; Ruyter, A. Metal-insulator transition in V$_2$O$_3$ thin film caused by tip-induced strain. *Appl. Phys. Lett.* 2018, 113, 241603. [CrossRef]

206. Finger, L.W.; Hazen, R.M. Crystal structure and isothermal compression of Fe$_2$O$_3$, Cr$_2$O$_3$, and V$_2$O$_3$ to 50 kbars. *J. Appl. Phys.* 1980, 51, 5362–5367. [CrossRef]

207. Zhang, Q.; Wu, X.; Qin, S. Pressure-induced phase transition of V$_2$O$_3$. *Chin. Phys. Lett.* 2012, 29, 106101. [CrossRef]

208. Zhang, Q.; Wu, X.; Qin, S. A nine-fold coordinated vanadium by oxygen in V$_2$O$_3$ from first-principles calculations. *Eur. Phys. J. B* 2012, 85, 267. [CrossRef]

209. Aggarwal, P.S.; Goswami, A. An oxide of tervalent nickel. *J. Phys. Chem.* 1961, 65, 2105. [CrossRef]

210. Conell, R.S.; Corrigan, D.A.; Powell, B.R. The electrochromic properties of sputtered nickel oxide films. *Sol. Energy Mater. Sol. Cells* 1992, 25, 301–313. [CrossRef]

211. Jones, P.G.; Rumpel, H.; Schwarzmann, E.; Sheldrick, G.M. Gold (III) oxide. *Acta Cryst. B* 1979, 35, 1435–1437. [CrossRef]

212. Minomura, S.; Drickamer, H.G. Effect of Pressure on the Electrical Resistance of some Transition-Metal Oxides and Sulfides. *J. Phys. Chem.* 1963, 64, 3043–3048. [CrossRef]

213. Chenavas, J.; Joubert, J.C.; Marezio, M. Low-spin $\Rightarrow$ high-spin state transition in high pressure cobalt sesquioxide. *Solid State Commun.* 1971, 9, 1057–1060. [CrossRef]

214. Rekhi, S.; Dubrovinsky, L.S.; Ahuja, R.; Saxena, S.K.; Johansson, B. Experimental and theoretical investigations on eskolaite (Cr$_2$O$_3$) at high pressures. *J. Alloy. Compd.* 2000, 302, 16–20. [CrossRef]

215. Kato, Y.; Yoshimori, Y.; Imamura, H.; Kimura, T. Enhancement of magnetoelectric operating temperature in compressed Cr$_2$O$_3$ under hydrostatic pressure. *Appl. Phys. Lett.* 2017, 110, 042902. [CrossRef]

216. Kantor, A.; Kantor, I.; Merlini, M.; Glazyrin, K.; Prescher, C.; Hanfland, M.; Dubrovinsky, L. High-pressure structural studies of eskolaite by means of single-crystal X-ray diffraction. *Am. Mineral.* 2012, 97, 1764–1770. [CrossRef]

217. Shim, S.H.; Duffy, T.S.; Jeanlou, R.; Yoo, C.S.; Iota, V. Raman spectroscopy and x-ray diffraction of phase transitions in Cr$_2$O$_3$ to 61 GPa. *Phys. Rev. B* 2004, 69, 144107. [CrossRef]

218. Dobin, A.Y.; Duan, W.; Wentzcovitch, R.M. Magnetostructural effects and phase transition in Cr$_2$O$_3$ under pressure. *Phys. Rev. B* 2000, 62, 11997–12000. [CrossRef]

219. Golosova, N.O.; Kozlenko, D.P.; Kichanov, S.E.; Lukin, E.V.; Liermann, H.-P.; Glazyrin, K.V.; Savenko, B.N. Structural and magnetic properties of Cr$_2$O$_3$ at high pressure. *J. Alloy. Compd.* 2017, 722, 593–598. [CrossRef]

220. Nishio-Hamane, D.; Katagiri, M.; Niwa, K.; Sano-Furukawa, A.; Okada, T.; Yagi, T. A new high-pressure polymorph of Ti$_2$O$_3$: Implication for high-pressure phase transition in sesquioxides. *High Press. Res.* 2009, 29, 379–388. [CrossRef]
221. Umemoto, K.; Wentzcovitch, R.M. Prediction of an U2S3-type polymorph of Al2O3 at 3.7 Mbar. Proc. Natl. Acad. Sci. USA 2008, 105, 6526–6530. [CrossRef] [PubMed]

222. Ovsyannikov, S.V.; Wu, X.; Shchennikov, V.V.; Karkin, A.E.; Dubrovinskaia, N.; Garbarino, G.; Dubrovinsky, L. Structural stability of a golden semiconducting orthorhombic polymorph of Ti2O3 under high pressures and high temperatures. J. Phys. Condens. Matter 2010, 22, 375402. [CrossRef] [PubMed]

223. Zheng, F.L.; Li, G.R.; Ou, Y.N.; Wang, Z.L.; Su, C.Y.; Tong, Y.X. Synthesis of hierarchical rippled BiOBr nanobelts for supercapacitor applications. Chem. Commun. 2010, 46, 5021–5023. [CrossRef] [PubMed]

224. Biesterbos, J.W.M.; Hornstra, J. The Crystal Structure of the high-temperature low-pressure form of Rh2O3. J. Less Common Met. 1973, 30, 121–125. [CrossRef]

225. Shannon, R.D.; Prewitt, C.T. Synthesis and structure of a new high-pressure form of Rh2O3 at 3.7 Mbar. J. Solid State Chem. 1970, 2, 134–136. [CrossRef]

226. Zhao, Z.; Zeng, Q.; Zhang, H.; Wang, S.; Hirai, S.; Zeng, Z.; Mao, W.L. Structural transition and amorphization in compressed β-Sb2O3. Phys. Rev. B 2015, 91, 184112. [CrossRef]

227. Shen, Z.-X.; Chen, G.-Q.; Ni, J.-H.; Li, X.-S.; Xiong, S.-M.; Qiu, Q.-Y.; Zhu, J.; Tang, W.; Sun, G.-L.; Yang, K.-Q.; et al. Use of Arsenic Trioxide (As2O3) in the Treatment of Acute Promyelocytic Leukemia (APL): II. Clinical Efficacy and Pharmacokinetics in Relapsed Patients. Blood 1997, 89, 3354–3360. [CrossRef]

228. Shen, Z.-X.; Shi, Z.-Z.; Fang, J.; Gu, B.-W.; Li, J.-M.; Zhu, Y.-M.; Shi, J.-Y.; Zheng, P.-Z.; Yan, H.; Liu, Y.F.; et al. All-trans retinoic acid/As2O3 combination yields a high quality remission and survival in newly diagnosed acute promyelocytic leukemia. Proc. Natl. Acad. Sci. USA 2004, 101, 5328–5335. [CrossRef] [PubMed]

229. Matsumoto, A.; Koyama, Y.; Tanaka, I. Electronic structures of dynamically stable As2O3, Sb2O3, and Bi2O3 crystal polymorphs. Phys. Rev. B 2011, 83, 214110. [CrossRef]

230. Matsumoto, A.; Koyama, Y.; Tanaka, I. Structures and energetics of Bi2O3 polymorphs in a defective fluorite family derived by systematic first-principles lattice dynamics calculations. Phys. Rev. B 2010, 81, 094117. [CrossRef]

231. Zhao, Z.; Zeng, Q.; Zhang, H.; Wang, S.; Hirai, S.; Zeng, Z.; Mao, W.L. Structural transition and amorphization in compressed β-Sb2O3. Phys. Rev. B 2015, 91, 184112. [CrossRef]

232. Wu, X.; Karkin, A.E.; Shchennikov, V.V.; Manthilake, G.M. Temperature-pressure phase diagram of Ti2O3 and physical properties in the golden Th2S2-type phase. Phys. Rev. B 2012, 86, 024106. [CrossRef]

233. Datta, A.; Giri, A.K.; Chakravorty, D. AC conductivity of Sb2O3 glasses. Phys. Rev. B 1993, 47, 16242. [CrossRef]

234. Ai, Z.; Huang, Y.; Lee, S.; Zhang, L. Monoclinic α-Bi2O3 photocatalyst for efficient removal of gaseous NO and HCHO under visible light irradiation. J. Alloy. Compd. 2011, 509, 2044–2049. [CrossRef]

235. Zheng, F.L.; Li, G.R.; Ou, Y.N.; Wang, Z.L.; Su, C.Y.; Tong, Y.X. Synthesis of hierarchical rippled Bi2O3 nanobelts for supercapacitor applications. Chem. Commun. 2010, 46, 5021–5023. [CrossRef] [PubMed]

236. Hu, M.; Jiang, Y.; Sun, W.; Wang, H.; Jin, C.; Yan, M. Reversible Conversion-Alloying of Sb2O3 as a High-Capacity, High-Rate, and Durable Anode for Sodium Ion Batteries. ACS Appl. Mater. Interfaces 2014, 6, 19449–19455. [CrossRef] [PubMed]

237. Datta, A.; Giri, A.K.; Chakravorty, D. AC conductivity of Sb2O3-P2O5 glasses. Phys. Rev. B 1993, 47, 16242. [CrossRef]

238. Shen, Z.-X.; Chen, G.-Q.; Ni, J.-H.; Li, X.-S.; Xiong, S.-M.; Qiu, Q.-Y.; Zhu, J.; Tang, W.; Sun, G.-L.; Yang, K.-Q.; et al. Use of Arsenic Trioxide (As2O3) in the Treatment of Acute Promyelocytic Leukemia (APL): II. Clinical Efficacy and Pharmacokinetics in Relapsed Patients. Blood 1997, 89, 3354–3360. [CrossRef]

239. Shen, Z.-X.; Shi, Z.-Z.; Fang, J.; Gu, B.-W.; Li, J.-M.; Zhu, Y.-M.; Shi, J.-Y.; Zheng, P.-Z.; Yan, H.; Liu, Y.F.; et al. All-trans retinoic acid/As2O3 combination yields a high quality remission and survival in newly diagnosed acute promyelocytic leukemia. Proc. Natl. Acad. Sci. USA 2004, 101, 5328–5335. [CrossRef] [PubMed]

240. Matsumoto, A.; Koyama, Y.; Tanaka, I. Electronic structures of dynamically stable As2O3, Sb2O3, and Bi2O3 crystal polymorphs. Phys. Rev. B 2011, 83, 214110. [CrossRef]

241. Matsumoto, A.; Koyama, Y.; Tanaka, I. Structures and energetics of Bi2O3 polymorphs in a defective fluorite family derived by systematic first-principles lattice dynamics calculations. Phys. Rev. B 2010, 81, 094117. [CrossRef] [PubMed]
242. Pereira, A.L.J.; Gracia, L.; Santamaría-Pérez, D.; Vilaplana, R.; Manjón, F.J.; Errandonea, D.; Nalin, M.; Beltrán, A. Structural and vibrational study of cubic Sb$_2$O$_3$ under high pressure. *Phys. Rev. B* **2012**, *85*, 174108. [CrossRef]

243. Pereira, A.L.J.; Sans, J.A.; Vilaplana, R.; Gomis, O.; Manjón, F.J.; Rodriguez-Hernández, P.; Muñoz, A.; Popescu, C.; Beltrán, A. Isostructural Second-Order Phase Transition of β-B$_2$I$_2$O$_3$ at High Pressures: An Experimental and Theoretical Study. *J. Phys. Chem. C* **2014**, *118*, 23189–23201. [CrossRef]

244. Orosel, D.; Dinnebier, R.E.; Blatov, V.A.; Jansen, M. Structure of a new high-pressure–high-temperature modification of antimony(III) oxide, γ-Sb$_2$O$_3$, from high-resolution synchrotron powder diffraction data. *Acta Cryst. B* **2012**, *68*, 1–7. [CrossRef]

245. Cornei, N.; Tancret, N.; Abraham, F.; Mentré, O. New c-Bi$_2$O$_3$ Metastable Polymorph. *Inorg. Chem.* **2006**, *45*, 4886–4888. [CrossRef]

246. Geng, A.-H.; Cao, L.-H.; Ma, Y.-M.; Cui, Q.-L.; Wan, C.-M. Experimental Observation of Phase Transition in Sb$_2$O$_3$ under High Pressure. *Chin. Phys. Lett.* **2016**, *33*, 097401. [CrossRef]

247. Harwig, H.A. On the Structure of Bismuthsesquioxide: The α, β, γ, and δ-Phase. *Z. Anorg. Allg. Chem.* **1978**, *444*, 151–166. [CrossRef]

248. Gavriliuk, A.G.; Struzhkin, V.; Lyubutin, S.; Eremets, I.; Trojan, A.; Artemov, V. Equation of state and high-pressure irreversible amorphization in Y$_3$Fe$_5$O$_{12}$. *JETP Lett.* **2006**, *83*, 37–41. [CrossRef]

249. Pereira, A.L.J.; Gracia, L.; Gomis, O.; Manjón, F.J.; Muñoz, A.; et al. Structural study of α-Bi$_2$O$_3$ under pressure. *J. Phys. Condens. Matter* **2013**, *25*, 475402. [CrossRef] [PubMed]

250. Gavriliuk, A.G.; Struzhkin, V.; Lyubutin, S.; Eremets, I.; Trojan, A.; Artemov, V. Equation of state and high-pressure irreversible amorphization in Y$_3$Fe$_5$O$_{12}$. *JETP Lett.* **2006**, *83*, 37–41. [CrossRef]

251. Loccher, T.; Dasari, L.; Prasad, V.K.; Dinnebier, R.; Wedig, U.; Jansen, M. High-pressure structural evolution of HP-Bi$_2$O$_3$. *Phys. Rev. B* **2011**, *83*, 214102. [CrossRef]

252. Ghedia, S.; Loccher, T.; Dinnebier, R.; Prasad, D.L.V.K.; Wedig, U.; Jansen, M.; Senyshyn, A. High-pressure and high-temperature multianvil synthesis of metastable polymorphs of Bi$_2$O$_3$: Crystal structure and electronic properties. *Phys. Rev. B* **2010**, *82*, 024106. [CrossRef]

253. Frueh, A.J., Jr. The crystal structure of claudetite (monoclinic As$_2$O$_3$). *Am. Miner.* **1951**, *36*, 833–850.

254. Frueh, A.J., Jr. The crystal structure of claudetite (monoclinic As$_2$O$_3$). *Am. Miner.* **1951**, *36*, 833–850. [CrossRef]

255. Soignard, E.; Amin, S.A.; Mei, Q.; Benmore, C.J.; Yarger, J.L. High-pressure behavior of As$_2$. *Phys. Rev. B* **2008**, *77*, 144113. [CrossRef]

256. Guřka, P.A.; Dranka, M.; Piechota, J.; Żukowska, G.Z.; Zalewska, A.; Zachara, J. As$_2$O$_3$ Polymorphs: Theoretical Insight into Their Stability and Ammonia Templated Claudetite II Crystallization. *Cryst. Growth Des.* **2012**, *12*, 5663–5670. [CrossRef]

257. Guřka, P.A.; Dranka, M.; Hanfland, M.; Dzubiak, K.F.; Katusiak, A.; Zachara, J. Cascade of High-Pressure Transitions of Claudetite II and the First Polar Phase of Arsenic(III) Oxide. *Cryst. Growth Des.* **2015**, *15*, 3950–3954. [CrossRef]

258. Jansen, M.; Moëbs, M. Structural Investigations on Solid Tetraphosphorus Hexaoxide. *Inorg. Chem.* **1984**, *23*, 4486–4488. [CrossRef]

259. Clark, G.L.; Schiltz, N.C.; Quirke, T.T. A New Study of the Preparation and Properties of the Higher Oxides of Lead. *J. Am. Chem. Soc.* **1937**, *59*, 2303–2308. [CrossRef]

260. Bouvaist, J.; Weigel, D. Sesquioxyde de plomb, Pb$_2$O$_3$. I. Determination de la structure. *Acta Cryst. A* **1970**, *26*, 501–510. [CrossRef]

261. Seko, A.; Togo, A.; Oba, F.; Tanaka, I. Structure and Stability of a Homologous Series of Tin Oxides. *Phys. Rev. Lett.* **2008**, *100*, 045702. [CrossRef] [PubMed]

262. Zhao, J.-H.; Tan, R.-Q.; Yang, Y.; Xu, W.; Li, J.; Shen, W.-F.; Wu, G.-Q.; Yang, X.-F.; Song, W.-J. Synthesis mechanism of heterovalent Sn$_2$O$_3$ nanosheets in oxidation annealing process. *Chin. Phys. B* **2015**, *24*, 070505. [CrossRef]

263. Kuang, X.L.; Liu, T.M.; Zeng, W.; Peng, X.H.; Wang, Z.C. Hydrothermal synthesis and characterization of novel Sn$_2$O$_3$ hierarchical nanostructures. *Mat. Lett.* **2016**, *165*, 235–238. [CrossRef]

264. Imre, A.R. On the existence of negative pressure states. *Phys. Stat. Sol. (b)* **2007**, *244*, 893–899. [CrossRef]
265. McMillan, P.F. New materials from high-pressure experiments. *Nat. Mater.* **2002**, *1*, 19–25. [CrossRef]

266. Manjón, F.J.; Errandonea, D.; López-Solano, J.; Rodríguez-Hernández, P.; Muñoz, A. Negative pressures in CaWO₄ nanocrystals. *J. Appl. Phys.* **2009**, *105*, 094321. [CrossRef]

267. Matsui, T.; Yagasaki, T.; Matsumoto, M.; Tanaka, H. Phase diagram of ice polymorphs under negative pressure considering the limits of mechanical stability. *J. Phys. Chem.* **2019**, *150*, 041102. [CrossRef]