High-pressure behavior of gasparite-(Ce) (nominally CeAsO₄), a monazite-type arsenate

Francesco Pagliaro¹ · Paolo Lotti¹ · Davide Comboni² · Tommaso Battiston¹ · Alessandro Guastoni³ · Patrizia Fumagalli¹ · Nicola Rotiroti¹ · G. Diego Gatta¹

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Abstract
The high-pressure behavior of the natural arsenate gasparite-(Ce) [Ce₀.₄₃La₀.₂₄Nd₀.₁₅Ca₀.₁₁Pr₀.₀₄Sm₀.₀₂Gd₀.₀₁(As₀.₉₉Si₀.₀₃O₄)] from the Mt. Cervandone mineral deposit (Piedmont Lepontine Alps, Italy), has been studied by in situ single-crystal synchrotron X-ray diffraction up to 22.01 GPa. Two distinct high-pressure ramps have been performed, using a 16:3:1 methanol:ethanol:water solution and helium as P-transmitting fluids, respectively. No phase transition occurs within the pressure range investigated, whereas a change in the compressional behavior has been observed at ~ 15 GPa. A second-order Birch-Murnaghan EoS was fitted to the P-V data, leading to a refined bulk modulus of 109.4(3) GPa. The structural analysis has been carried out on the basis of the refined structure models, allowing the description of the deformation mechanisms accommodating the bulk compression in gasparite-(Ce) at the atomic scale, which is mainly controlled by the compression of the Rare Earth Elements coordination polyhedra, while the AsO₄ tetrahedra behave as a quasi-rigid units. A micro-Raman spectroscopy analysis, performed at ambient conditions, suggests the presence of hydroxyl groups into the structure of the investigated gasparite-(Ce).

Keywords Gasparite-(Ce) · Rare earth elements · Arsenate · Monazite · Synchrotron · High-pressure

Introduction
The ATO₄ compounds (where A = Sc, Y, La-Lu series (Ln), Ca, U and Th, whereas T stands for tetrahedrally-coordinated cations) represent a large group of minerals. The ATO₄ group embodies several Rare Earth Elements (REE) bearing phosphates, arsenates and vanadates, in addition to, among the others, silicates, chromates and selenates. The REETO₄₄ phosphates, arsenates and vanadates can crystallize in both a zircon-type structure (also called xenotime-type) and in a monazite-type structure (Clavier et al. 2011). The zircon-type-structure is characterized by a tetragonal unit-cell (space group I₄₁/amd; Z=4) and, in general, hosts the smaller Heavy Rare Earth Elements (HREE; Tb-Lu and Y, according to the classification provided by the U.S. Geological Survey, 2011) or Sc. Conversely, the monazite-type-structure REE-bearing minerals, with a monoclinic lattice (space group P2₁/n) (Z=4), typically host Light Rare Earth Elements (LREE; Ce-Gd, i.e., the lanthanides with unpaired 4f electrons, according to U.S. Geological Survey, 2011). The first description of the monazite-type structure has been reported by Mooney (1948), who investigated the La, Ce, Pr and Nd phosphates. The structure has been later described correctly by Beall et al. (1981), Mullica et al. (1984) and Ni et al. (1995), whereas an exhaustive review of the monazite-structure topology has been carried out by Boatner (2002) and then by Clavier et al. (2011). The monazite-type structure is characterized by infinite chains running along the [001] direction (c axis), composed by the alternation of the A-coordination polyhedra (hereafter REE-coordination polyhedra) and the T-hosting tetrahedra (Fig. 1). The REE-polyhedron coordination environment is made by nine oxygen atoms. According to Mullica et al. (1984), the REEO₄ polyhedron can be described as an equatorial pentagon (sharing vertices with five TO₄ tetrahedra of five adjacent chains),
interpenetrated by a tetrahedron (made by the O$_{1a}$, O$_{2a}$, O$_{3a}$ and O$_{4a}$ oxygen atoms, see Fig. 1a), which is in contact, along the [001] direction, with two subsequent TO$_4$ tetrahedra, leading to the formation of the infinite chain units. As reported in Fig. 1a, the REE-O$_{2a}$ bond length is sharply longer than the other REE-O bonds, contributing to a significant distortion of the REEO$_9$ polyhedron (Clavier et al. 2011; Ni et al. 1995; Beall et al. 1981). Whether the monazite or the zircon structure is stable at ambient conditions strongly depends on the ionic radii of either oxygen, A- and T-site cations. This relation has been enlightened by Muller and Roy (1974), Fukunaga and Yamaoka (1979) and Bastide (1987). Pure REEAsO$_4$ compounds have been synthesized by Glushko et al. (1972), who observed the presence of both the monazite- and zircon-type structure topologies as a function of the radii of the REE-atoms. Whether the REE is one of the larger REE-cations, as La, Ce, Pr, and Nd, the lattice is monoclinic, whereas when REE = Y, Sc, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu the tetragonal zircon-type structure occurs in arsenates (Glushko et al. 1972; Ushakov et al. 2001; Boatner, 2002; Kolitsch and Holstam, 2004). Chernovite-(Y) and gasparite-(Ce) are the natural arsenates with zircon- and monazite-type structure, respectively, and they are both rare minerals. As underlined by Vereshchagin et al. (2019), gasparite-(Ce), similarly to the Y- and HREE-bearing arsenate chernovite-(Y), seems strongly linked to post-magmatic and metasedimentary environments, influenced by late hydrothermal processes. The monazite-type structure in REE-bearing arsenates had been firstly described from synthetic CeAsO$_4$ by Beall et al. (1981) and only after Graeser and Schwander (1987) it has been reported in nature, in the mineral named gasparite-(Ce), occurring within the hydrothermal Alpine fissures of Mt. Cervandone (Italy) and adjacent Binn Valley (Switzerland). For a complete overview about the sites where gasparite-(Ce) occurs, refer to Ondrejka et al. (2007), Anthony et al. (2000), Kolitsch et al. (2004), Mills et al. (2010), Mancini (2000), Vereshchagin et al. (2019), Cabella et al. (1999).

The high-pressure behavior of monazite-type phosphates has been object of numerous studies (Lacomba-Perales et al. 2010; Errandonea et al. 2018; Errandonea 2017; Feng et al. 2013; Ruiz-Fuertes et al. 2016; Heffernan et al. 2016; Huang et al. 2010; Li et al. 2009), while the literature available on arsenates is rather limited (Metzger et al. 2016; Li et al. 2009). A comprehensive theoretical study on the high-pressure behavior of all the REE-bearing arsenates and phosphates, with both zircon- and monazite-type structure, has been reported by Li et al. (2009), whereas an extensive review on the high-pressure behavior of monazite-type ATO$_4$ compounds has been carried out by Errandonea (2017). Generally, what has been observed in synthetic REE-phosphates end members (Lacomba-Perales et al. 2010; Feng et al. 2013; Li et al. 2009; Errandonea 2017) is that the bulk modulus increases (i.e., the compressibility decreases) when the atomic radius of the REE cation decreases, from LaPO$_4$ to GdPO$_4$. In the same way, the pressure stability field of the monazite-structured phosphates increases to higher pressures from LaPO$_4$ to GdPO$_4$. For LaPO$_4$, a phase transition at a pressure exceeding 27.1 GPa to a post-barite-type structure ($P2_1_2_1_2_1$ space group) occurs and the same phase transition is predicted to occur at 35 and 45 GPa for NdPO$_4$ and GdPO$_4$, respectively (Lacomba-Perales et al. 2010; Ruiz-Fuertes et al. 2016; Errandonea 2017). Whereas several
studies have been dedicated to the compressional behavior of the monazite-structure analogs, a few of them explore the structural mechanisms responsible for the high-pressure bulk compression and deformation. Heffernan et al. (2016) studied the structural (at the atomic scale) response of GdPO$_4$ under high-pressure conditions up to 7.062 GPa. Either Heffernan et al. (2016), Errandonea et al. (2018) and Muñoz and Rodríguez-Hernández (2018) point out the relevant role played by the compression of the REEO$_9$ polyhedron, whereas the PO$_4$ tetrahedra substantially act as rigid bodies. Heffernan et al. (2016) also show that the anisotropic behavior of GdPO$_4$ is mainly controlled by the variations of the O–Gd–P linkages, resulting from the distortion of the GdO$_9$ polyhedra. So far, no experimental variations of the O−Gd−P linkages, resulting from the gasparite-(Ce) and other monazite-type O$_4$ compounds.

In this study, we have investigated the high-pressure behavior of a natural gasparite-(Ce), with a multi-elemental composition of the REE-bearing A site, by means of in situ single-crystal synchrotron X-ray diffraction with a diamond anvil cell (DAC). The elastic parameters and a description of the deformation mechanisms accommodating and controlling, at the atomic scale, the bulk compression are provided, along with a comparative analysis of the high-P behaviors of gasparite-(Ce) and other monazite-type ATO$_4$ compounds. Moreover, the Raman spectrum of gasparite-(Ce) has been collected at ambient conditions, with the aim to provide a comprehensive chemical description of this mineral. This manuscript belongs to an ongoing long-term project studying the crystal chemistry and the behavior at non-ambient conditions of REE-bearing minerals (Gatta et al. 2019, 2021; Pagliaro et al. 2022).

### Materials and methods

Natural samples of hydrothermal gasparite-(Ce) from the Mt. Cervandone (Lepontine Alps, Italy) mineral deposit have been studied. Further information concerning the mineralogy of the REE-bearing deposit are reported by Dal Piaz (1975), Graesser and Roggiani (1976), Graesser and Albertini (1995), Guastoni et al. (2006), Demartin et al. (1991a, 1991b). The chemical composition of the samples of gasparite-(Ce) used in this study has been previously determined by electron probe microanalysis in wavelength dispersion mode (EPMA-WDS) based on eight points of analysis: Ce$_{0.43}$La$_{0.23}$Nd$_{0.15}$Ca$_{0.11}$Pr$_{0.04}$Sn$_{0.02}$Gd$_{0.01}$($\lambda E_0.09S_0.03$O$_4$). Further information on the adopted experimental protocol is reported in Pagliaro et al. (2022).

### Raman spectroscopy

Unoriented micro-Raman spectroscopy analysis of gasparite-(Ce) has been carried out, at room conditions, at the Earth Science Department “A. Desio” of the University of Milano, using a Horiba LabRam HR Evolution micro-Raman spectrometer, equipped with an Nd:YAG 532 nm/100 mW, a Peltier-cooled charge-coupled device (CCD) detector, an Olympus microscope having 100× objectives and Ultra Low Frequency (ULF) filters. In addition, the 10% laser power filter used yields to an esteemed power of 6 mW on the sample surface. The spectra were collected with the Labspec software in the region between 30 and 1200 cm$^{-1}$ and in the range 3200–4000 cm$^{-1}$, both with a step size of 1.8 cm$^{-1}$ and 20 s of acquisition time. The two sections of the micro-Raman spectrum of gasparite-(Ce) are reported in Fig. 2a and Fig. 2b. Peak analysis has been conducted using the OriginPro suite (OriginLab Corporation 2019).

### In situ high-pressure X-ray diffraction experiments

In situ high-pressure single-crystal synchrotron X-ray diffraction experiments have been conducted at the ID15b beamline of the European Synchrotron Radiation Facility, ESRF (Grenoble, France). Single crystals of gasparite-(Ce) (ca 20 × 15 × 10 µm$^3$ in size) were selected for two separate high-pressure experiments, performed using a 16:3:1 methanol:ethanol:H$_2$O mixture (hereafter m.e.w., Angel et al. 2007), up to 9.31(5) GPa, and helium (Klotz et al. 2009), up to 22.76(5) GPa, as P-transmitting fluids, respectively. A convergent monochromatic X-ray beam with an energy of 30.2 keV ($\lambda = 0.41046$ Å) was used. For each P-point, the collection strategy consisted in a step-wise $\omega$-scan in the range ± 30°, with a step-width of 0.5° and an exposure time of 0.5 s/frame (m.e.w. ramp) and 0.25 s/frame (He ramp). The pressure increase was controlled through a remote, automated pressure-driven system. X-ray diffraction patterns were collected with a MAR555 flat-panel detector, set at 260.32 mm from the sample position. The sample-to-detector distance was calibrated using a Si standard. Further details concerning the beamline setup are reported in Merlino and Hanfland (2013). For both the experiments, gasparite-(Ce) crystals were loaded in a membrane-driven diamond anvil cell (DAC), equipped with Boehler-Almax designed diamonds/seats with 60° opening and 600 µm culets size. Stainless-steel foils (with thickness ~ 250 µm) were pre-indented to ca. 70 µm and then drilled by spark-erosion to obtain P-chambers of 300 µm and 150 µm in diameter, for the m.e.w. and He ramps, respectively. Few ruby spheres were used as pressure calibrants (pressure uncertainty ±0.05 GPa; Mao et al. 1986; Chervin et al. 2001). Indexing of the X-ray diffraction peaks, unit-cell refinements and intensity data reductions were performed using the CrysAlisPro.
package (Rigaku Oxford Diffraction 2019). Absorption effects, due to the DAC components, were corrected using the semi-empirical ABSPACK routine, implemented in CrysAlisPro.

**Structure refinements**

The experimental X-ray diffraction patterns were always compatible with the monoclinic $P2_1/n$ symmetry of gasparite-(Ce). All the structure refinements were performed using the package JANA2006 (Petříček et al. 2014), in the space group $P2_1/n$, using, as starting model, the atomic coordinates reported by Pagliaro et al. (2022). Only the structure refinements performed on the m.e.w.-ramp XRD data are fully reported (see High-pressure structure deformation for further details). The occupancies of all the crystallographic sites were fixed according to the measured chemical data, applying a cut-off on atomic species with abundance lower than 0.03 atoms per formula unit (apfu). Calcium was also excluded from the refinements, as this led to better figures of merit (further details on this protocol can be found in Pagliaro et al. 2022). For all the refinements based on in situ high-pressure diffraction data, to reduce the number of refined variables, the atomic displacement parameters (ADP) were refined as isotropic. At any $P$ point, no restraints on bond distances or angles have been applied and all the refinements converged with no significant correlations among the refined variables. The refined structure models are deposited as supplementary materials (CIF files). Relevant statistical parameters of the refinements are reported in Table S1.

**Results and discussion**

**Micro-Raman spectroscopy**

Figure 2 shows the experimental micro-Raman spectra of gasparite-(Ce). Conversely to the previously studied monazite-type LREE-bearing arsenates (Vereshchagin et al. 2019; Botto and Baran 1982), gasparite-(Ce) from Mt. Cervandone, in the range between 3200 and 4000 cm$^{-1}$ (Fig. 2b), shows the presence of slightly intense peaks, ascribed to OH$^-$ groups. The partial replacement of oxygen atoms by hydroxyl groups may explain some features of the chemical data of gasparite-(Ce), characterized by a slight charge defect, for to the combined presence of Ca$^{2+}$ within the A site (in place of REE$^{3+}$) and Si$^{4+}$ within the tetrahedral T-site (in place of As$^{5+}$), apparently not counterbalanced (Pagliaro et al. 2022). As reported by Pagliaro et al. (2022), this may be explained by the following charge compensating mechanism:

$$2(\text{OH})^- + \text{Ca}^{2+} + \text{Si}^{4+} = 2\text{O}^{2-} + \text{REE}^{3+} + (\text{As})^{5+},$$

which is further supported by the present Raman spectrum of gasparite-(Ce).

Further information about the Raman spectroscopy data are reported as supplementary material (see Table S2).

**High-pressure behavior**

**Compressional behavior**

Figure 3 and 4 and Table S3 show the compressional behavior of the unit-cell of gasparite-(Ce) up to 21.05 GPa.
Gasparite-(Ce) is characterized by an anisotropic compressional behavior, with a lower compressibility along [001], a maximum shortening along [100], whereas along [010] displays an intermediate compressibility (Fig. 3a). At a first approximation, gasparite-(Ce) shows a similar compressional behavior with the other $\text{A}_2\text{O}_4$ compounds sharing a monazite-type structure (Errandonea 2017). The monoclinic $\beta$ angle linearly decreases with pressure up to ~15 GPa, as shown in Fig. 3b. Above ~15 GPa an increase in the rate of unit-cell volume compression can also be observed. The compressional behavior of gasparite-(Ce) has been modeled with both a second-order Birch-Murnaghan Equation of State (BM2-EoS) and a third-order Birch-Murnaghan Equation of State (BM3-EoS) (Birch 1934; Angel 2000), using the Eos_Fit7c_GUI software (Angel et al. 2014; Gonzalez-Platas et al. 2016), based on both the m.e.w. and helium ramps unit-cell data (normalized to corresponding ambient-$P$ values). The experimental data collected at pressures exceeding 15.22 GPa have not been taken into account, due to the observed change in the compressional behavior (Fig. 3b and Fig. 4). The fit of the BM-EoS to the experimental data yielded the following refined parameters:

- $K_{P0,T0} = 109.4(3)$ GPa ($\beta_{V} = 0.00914(3)$ GPa$^{-1}$) and $V_0 = 320.58(3)$ Å$^3$ for the BM2-EoS,
- $K_{P0,T0} = 108.3(10)$ GPa ($\beta_{V} = 0.00923(9)$ GPa$^{-1}$), $K' = 4.2(2)$ and $V_0 = 320.59(3)$ Å$^3$ for the BM3-EoS.

An analysis of the finite Eulerian strain ($\epsilon_e$) vs. the normalized pressure ($\epsilon_n$) plot [Figure S1; see Angel (2000) for further details] suggests that the refined BM2-EoS curve (reported in Fig. 4) properly describes the elastic compressional behavior of gasparite-(Ce). In addition, the compressional behaviors along the three principal crystallographic directions have been modeled with BM2-EoS. As for the $P$–$V$ data, the fit of the BM2-EoS has been conducted on the normalized data up to 13.70 GPa, yielding the following results, where $K_0$ is the refined linearized bulk modulus [see Angel (2000) for further details]: $K_a = 93(4)$ GPa ($\beta_a = 0.00357(9)$ GPa$^{-1}$) and $a_0 = 6.9286(13)$ Å; $K_b = 105(4)$ GPa ($\beta_b = 0.00318(9)$ GPa$^{-1}$) and $b_0 = 7.1265(9)$ Å; $K_c = 122(4)$ GPa ($\beta_c = 0.00273(9)$ GPa$^{-1}$) and $c_0 = 6.7120(10)$ Å. Given the monoclinic symmetry of gasparite-(Ce), the
compressibility along the unit-cell axes does not allow a comprehensive description of the elastic anisotropy, due to the variation of the \( \beta \) angle as a function of pressure. Therefore, magnitude and orientation of the finite Eulerian unit-strain tensor have been calculated based on the data from the helium ramp, between 0.0001 and 15.22 GPa, using the software Win_Strain (Angell 2011). The average compressibility values along the axes of the strain ellipsoid (with \( \varepsilon_1 > \varepsilon_2 > \varepsilon_3 \)) are: \( \varepsilon_1 = 0.00303(1) \text{ GPa}^{-1}, \varepsilon_2 = 0.002546(9) \text{ GPa}^{-1}, \varepsilon_3 = 0.001711(8) \text{ GPa}^{-1} \), leading to the following anisotropic scheme \( \varepsilon_1:\varepsilon_2:\varepsilon_3 = 1.77:1.49:1 \). The following matrix describes the geometric relations between the crystallographic axes and the strain ellipsoid orientation (where \( X/\alpha^* \) and \( Y/\beta^* \)):

\[
\begin{pmatrix}
\varepsilon_1 & 23.7(2)^\circ & 90^\circ & 127.4(2)^\circ \\
\varepsilon_2 & 90^\circ & 180^\circ & 90^\circ \\
\varepsilon_3 & 113.7(2)^\circ & 90^\circ & 142.6(2)^\circ
\end{pmatrix}
\begin{pmatrix}
a \\
b \\
c
\end{pmatrix}
\]

The matrix shows that both the directions of maximum and minimum compressibility lay on the (010) plane.

As previously mentioned, the monazite-type structure of gasparite-(Ce) undergoes a change in the compressional behavior, pointed out by the significant deviation in the \( \beta, V \) vs. \( P \) trends at \( P > 15.22 \text{ GPa} \). It is worth to underline that a similar behavior of the \( \beta, V \) vs. \( P \) trends was also described by Huang et al. (2010) for the synthetic powder samples of CePO_4 at about 11.5 GPa, compressed in methanol-ethanol (4:1) mixture. A careful analysis of the systematic absences in the experimental single-crystal diffraction patterns of this study suggests that no change in symmetry occurs coupled with the change in compressibility. In this case, as the experiment was conducted using a single crystal compressed in helium, we can exclude that the observed change in the compressional behavior may be ascribed to non-hydrostatic conditions. The structural mechanism likely responsible for this change in the elastic behavior is discussed in the next High-pressure structure deformation Section.

As discussed in Introduction Section, no experimental data about the elastic properties of the monazite-type arsenates have ever been experimentally obtained. The bulk modulus of gasparite-(Ce) \( (K_{0V} = 109.4 \text{ GPa}) \) is lower than the theoretical bulk moduli determined by Li et al. (2009) for both LaAsO_4 and CeAsO_4 \( (K_{0V} = 124.5 \text{ GPa} \) and \( K_{0V} = 125.1 \text{ GPa} \), respectively). On the other hand, it is worth to mention that also the theoretical bulk moduli obtained by Li et al. (2009) for monazite-type phosphates usually overestimate the experimental ones. Moreover, since different bulk moduli have been refined or calculated for CePO_4, ranging from 109(1) to 122 GPa (Errandonea et al. 2017; 2018; Huang et al. 2010), it is not straightforward to provide a comparison between gasparite-(Ce) and the large family of synthetic monazite-type REEPO_4, also in the light of the multi-elemental composition of the \( A \) site of the investigated natural sample. Considering the most recent and complete data, provided by Errandonea et al. (2018) on CePO_4 \( (K_{0V} = 117.3(5) \text{ GPa}, K' = 4.54(3) \text{ refined with a BM3-EoS}) \), the high-pressure compressibility of gasparite-(Ce) is slightly higher. This difference could be ascribed to the complex composition of the REE-bearing site in gasparite-(Ce) or to the presence of arsenic in place of phosphorous at the tetrahedral site, or by a combination of the two factors. Several authors (Li et al. 2009; Errandonea et al. 2011a; b) pointed out that, at a given composition of the REE cation, the arsenates are always more compressible than the phosphates counterparts, due to the higher compressibility of the AsO_4 with respect to the PO_4 tetrahedron. In addition, as pointed out by Pagliaro et al. (2022), the T-site of arsenates and phosphates has a strong influence on the whole structural features and, in particular, on the volume of both the REE-coordination polyhedron and unit-cell. Thus, the REE polyhedron in monazite-(Ce) is smaller, if compared to the REE polyhedron in gasparite-(Ce), despite a very similar population of the REE site. In this light, being the PO_4 tetrahedra less compressible than the AsO_4 ones, the smaller REE polyhedron of phosphates is reasonably also less compressible than the larger REE polyhedron of arsenates.

Interestingly, the bulk modulus of gasparite-(Ce) is intermediate between those of synthetic REEPO_4 and LaVO_4 \( (K_{0V} = 95(5) \text{ GPa}; \text{Errandonea et al. 2016}) \): the volume of AsO_4 is, indeed, intermediate between those of the PO_4 and VO_4 tetrahedra \( (\text{LaVO}_4 \text{ is the only endmember vanadate crystallizing with the monazite-type structure, if synthesized under high-temperature conditions, according to Bashir and Khan (2006), Rice and Robinson (1976), Aldred (1984), Baran and Aymonino (1971)} ) \).

### High-pressure structure deformation

The analysis of the structural deformation mechanisms, acting at the atomic scale, is mainly based on the experimental data from the \( \text{m.e.w.} \) ramp. Indeed, most of the analysis of the refined structural models from the He ramp revealed a scattering of the \( P \)-induced evolution of relevant structural parameters. Figure 5 and Table S4 show the high-pressure volume evolution for both the REEO_3 and the AsO_4 coordination polyhedra. The volumes of the coordination polyhedra have been measured by means of the routine implemented in the Vesta 3 software (Momma and Izumi 2011).

A second-order Birch-Murnaghan EoS \( (K' = 4) \) fitted to the \( P-V \) data of the REEO_3 polyhedron leads to a refined bulk modulus of \( K_{0P,T0} = 99(3) \text{ GPa} \) \( (\beta_V = 0.0101(9) \text{ GPa}^{-1}; V_0 = 33.02(4) \text{ Å}^3) \). The AsO_4 tetrahedron clearly shows a discontinuity in the compressional behavior, with a significant compression until 2.30 GPa, followed by a stiffening that makes this structural unit substantially uncompressible.
between 2.30 and 9.31 GPa, preventing a modeling of its elastic behavior by an EoS. As the bulk compressibility of gasparite-(Ce) ($\beta_V=0.00923(9)$ GPa$^{-1}$) is lower with respect to the compressibility of the REEO$_9$ coordination polyhedron ($\beta_{V,\text{REEO}_9}=0.0101(9)$ GPa$^{-1}$), it follows that the latter plays a key role in accommodating the unit-cell volume compression.

As reported in Fig. 6b and Table S5, the analysis of the high-pressure behavior of the REE-O bond distances shows that the REEO$_9$ polyhedron is characterized by a clear anisotropic behavior. The two REE-O bond distances involving the O3 atoms are the less compressible, with the REE-O3$_a$ bond distance even showing an expansion with the pressure increase. According to the notation reported in Fig. 1a, the REE-O3$_a$ bond distances, along with REE-O2$_a$ and REE-O4$_a$, represent the connection between the REEO$_9$ polyhedron and the AsO$_4$ tetrahedra along the c axis. The expansion of the REE-O3$_a$ bond distance, coupled with the contraction along the REE-O1$_a$ bond, leads to a tilting of the AsO$_4$ tetrahedra, with a slight closure of the REE-As-REE interatomic angle (Fig. 7d, Table S4). Therefore, we can conclude that the major mechanism responsible for the contraction along the c crystallographic direction is the bulk compression of the REEO$_9$ polyhedron, whereas a slight tilting of the AsO$_4$ polyhedron tends to accommodate this linear contraction.

In addition, the evolution with pressure of the REE-O3$_c$ interatomic distance, as it is defined in Fig. 8a, has been investigated. As shown in the normalized diagram in Fig. 8b, the REE-O3$_c$ interatomic distance is significantly more compressible compared to any other REE-O bond distance in the coordination sphere of the REE site and it shows a similar and rather significant compressional trend both in the m.e.w. and helium ramps. Between 13.72 and 17.22 GPa, the shortening of the REE-O3$_c$ undergoes a saturation before showing an abrupt compression above ~17 GPa, reaching the minimum value of 2.85(3) Å at 21.05 GPa. As the O3$_c$ oxygen (as defined in Fig. 8a) does not belong to the coordination sphere of the REE site at ambient conditions, we can conclude that, at ca. 15 GPa, the REEO$_9$ coordination polyhedron in gasparite-(Ce) experiences an increase in its coordination number from CN = 9 to CN = 10. This structural mechanism is likely responsible for the change in the compressional behavior shown in Fig. 3 and previously discussed.

Eventually, for a comprehensive understanding of the deformation mechanisms occurring in gasparite-(Ce) at high pressure, and to explain the anisotropic behavior described...
Fig. 7  Representation of the crystal structure of gasparite-(Ce), showing the four independent lozenge-like units in purple (a, b and c) and high-pressure evolution of relevant interatomic angles (d); section of the Eulerian strain ellipsoid in the (010) plane (a).

Fig. 8  a Crystal structure of gasparite-(Ce) in the surrounding of the REE-bearing A-site: in purple is reported the longest REE-O3c interatomic distance, in sky blue the REE-O distances of the equatorial pentagon, while in green are reported the four REE-O chain-connecting bonds; b evolution with pressure of the ten REE-O interatomic distances (for the REE-O3c interatomic distance, the black and grey circles refer to the m.e.w. and He ramp respectively)
by the finite-strain tensor analysis, it is essential to introduce the REE-Ox-REE angles (Fig. 7a,b,c, Table S4), which represent the lozenge-like connection between adjacent chains. Six independent angular units, defining 4 independent lozenge-like connections (i.e., REE-O4-REE–REE-O2-REE (I); REE-O1-REE–REE-O2-REE (II), REE-O2-REE–REE-O2-REE (III); REE-O3-REE–REE-O3-REE (IV)) can be described as reported in Fig. 7a,b,c and Table S4. The only mechanism significantly contributing to the anisotropic compression involves the lozenge-like unit I, defined by the couple of interatomic angles REE-O2-REE and REE-O4-REE. These lozenge-like units define a slightly sinuousoidal chain system running along the [010] direction, as reported in Fig. 7a. The opening of these two angles in response to the pressure increase, as shown in Fig. 7d, leads to a stretching of the chain. This deformation mechanism, coupled with the slight shortening of the REE-As-REE (Fig. 7d) chains running along the [010], provides the rationale for the anisotropic scheme defined by the finite-strain Eulerian tensor reported in Fig. 7a.

Concluding remarks

The compressional behavior of the natural REE-bearing arsenate gasparite-(Ce) has been studied up to 21.05 GPa. The bulk compression of gasparite-(Ce) has been described with both a 2nd and 3rd order Birch-Murnaghan EoS up to 15.22 GPa, leading to a bulk modulus of $K_{P_0,T_0} = 109.4(3)$ GPa ($V_0 = 320.58(3) \ \text{Å}^3$, $K' = 4$) and $K'_{P_0,T_0} = 108.3(10)$ GPa ($K' = 4.23(20)$) and $V_0 = 320.59(3) \ \text{Å}^3$), respectively. At pressure exceeding ~15 GPa, gasparite-(Ce) undergoes a change in the compressional behavior, clearly marked by a discontinuity in the compressional path of the $\beta$-angle (Fig. 3b), as previously also described for the isostructural synthetic CePO$_4$ (Huang et al. 2010). The analysis of the refined structure models suggests that this change of the compressional behavior is related to the increase in the coordination number of the A-site from 9 to 10 at $P > 15$ GPa, with the O$_3$ oxygen (Fig. 8) entering the coordination sphere of the REE cation in response to the $P$-induced structure deformation. The structural refinements show that the compression of the REEO$_9$ coordination polyhedron ($K_{P_0,T_0} = 99(3)$ GPa; $V_0 = 33.02(4) \ \text{Å}^3$) mostly accommodates the bulk compression of gasparite-(Ce), whereas the AsO$_4$ units behave as almost rigid bodies at $P$ exceeding 2.30 GPa. Moreover, the structural analysis also showed that a modest tilting occurs within the [001] chain units, represented by the evolution of REE-As-REE interatomic angle (Fig. 7). Finally, the high-pressure evolution of six independent REE-O-REE bond angles, previously described (Fig. 7), has been taken into account to explain the anisotropy of the gasparite-(Ce) compressional behavior. It has been observed that the angular deformation of the couple made by the REE-O2-REE and REE-O4-REE angles is responsible for a stretching of the structure along the [010] direction, in agreement with the anisotropic scheme defined by the finite Eulerian strain tensor.

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Declarations

Conflict of interest The authors have no financial and competing interests to declare that are relevant to the content of this article.

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