Transition of strong, wide band-gap oxide insulators to metallic glasses at 100 GPa (Mbar) pressures, etc

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Abstract. This paper is a review of experimental results observed for shock and statically compressed sapphire (single-crystal Al₂O₃) and implications of these results. Many of these were unexpected prior to experiments: (i) Hugoniot and 300-K theoretical isotherm are nearly coincident to 340 GPa, (ii) shock-compressed sapphire probably achieves minimum metallic conductivity (MMC) at ~300 GPa, as does fluid H at 140 GPa, (iii) Both crossovers are driven by shock dissipation and both probably occur by a bonds to bands transition (BtBT), (iv) the BtBT is driven by shock-induced damage which breaks bonds at such high densities that wave functions of atoms so formed hybridize into energy bands; (v) disorder caused by sluggish phase transitions in a DAC suggest sapphire also reaches MMC in a DAC at ~300 GPa; (vi) the structural ground states of all solids at very high pressures might be metallic glasses; (vii) Super Earths can have magnetic fields caused only by convecting conducting oxides without the need for Fe; (viii) alumina powders in a DAC might attain MMC at ~300 GPa and perhaps at pressures as low as ~200 GPa. Al₂O₃ is probably amorphous in a DAC at 200 GPa

1. Introduction
Extreme conditions of density and temperature produced by high pressures achieve novel states of matter. Dynamic pressure achieves compression and temperature simultaneously and adiabatically. The latter results from the short experimental lifetimes, typically of order 1 to 100 ns, which are too brief for significant thermal transport in or out of a sample. Thus, heating produced by dynamic compression is retained during experimental lifetimes. The experimental lifetimes are also sufficiently brief to preclude mass diffusion out of a sample holder. The fast time scale also means that dynamic compression is irreversible and dissipative. Dissipation energy goes into something other than compression, in this case heating and disorder. Consider, for example, fast compression of an ordered crystalline solid. If compression is sufficiently fast, an ordered crystal structure cannot survive that fast application of pressure, nor can the initial order be regained on the associated fast release (~100 ns) of dynamic pressure. Fast dynamic compression is commonly known as shock or multiple-shock compression. Shock wave velocities are supersonic. In general, a shock-compressed fluid is in thermal equilibrium and thus shock compression produces a shock temperature T and entropy S in bulk fluid. However, a shock-compressed strong solid is not generally in thermal equilibrium up to a stress of a few multiples of its elastic strength under shock, called the Hugoniot elastic limit (HEL). In this case shock heating and damage are heterogeneous. Densities and temperatures achieved dynamically can be tuned to a significant degree by tuning the temporal shape of the pressure pulse applied to a sample.
Static compression is isothermal because experimental lifetime is sufficiently long to enable heat produced by compression to be transported out of a pressure cell prior to making measurements. Temperature is varied independently by heating or cooling the sample or the entire cell. Experimental lifetimes for static compression range from seconds to years. Such long lifetimes enable light, mobile elements, such as H, to rapidly diffuse out of a static-pressure cell.

Work on strong oxide insulators discussed herein was motivated initially by experiments that synthesized metallic fluid hydrogen by reverberating a shock wave in liquid H₂ at 20 K contained between two c-cut sapphire (single-crystal Al₂O₃) disks [1]. The reverberating shock compresses the hydrogen with multiple shocks, which tunes the final temperature to ~1/10 what would be achieved with a single shock to the same final pressure. At 140 GPa, 10-fold compressed liquid density, and ~3000 K, fluid hydrogen achieves minimum metallic conductivity (MMC). In the process, however, transparent colorless sapphire becomes opaque because of shock-induced damage. Because sapphire becomes opaque, thermal emission from the dense hydrogen cannot exit the sample holder, and so its temperature cannot be determined from gray body spectra. In order to determine if some direction of shock propagation, other than along the c axis, might produce a more transparent anvil, shock propagation in seven crystallographic directions was investigated experimentally [2]. The nature of those shock waves in sapphire proved to be contrary to expectations prior to those measurements and showed that strong sapphire damages substantially at stresses above its HEL [3].

One widely accepted view is that shock compression produces shock heating, which produces thermal pressures in addition to pressures produced by “cold compression” at ambient temperature. As a result shock pressures are widely assumed to be much greater than pressures achieved by static compression to the same density, particularly at 100 GPa pressures. However, extreme conditions produce unusual and unexpected results. In the case of oxides, dynamic and static compression produce similar results at 100 GPa pressures. This paper reviews a number of unexpected results discovered for sapphire at ~100 GPa pressures. Similar results have been observed for Gd₃Ga₅O₁₂.

2. Virtual coincidence of Hugoniots and isotherm of oxides at high pressure and implications

The Hugoniot of sapphire was measured up to 340 GPa [4], no phase transitions or cross overs are apparent on the Hugoniot, and the Hugoniot is virtually identical to the theoretical 300-K isotherm up 340 GPa [3,5]. (A crossover is a transition that occurs over some range of pressure, density, and temperature, as opposed to a sharp first-order phase transition with a discontinuity in density.) The Hugoniot of sapphire does not deviate significantly from the theoretical 300-K isotherm until shock pressure exceeds ~400 GPa [6]. This fact suggests dissipation on the sapphire Hugoniot is dominated by disorder up to ~400 GPa and once disorder is complete additional dissipation goes into temperature above ~400 GPa. Electrical conductivities of shocked sapphire have been measured up to 220 GPa [7]. Measured conductivities of shocked sapphire extrapolate to MMC at ~300 GPa. Sapphire was not expected to have metallic conductivity at such a relatively low pressure. Remarkably, sapphire might attain MMC under static compression at ~300 GPa as well.

In a diamond anvil cell (DAC) the as-compressed phase of sapphire is only corundum (α-Al₂O₃) up to a static pressure of 180 GPa. Predicted phase transitions occur but only with laser-heating and thermal quenching at high pressures. The predicted corundum (α-Al₂O₃) to Rh₂O₃ (II)-type transition occurs at 103 GPa and the Rh₂O₃(II)-type to CaIrO₃-type transition occurs at 130 GPa and persists to 180 GPa. X-ray spectra of laser-heated and thermally quenched samples consist of broad individual diffraction peaks superimposed on a significant broad background, indicative of disordered structures with short-range order. Above 180 GPa, even with laser heating, sapphire is apparently amorphous because no crystal-structure type has been reported above 180 GPa [8]. Al₂O₃ in a DAC is substantially disordered, as is shocked sapphire. Since both shock and statically compressed sapphire
are highly disordered and their pressure-density curves are quite similar up to 180 GPa [9], it is quite possible that amorphous Al$_2$O$_3$ in a DAC achieves MMC at ~300 GPa, as shocked Al$_2$O$_3$ might do. That is, Al$_2$O$_3$ in a DAC at ~300 GPa might well be a metallic glass in the solid at 300 K.

Analysis of a large amount of data on dynamically compressed soft fluids (H$_2$, etc) and strong oxides (Al$_2$O$_3$, etc) lead to the realization that these two apparently different types of materials probably become poor metals by essentially the same mechanism at ~100 GPa pressures. Remarkably, the H-H and Al-O bond strengths are both 4.5 eV. This common mechanism is probably the bonds to bands transition (BtBT). That is, once strong bonds in Al$_2$O$_3$ and Gd$_3$Ga$_5$O$_{12}$ break under dynamic compression, electronic wave functions of resulting atoms overlap at sufficiently high density to form a disordered metal or metallic glass [9-11]. At some high pressure bonds in all insulators break to form a poor metal. Material strength determines the pressure at which the BtBT occurs but not whether it occurs. Because of shock-induced disorder, maximum electrical conductivity is MMC. Sluggish phase transitions induce disorder into sapphire compressed in a DAC [8,10] so that sapphire probably attains MMC under static pressure as well as dynamic.

3. **Ground-state structure at very high pressures and 0 K**

The prominence of disorder at high pressures discussed above raises a fundamental question. At very high pressures, densities are sufficiently high for all materials to be metals. So one question is whether the structural ground state of all solids is well-ordered metal or a metallic glass at sufficiently high pressures and densities? A metallic glass is an amorphous metal, which is a poor metal with MMC because of strong electron scattering caused by disorder. To my knowledge there is no known a priori reason to assume that solids at very high pressures are perfectly-ordered crystals. Calculations of high-pressure structures assume perfectly ordered structures, total energy is calculated for each, the one with least total energy is declared the likely equilibrium structure, and pressure is the mathematical derivative of energy with respect to volume. Amorphous structures have yet to be included in such comparisons. To my knowledge, the mechanical stability of such structures under pressure is not calculated. That is, what happens dynamically if a bond is tilted slightly from its direction in a perfectly ordered crystal at high pressures? Such a disturbance might happen, for example, as atoms in one structure start moving in a transition to another structure. The key question is whether high-pressure structures are in stable equilibrium or not?

4. **Can Super Earths have magnetic fields caused only by convecting molten oxides, without Fe?**

Yes, it is possible and thus probable. A Super Earth is a planet with a mass up to ten times greater than that of Earth. Planetary magnetic fields are caused by dynamos, which are convecting conducting material. The magnetic fields of Earth and Jupiter are caused by convection of liquid Fe and metallic liquid hydrogen, respectively with MMC [12].

The highest pressure and temperature of rock (oxides) inside Earth are 130 GPa and 3000 K at the core-mantle boundary between the solid-rock mantle and the liquid Fe outer core. In planets larger than Earth interior pressures and temperatures are larger than in Earth. In some of them temperatures in oxides will exceed melting temperatures of rock at pressure and then that molten rock can convect. Because of very high pressures those molten oxides will probably decompose into a mixture of atoms. Wave functions of outermost electrons of those atoms could overlap to form metallic liquid metal with MMC, as suggested above occurs in Al$_2$O$_3$. Such a liquid metallic alloy would have a conductivity of MMC, no matter what the exact chemical composition of the oxide might be. Thus, molten rock could convect and conduct and so produce an external magnetic field by dynamo action. The actual magnitude of magnetic field would depend on details of conductivity and convecting hydrodynamic flows [13].
Solid rock deep in Super Earths might be metallic glasses at pressures less than required for melting. Structural defects, dislocations, grain boundaries, sluggish phase transitions, and chemical impurities cause such bond distortions in ideal ordered structures. Under high physical pressures bonds might creep into an amorphous phase. While planetary interiors are at high temperatures, annealing effects depend sensitively on details of temperature, density, electronic structure (strong chemical bonds or metallic bonding) and creep. Within a given Super Earth it is not possible to say, but in principle metallic-glass oxides probably exist inside some Super Earths.

5. Does an oxide exist that is an electrical insulator above ~200 GPa? Alumina powder is used as an electrical insulator in a DAC at ~100 GPa pressures. Given the possibility that sapphire might become a poor metal at ~300 GPa in a DAC and given that sapphire is highly disordered in a DAC at 180 GPa [8], it would seem prudent to measure electrical conductivities of powders used as electrical insulators in a DAC at high pressures to be sure such powders are insulators at pressures in which they are to be used. If the BtBT occurs at 300 K in a DAC for some reason, it is quite possible such powders could become poor metals. This question can only be answered by experiment.

6. References
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