

Structural mechanisms of pressure-induced isosymmetric second-order phase transitions

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ABSTRACT

Pressure-induced polymorphic phase transitions are important in fundamental physics, chemistry, materials science, and geoscience. The isosymmetric phase transition is unique in that it retains crystal symmetry through the transition and exhibits either first- or second-order characteristics. However, the underlying mechanisms of the isosymmetric second-order phase transition have not been well constrained under high pressures. Here, we report a novel case of pressure-induced isosymmetric phase transition in cerite, a rare earth element (REE) mineral, using a diamond-anvil cell combined with in situ synchrotron single-crystal X-ray diffraction. This phase transition is triggered by an increase in coordination number (CN) and exhibits the second-order characteristics. By combining our findings with previous studies, we identify five distinct types of pressure-induced isosymmetric phase transitions. Furthermore, we propose an explanation for the nature (first- or second-order) of phase transitions triggered by increases in coordination number under pressure. The complexity of a mineral structure plays a crucial role in determining the type of isosymmetric phase transition observed. Crystal structures composed of single-building units tend to exhibit first-order transitions, while those with multiple building units exhibit greater flexibility and are more prone to second-order transitions. This study provides new evidence for isosymmetric second-order phase transitions triggered by pressure and an increase in coordination number, while offering valuable insights into the mechanisms governing such transitions.

Keywords: Isosymmetric phase transition, coordination number increase, high pressure, second-order phase transition, phase transition mechanisms

INTRODUCTION

Materials undergoing phase transitions under high pressure are of significant scientific and technological importance. High pressure can induce changes in the crystal structure of materials (Hemley 2000; Lei et al. 2009; Wang and Ma 2014; Salmon et al. 2019; Li et al. 2024), leading to subsequent modifications in their physical and chemical properties (Hemley 2000; Wang and Ma 2014; Li et al. 2024). These changes encompass pressure-induced magnetic transitions (Ding et al. 2008; Gao et al. 2008), metallization (Zhao et al. 2015; Barreda-Argüeso et al. 2019), and superconductivity (Li et al. 2018, 2022; Pei et al. 2021).

Crystal polymorphism refers to the ability of a substance with a consistent chemical composition to exist in multiple crystal structures (Anwar and Zahn 2017; Li et al. 2024). In the realm of mineral physics, common polymorphic phase transitions of crystals encompass both first-order and second-order phase transitions, and some can also be tricritical (Salje 1990; Ardit et al. 2015; Whitfield et al. 2016). First-order phase transitions in

crystals are typically accompanied by a significant discontinuity in the unit-cell volume. For instance, the pressure-induced phase transitions in orthopyroxene (opx) from α -opx to β -opx and γ -opx (Dera et al. 2013; Finkelstein et al. 2015; Xu et al. 2022b) and the ilvaite-II $\rightarrow$ ilvaite-III transition (Xu et al. 2022a) exemplify such transitions. In contrast, second-order phase transitions are characterized not by volume discontinuity but rather by an abrupt alteration in the second derivative of the free energy. An example of this transition is the pressure-induced transition from a body-centered cubic (bcc) to a tetragonal structure in cesium halides (Cedillo et al. 1991).

Isosymmetric phase transitions stand out among other phase transitions for maintaining crystal symmetry throughout the transition process (Christy 1995). This type of transition can be induced by temperature (Miyake et al. 2004; Ohi et al. 2008; Ohi and Miyake 2016) or pressure. Pressure-induced isosymmetric phase transitions, in particular, have garnered significant attention. Notable examples include the tilting and rotation of SiO_4 tetrahedra in certain silicate minerals like kalsilite (Gatta et al. 2011), the shearing movement of the charge reservoir layer in 111-type $\text{Na}_{1-x}\text{FeAs}$ (Liu et al. 2011), coordination number increase in PbF_2 (Haines et al. 1998), a change in the relative strengths

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of the ionic-covalent bonds along the $[\text{Ca}_3\text{Si}(\text{OH})_6(\text{H}_2\text{O})_{12}]^{4+}$ columns parallel to the *c*-axis in thaumasite (Ardit et al. 2014), and the layer shift in In_2Se_3 and dickite (Dera et al. 2003; Ke et al. 2014). The aforementioned examples pertain to isosymmetric first-order phase transitions. However, isosymmetric phase transitions can also be second-order, as observed in the pressure-induced spin crossover transitions in many Fe-bearing minerals (Lin et al. 2005; Merlini et al. 2010; Chen et al. 2012). Although there have been several reports of first-order phase transitions, i.e., an isostructural volume collapse due to spin crossover in $\epsilon\text{-FeOOH}$ (Thompson et al. 2020), changes in electronic structure in $\alpha\text{-Ag}_2\text{S}$ (Liang et al. 2020), Li^+ migration in the LiNbO_3 ionic conductor (Tao et al. 2024), and coordination number increase in Na-pyroxene (aegirine, NaFeSi_2O) (Xu et al. 2017). Compared to other types of phase transitions, there have been relatively few reports on pressure-induced isosymmetric second-order phase transitions, apart from spin crossover transition and charge transfer. To the best of our knowledge, isosymmetric second-order phase transitions triggered by coordination number increase have only been reported for Na-pyroxene (Xu et al. 2017).

Despite a wealth of previous research on pressure-induced isosymmetric phase transitions, several key aspects concerning the underlying transition mechanisms remain unresolved. Specifically, why does an increase in chemical bonding induced by pressure trigger first-order phase transitions in specific crystalline materials, while simultaneously exhibiting second-order phase transitions in others? To address this knowledge gap, we investigated a particular crystalline phase, cerite, a rare earth element (REE) mineral known for its trigonal crystal system and $R3c$ space group. We chose cerite due to its unique eightfold to 10-fold coordination numbers for the REE cations (further elaborated in the subsequent paragraph), indicating the possibility of the low-coordinated (specifically eightfold coordination) REE cation-bearing cerite experiencing an increase in coordination number under high pressure.

Naturally occurring cerites exhibit variations in the coordination number of their REE cations in different geological settings. Three types of cerite have been documented: (1) in the first type, all REE cations are eightfold coordinated (Moore and Shen 1983); (2) the second type comprises a mixture of eightfold and ninefold coordinated REE cations (Nestola et al. 2009); and (3) the third type consists of exclusively ninefold or 10-fold coordinated REE cations (Pakhomovsky et al. 2002; Atencio and Azzi 2020; Qu et al. 2020; Campostrini et al. 2023). Furthermore, cerite formed under relatively high-pressure conditions exhibits a higher coordination number of REE cations (Pakhomovsky et al. 2002; Qu et al. 2020). This variation in the coordination number makes low-coordinated cerite an ideal material for our study. Therefore, in this study, we selected a natural type-II cerite sample and conducted synchrotron single-crystal X-ray diffraction (SCXRD) experiments using a diamond-anvil cell (DAC) to investigate its structural evolution under high pressure.

EXPERIMENTAL METHODS

Sample

A natural type-II cerite was selected for this study. The cerite crystal was a natural specimen of unknown origin. A large crystal, ~ 2 mm in size, was

fragmented into smaller crystal grains for this investigation. Several grains were selected for EMPA analysis to determine their chemical composition, and the remaining crystal grains were used for the subsequent SCXRD experiments. Chemical analyses were performed using a JXA8230 tungsten filament electron microscope at the Institute of Geochemistry, Chinese Academy of Sciences. The microscope operated at an acceleration voltage of 25 kV, with a beam current of 20 nA, and a beam diameter of 1 μm . Online Materials¹ Table S1 presents the chemical data and standards employed in the analysis. The general structural formula of cerite is $\text{REE}_9\text{MX}(\text{SiO}_4)_6(\text{SiO}_3\text{OH})(\text{OH})_3$ (Moore and Shen 1983). Based on the electron microprobe results (Online Materials¹ Table S1), the chemical formula of cerite was determined to be $(\text{La}_{1.94}\text{Ce}_{3.75}\text{Pr}_{0.38}\text{Nd}_{1.40}\text{Sm}_{0.32}\text{Gd}_{0.15}\text{Ca}_{0.79}\text{X}_{0.27})(\text{Fe}_{0.24}\text{Mg}_{0.78})(\text{SiO}_4)_6(\text{SiO}_3\text{OH})[(\text{OH})_{1.17}\text{F}_{1.83}]$, where X indicates the presence of an unidentified element or elements necessary to bring the total of elements in the REE position up from 8.73 to around 9.

Methods

In situ high-pressure synchrotron SCXRD experiments were carried out at the GSECARS (Sutton et al. 2022) 13-BM-C beamline of the Advanced Photon Source, Argonne National Laboratory. SCXRD images were acquired using a PILATUS 1M detector mounted on a six-circle diffractometer (Zhang et al. 2022). The incident X-ray wavelength was 0.4340 Å, and the beam size was 12×18 μm . Calibration of the detector tilts, rotations, and sample-to-detector distances was performed using a LaB_6 powder standard (Zhang et al. 2017; Xu et al. 2022a). The Φ rotation step size was 0.5° , and the measurement exposure time was 1°/s.

We performed in situ high-pressure experiments using a DAC equipped with a pair of Boehler-Almax-type WC seats and diamonds. The diamond culet diameter was 300 μm . To create the sample chamber, a 180 μm diameter hole was drilled in the pre-indented Re gasket, which had a thickness of ~ 45 μm . Two cerite crystals, each with dimensions of ~ 30 – 40 μm on their sides and a thickness of 10–15 μm , devoid of any inclusions and exhibiting high diffraction quality (Fig. 1), were carefully placed into the DAC chamber (Fig. 1) for the high-pressure single-crystal X-ray diffraction experiments. A ruby sphere served as a pressure marker, and its fluorescence spectra were utilized for pressure measurements (Shen et al. 2021). The pressure was measured before and after data collection, and the average value was used. The pressure uncertainty reported is half of the pressure change before and after sample data collection. When it was smaller than 0.1 GPa, 0.1 GPa was reported as the pressure uncertainty. To achieve a quasi-hydrostatic high-pressure condition in the sample chamber, Ne gas was loaded as the pressure medium (Klotz et al. 2009).

During the experiments, SCXRD data were collected at 25 different pressures ranging from ambient pressure to 29.8 GPa. The APEX 4.0 software suite was employed for experimental data reduction and to determine the unit-cell parameters and volumes (Table 1). Crystal structure refinement was carried out using the SHELX software package (Sheldrick 2008), facilitated by the Olex 2 user interface (Dolomanov et al. 2009). The starting model for refinement was the crystal structure of cerite-(La) proposed by Pakhomovsky et al. (2002). Refinement was performed only for data up to 26.3 GPa, as the data collected at higher pressures were insufficient for reliable structural refinement.

According to the structural refinement conducted by Pakhomovsky et al. (2002), the REE and Ca atoms occupy three distinct crystallographic positions [REE1(R1), REE2(R2), and REE3(R3)], where the larger La atom mainly occupies R1, while the smaller Ca atom mainly occupies R2 and R3. The M position is occupied by Fe and Mg atoms. Therefore, based on the obtained electron microprobe data, the site occupancies for the structural refinement in this study were set as follows. We assumed that Ca exclusively occupies R2 and R3 ($\text{Ca} = 0.13$), with REEs other than La (Ce–Nd) evenly distributed among R1, R2, and R3, specifically $\text{Ce} = 0.42$, $\text{Pr} = 0.04$, $\text{Nd} = 0.16$, $\text{Sm} = 0.04$, and $\text{Gd} = 0.02$. Consequently, La was calculated as 0.33 on R1 ($\text{La} = 1 - 0.42 - 0.04 - 0.16 - 0.04 - 0.02$). The remaining La was then equally distributed between R2 and R3, resulting in $\text{La} = 0.16$ for both R2 and R3. Furthermore, the M position was entirely occupied by Fe and Mg, while all the Si positions were fully occupied by Si. As a result, Mg was calculated to be 0.77 on M [$\text{Mg} = 0.78/(0.24 + 0.78)$], resulting in Fe being 0.23 for M ($\text{Fe} = 1 - 0.77$). The OH/F anion substitution was not considered as they have similar electron numbers. It is worth noting that Pakhomovsky et al. (2002) suggested a low-occupancy Ca position (X) in their cerite structure, but our structural refinement indicated the absence of Ca at this position. Due to the limited number of diffraction peaks collected in the DAC during the experiment, anisotropic atomic displacement parameters (ADPs) were only applied to cations in the three REE positions during refinement.

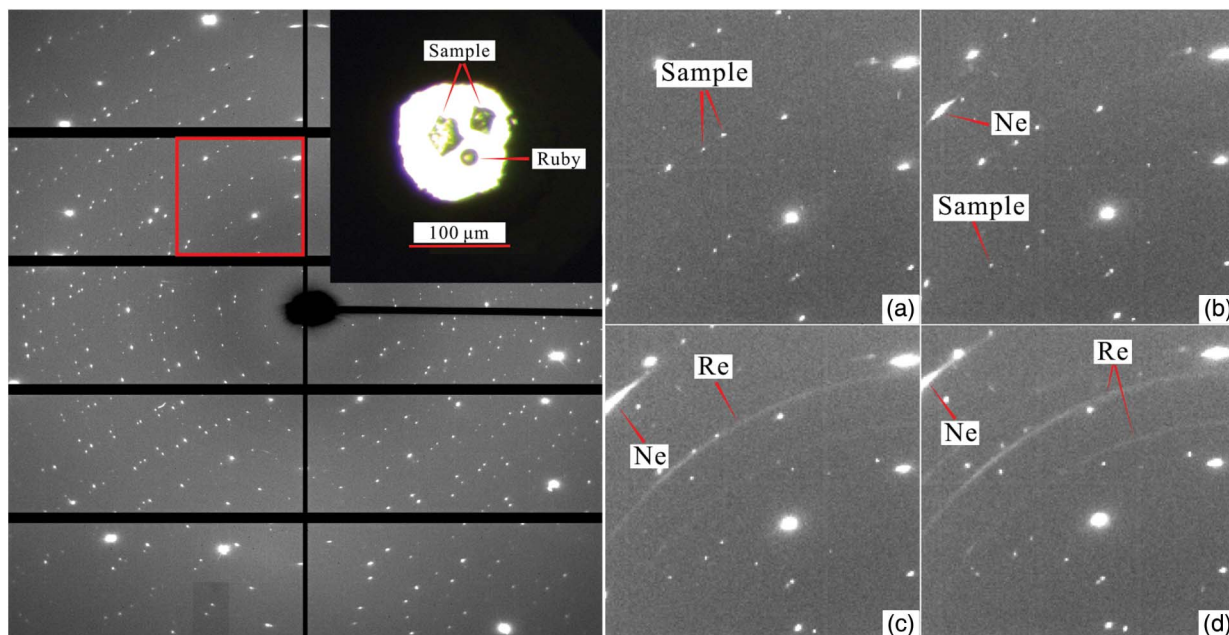


FIGURE 1. Left: a representative diffraction image of cerite at 0.9 GPa, and the insert figure is a sample photo taken at 0.9 GPa. The red rectangle indicates the zoomed-in regions that are compared on the right. Right: magnified diffraction images for the ease of comparison at (a) 0.9 GPa; (b) 10.4 GPa; (c) 20.5 GPa; (d) 29.8 GPa. (Color online.)

Similarly, O10, O11, O12, and O13 were assumed to share the same ADPs due to the aforementioned limitations. Despite collecting diffraction data for two crystals in our experiment, we exclusively utilized the data from one cerite crystal to ensure consistency.

The results of structural refinement under different pressures are detailed in Table 2. The R_1 values varied from 4.03% to 8.17%. Interatomic distances and polyhedral parameters (Online Materials¹ Tables S2–S4) were calculated using the VESTA software (Momma and Izumi 2011).

TABLE 1. Unit-cell parameters and volume of cerite at different pressures

P (GPa)	a (Å)	c (Å)	V (Å ³)
0.0001	10.8235(3)	37.9948(10)	3854.68(14)
0.9(1)	10.7899(4)	37.9075(12)	3822.04(17)
1.6(1)	10.7652(4)	37.8523(14)	3798.99(19)
2.5(1)	10.7346(4)	37.7828(13)	3770.51(18)
3.1(1)	10.7178(4)	37.7470(14)	3755.10(18)
4.5(1)	10.6769(4)	37.6471(13)	3716.64(18)
5.5(1)	10.6464(4)	37.5728(13)	3688.15(17)
6.7(1)	10.6069(4)	37.4767(14)	3651.50(18)
7.8(1)	10.5756(4)	37.3917(14)	3621.74(18)
9.0(1)	10.5451(4)	37.3069(14)	3592.67(19)
10.4(1)	10.5071(5)	37.2053(17)	3557.20(20)
11.6(1)	10.4782(4)	37.1213(15)	3529.60(19)
12.6(1)	10.4522(4)	37.0478(14)	3505.16(17)
13.6(1)	10.4296(4)	36.9849(14)	3484.12(18)
14.6(1)	10.4060(4)	36.9127(14)	3461.55(18)
16.5(2)	10.3649(4)	36.7861(15)	3422.50(18)
17.7(1)	10.3362(4)	36.7017(14)	3395.74(18)
19.3(1)	10.3008(4)	36.5893(16)	3362.22(19)
20.5(1)	10.2751(4)	36.5107(15)	3338.15(18)
21.8(1)	10.2477(5)	36.4157(17)	3311.90(20)
23.7(1)	10.2095(5)	36.2881(18)	3275.70(20)
25.1(1)	10.1806(5)	36.1970(20)	3249.00(20)
26.3(1)	10.1562(6)	36.1120(20)	3225.80(20)
27.8(1)	10.1293(6)	36.0030(20)	3199.10(30)
29.8(1)	10.0948(7)	35.8760(30)	3166.10(30)

Note: Numbers in parentheses represent standard deviations to the last significant digit.

RESULTS

Equation of state

Unit-cell parameters of cerite at pressures up to 29.8 GPa are summarized in Table 1. At ambient pressure, the analysis of SCXRD data revealed that the cerite sample belongs to a trigonal system with an $R\bar{3}c$ space group. The unit-cell parameters and volume were determined to be $a = 10.8235(3)$ Å, $c = 37.9948(10)$ Å, and $V = 3854.68(14)$ Å³. With increasing pressure, both the unit-cell parameters a and c , as well as the volume V , consistently decrease (Fig. 2). To characterize the equation of state (EoS) for cerite, the pressure-volume (P - V) data were fitted to a third-order Birch-Murnaghan EoS (III-BM-EoS) (Angel 2000) using the EosFit7-GUI software (Angel et al. 2014). The III-BM-EoS is as follows:

$$P(V) = \frac{3}{2} K_0 \left[\left(\frac{V_0}{V} \right)^{\frac{7}{3}} - \left(\frac{V_0}{V} \right)^{\frac{5}{3}} \right] \times \left\{ 1 + \frac{3}{4} (K'_0 - 4) \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] \right\}$$

where V_0 , V , K_0 , and K'_0 represent the zero-pressure volume, high-pressure volume, isothermal bulk modulus, and its pressure derivative, respectively. The fitting yielded the following results: $V_0 = 3854.6(3)$ Å³, $K_0 = 116.8(6)$ GPa, and $K'_0 = 2.8(1)$.

The quality of the EoS fitting was assessed using the volume Eulerian finite strain $\{f_E = [(V_0/V)^{2/3} - 1]/2\}$ vs. “normalized stress” $\{F_E = P/[3f_E(2f_E + 1)^{5/2}]\}$ (Angel 2000). Figure 3a demonstrates the distribution of $f_E - F_E$ data from ambient pressure to 5.5 GPa, which follows a linear trend. This suggests that an III-BM-EoS sufficiently describes the P - V data within this pressure range. However, a noticeable discontinuity is observed

TABLE 2. Structural refinement details of cerite at different pressures

<i>P</i> (GPa)	0.0001	1.6(1)	3.1(1)	5.5(1)	7.8(1)	10.4(1)
<i>R</i> _{int} (%)	8.45	2.77	2.72	2.88	3.19	3.12
<i>R</i> ₁ (%)	8.17	4.03	4.27	4.40	4.55	4.80
<i>wR</i> ₂ (all reflections, %)	23.08	12.10	13.23	13.33	12.93	14.86
Goodness of fit	1.012	1.018	1.069	1.084	1.053	1.037
No. of total reflections	1202	1320	1298	1230	1216	1191
No. of reflections [<i>F</i> _o > 4σ(<i>F</i> _o)]	466	481	499	480	478	474
<i>P</i> (GPa)	12.6(1)	14.6(1)	17.7(1)	20.5(1)	23.7(1)	26.3(1)
<i>R</i> _{int} (%)	4.31	3.57	5.34	6.20	6.12	7.10
<i>R</i> ₁ (%)	4.88	4.66	5.07	5.37	6.02	7.25
<i>wR</i> ₂ (all reflections, %)	14.57	14.36	14.87	16.24	17.85	20.46
Goodness of fit	1.064	1.054	1.059	1.081	1.063	1.025
No. of total reflections	1180	1157	1162	1142	1109	1044
No. of reflections [<i>F</i> _o > 4σ(<i>F</i> _o)]	469	442	449	442	406	380

Note: Numbers in parentheses represent standard deviations to the last significant digit.

between 5.5 and 6.7 GPa, and within the high-pressure region (6.7–29.8 GPa), the data points form a nonlinear curve. These indicate that the *P*-*V* data within this pressure range can only be accurately described by employing a fourth-order Birch-Murnaghan EoS (IV-BM-EoS) (Angel 2000).

Hence, we conducted separate EoS fits for the *P*-*V* data below and above 5.5 GPa. For the *P*-*V* data collected between ambient pressure and 5.5 GPa, fitting with an III-BM-EoS yielded *V*₀ = 3854.7(1) Å³, *K*₀ = 105(3) GPa, and *K*'₀ = 8(1). Conversely, for the data within 6.7–29.8 GPa, an IV-BM-EoS was used for the EoS fitting:

$$P = 3K_0 f_E (1 + 2f_E)^{\frac{5}{3}} (1 + 3/2(K'_0 - 4)f_E + 3/2(K_0 K''_0 + (K'_0 - 4)(K'_0 - 3) + 35/9)f_E^2) f_E \\ f_E = [(V_0/V)^{2/3} - 1]/2$$

where *K*'₀ is the second-order derivative of *K*₀. The fitting yielded: *V*₀ = 3854.5(7) Å³, *K*₀ = 111(1) GPa, *K*'₀ = 4.5(2), and *K*'₀ = −0.20(3). As depicted in Figures 2a and 3a, the piecewise fitting properly describes the data.

Figures 2b and 2c illustrate the variations of the unit-cell parameters *a* and *c* of cerite with pressure. To determine the EoS parameters for *a* and *c*, we substituted the cube of the unit-cell parameters (*a* or *c*) for the unit-cell volume in the III- or IV-BM-EoS described above (Angel 2000), also using the EoSFit7-GUI software (Angel et al. 2014). Similar to the unit-cell volume, the *f*_E − *F*_E plots for *a* and *c* exhibit discontinuities within 5.5–6.7 GPa (Figs. 3b–3c). Consequently, separate EoS fits were performed for *a* and *c*. The fitting for data below 5.5 GPa yielded: *a*₀ = 10.8235(3) Å, *K*_{*a*0} = 281(7) GPa, and *K*'_{*a*0} = 21(4) for *a*, and *c*₀ = 37.9913(2) Å, *K*_{*c*0} = 410(25) GPa and *K*'_{*c*0} = 36(14) for *c*. In contrast, for the data within 6.7–29.8 GPa, the fitting yielded: *a*₀ = 10.8205(1) Å, *K*_{*a*0} = 289(10) GPa, *K*'_{*a*0} = 14(3), and *K*'_{*a*0} = −0.21(12) for *a*, and *c*₀ = 37.9881(2) Å, *K*_{*c*0} = 463(11) GPa, *K*'_{*c*0} = 8(2), and *K*'_{*c*0} = −0.12(5) for *c*.

Polyhedral compression

Table 2 presents the details of the structural refinement for cerite under various pressures, affirming that cerite retains its symmetry in the *R*3̄̄̄ space group throughout the pressure range investigated. The crystal structure of cerite at ambient pressure is depicted in Figure 4. With increasing pressure, the polyhedra (RO₉, MO₆, and SiO₄) display distinct compression behaviors.

RO₉. Based on the findings reported by Pakhomovsky et al. (2002), the cerite structure comprises three REE³⁺ surrounded by nine O^{2−} anions. Our results indicate that at ambient pressure, the average interatomic distances between REE and O atoms (*d*_{REO}) are 2.6291, 2.5330, and 2.6475 Å for the R1O₉, R2O₉, and R3O₉ polyhedra, respectively. However, for the R1O₉ and R3O₉ polyhedra, the specific REE-O distances, *d*_{R1-O9} [3.15(6) Å] and *d*_{R3-O1} [3.30(5) Å], are notably larger than their corresponding average REE-O interatomic distances. The respective volumes of the three RO₉ polyhedra at ambient pressure are *V*_{R1} = 34.97 Å³, *V*_{R2} = 31.73 Å³, and *V*_{R3} = 35.73 Å³.

With increasing pressure, the *d*_{REO} values of the three RO₉ polyhedra exhibit distinct characteristics (Fig. 5; Online Materials¹ Table S2). Specifically, for the R1O₉ polyhedron, all *d*_{R1-O} distances, except *d*_{R1-O9}, decrease irregularly as the pressure increases, leading to a reduction of only 2.9–7.0% from ambient pressure to 26.3 GPa. However, *d*_{R1-O9} shows a rapid decrease from ambient pressure to 5.5 GPa, contracting by 11.1% from 3.15(6) to 2.80(6) Å. Subsequently, with further pressure increase, *d*_{R1-O9} exhibits similar compressional behavior to other *d*_{R1-O} distances, as depicted in Figure 5a, decreasing by 3.9% from 5.5 to 26.3 GPa. Regarding the R2O₉ polyhedron, *d*_{R2-O9} displays the highest compressibility, experiencing a significant decrease of 21% from ambient pressure to 26.3 GPa. In contrast, the other eight *d*_{R2-O} distances decrease only by 0.8–8.4% within the same pressure range (Fig. 5b). For the R3O₉ polyhedron (Fig. 5c), the *d*_{R3-O1} value exhibits the greatest compressibility, decreasing by 18.8% from ambient pressure to 26.3 GPa and surpassing the reductions observed in the other eight *d*_{R3-O} distances (1.5–11.1%). Furthermore, all three RO₉ polyhedral volumes exhibit a steady decrease throughout the entire pressure range (Fig. 5d), contracting by 18%, 20%, and 22%, respectively.

MO₆. In the MO₆ octahedron, six O^{2−} anions coordinate with the cations, comprising three identical O4 anions and three identical O7 anions. At ambient pressure, the distances between the cations and O4/O7 anions (*d*_{M-O4} and *d*_{M-O7}, respectively) are 2.13(7) and 2.19(4) Å, resulting in an average of 2.16 Å. The polyhedral volume of the MO₆ octahedron is 13.30 Å³. As the pressure increases, both *d*_{M-O4} and *d*_{M-O7} decrease irregularly from ambient pressure to 26.3 GPa (Online Materials¹ Table S3 and Fig. S1). The *d*_{M-O4} experiences an 8.5% reduction, while *d*_{M-O7} decreases by 10.1%. Concurrently, the

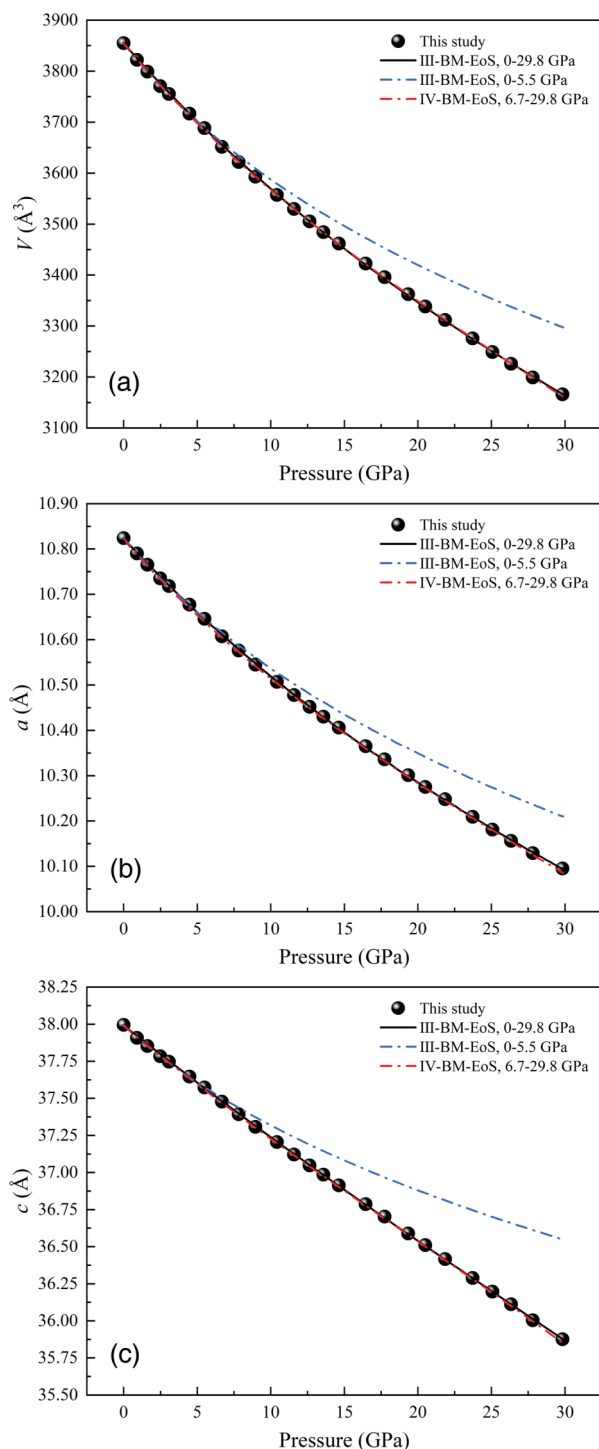


FIGURE 2. Illustration of the relationship between pressure and various parameters: unit-cell volume V (a), parameters a (b), and c (c). Black line represents the fitting of all data to an III-BM-EoS. Blue line represents the fitting of the data from ambient pressure to 5.5 GPa to an III-BM-EoS, while red line represents the fitting of the data within 6.7–29.8 GPa to an IV-BM-EoS. (Color online.)

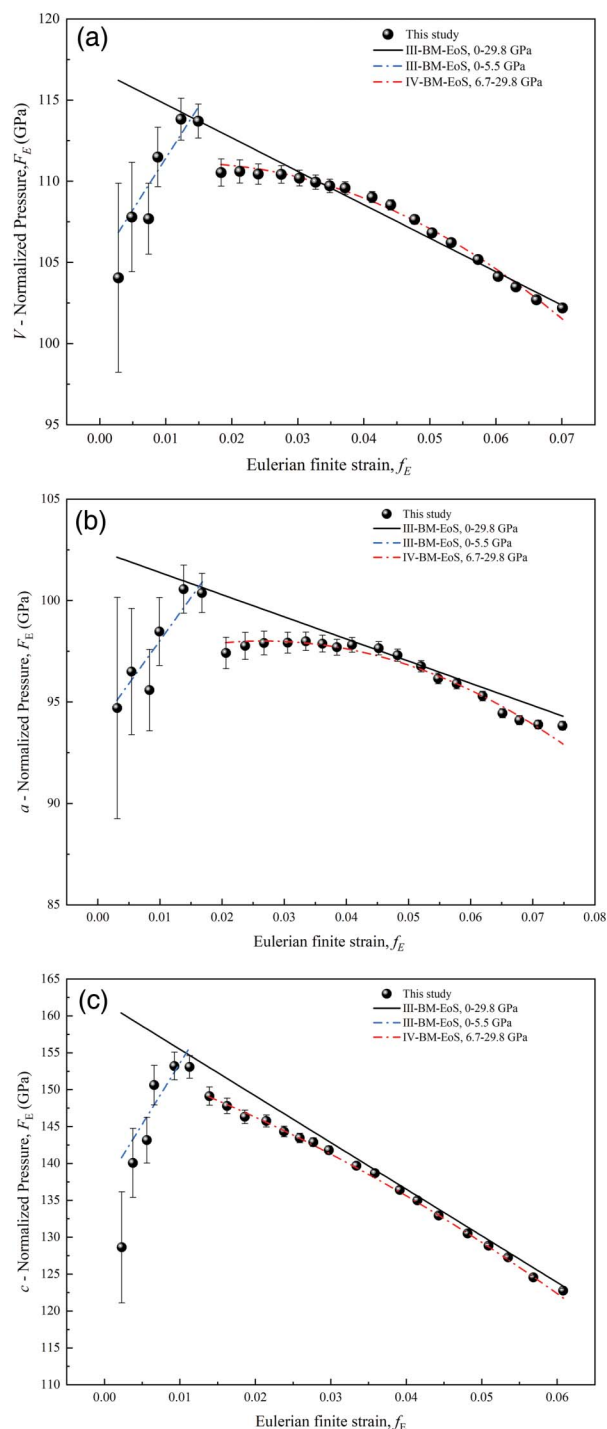


FIGURE 3. Eulerian strain-Normalized pressure ($f_E - F_E$) plots for unit-cell volume (a) and parameters a (b) and c (c). Black line corresponds to an III-BM-EoS fitting for all the data. Blue line represents the fitting of data below 5.5 GPa to an III-BM-EoS, while red line depicts the fitting of the data within 6.7–29.8 GPa to an IV-BM-EoS. (Color online.)

polyhedral volume of MO_6 octahedron decreases by 27%, demonstrating a highly comparable compressional behavior to that of the $d_{\text{M-O}}$ distances across the entire pressure range.

SiO₄. The cerite structure comprises three distinct SiO_4 tetrahedra. Si1 and Si2 are coordinated to four different O^{2-} anions, while Si3 is coordinated to three identical O9 anions and one O10 anion. At ambient pressure, the average $d_{\text{Si-O}}$ distances are $d_{\text{Si1-O}} = 1.5687 \text{ \AA}$, $d_{\text{Si2-O}} = 1.6305 \text{ \AA}$, and $d_{\text{Si3-O}} = 1.5243 \text{ \AA}$ for Si1O₄, Si2O₄, and Si3O₄, respectively. The corresponding volumes are $V_{\text{Si1}} = 1.96 \text{ \AA}^3$, $V_{\text{Si2}} = 2.19 \text{ \AA}^3$, and $V_{\text{Si3}} = 1.79 \text{ \AA}^3$, respectively. As the pressure increases, the interatomic distances within all three SiO_4 tetrahedra exhibit irregular variations (Online Materials¹ Table S4 and Fig. S2). These variations indicate a relatively minor dependence on pressure compared to the RO₉ and MO₆ polyhedra. For instance, the average $d_{\text{Si2-O}}$ decreases by only 2.6% as the pressure increases from ambient pressure to 26.3 GPa (Online Materials¹ Fig. S2b). Similarly, the volume compression of the Si2O₄ tetrahedron is negligible, as depicted in Online Materials¹ Figure S2d. Specifically, V_{Si2} decreases by only 7.4% from 2.19 to 2.03 $\text{\AA}^3$ across the entire pressure range. In contrast, the compressions of the Si1O₄ and Si3O₄ tetrahedra are even more insignificant, as illustrated in Online Materials¹ Table S4 and Figures S2a–S2b.

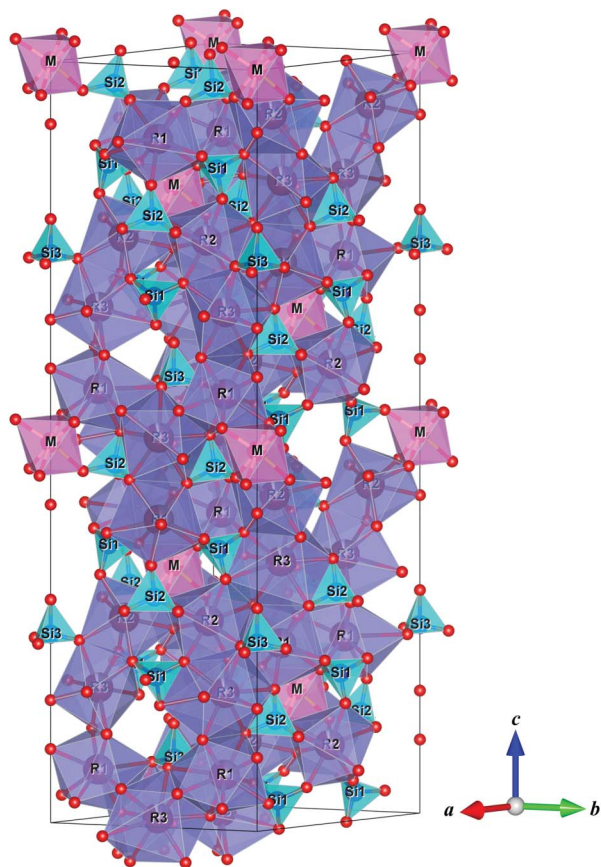


FIGURE 4. Crystal structure of cerite at ambient pressure. R1, R2, and R3 are the three crystallographically distinct sites occupied by REE^{3+} cations, and red spheres indicate O^{2-} or OH^- anions. (Color online.)

DISCUSSION

Compression mechanism and anisotropy

In the cerite structure, the compressional behaviors of the three types of polyhedra (SiO_4 , MO_6 , and RO_9) are significantly different, with RO_9 polyhedra and MO_6 octahedron demonstrating higher compressibility compared to SiO_4 tetrahedra (Fig. 5; Online Materials¹ Figs. S1–S2). The compression of the cerite unit cell primarily occurs due to a reduction in the volumes of MO_6 and RO_9 polyhedra (Online Materials¹ Fig. S3). Within the pressure range investigated here, the volumes of these polyhedra steadily decrease with increasing pressure, with the MO_6 octahedron showing the highest compressibility (Online Materials¹ Fig. S3). Among the three RO_9 polyhedra, R1O₉ and R3O₉ display greater compressibility than R2O₉. Furthermore, the RO_9 polyhedra occupy more space within the cerite structure and are comparatively larger than the MO_6 octahedra (Fig. 4). Consequently, the volume compression of the RO_9 polyhedra plays a more significant role in the overall compression of the unit cell.

Online Materials¹ Figure S4 compares the axial compressions along the *a*- and *c*-axes, revealing that the unit-cell parameter *a* is more compressible than *c*. This anisotropy arises from the characteristics of the cerite structure. Within the structure, the interatomic distances $d_{\text{R1-O9}}$, $d_{\text{R2-O9}}$, and $d_{\text{R3-O1}}$ exhibit significantly higher compressibility compared to other $d_{\text{R-O}}$ distances. Additionally, these three distances are nearly parallel to the *a*-*b* plane, except $d_{\text{R2-O9}}$, which still maintains a smaller angle with the *a*-*b* plane than with the *c*-axis (Online Materials¹ Fig. S5). In contrast, while the MO_6 octahedron also experiences compressibility relative to the RO_9 polyhedra, it demonstrates compressional isotropy (Online Materials¹ Fig. S1). As a result, it does not contribute to the unit-cell compressional anisotropy.

Isosymmetric second-order phase transition triggered by pressure-induced coordination number increase

The $f_E - F_E$ plot of the unit-cell volume (Fig. 3a) exhibits a notable discontinuity at 5.5 GPa, indicating a change in the compression mechanism of cerite at this pressure. This change does not cause a discontinuity in the unit-cell volume (Fig. 2a) or alter the crystal symmetry. However, it is associated with an apparent discontinuity in the pressure-bulk modulus relationship. As shown in Online Materials¹ Figure S6, the bulk modulus increases rapidly with pressure below 5.5 GPa, while at pressures higher than 5.5 GPa, it shows nonlinear increases. Furthermore, the rate of increase in the bulk modulus between 5.5 and 29.8 GPa is lower than that at pressures below 5.5 GPa. This behavior suggests that cerite undergoes an isosymmetric second-order phase transition at 5.5 GPa.

Isosymmetric phase transitions are commonly observed in mineral physics studies. The reasons for pressure-induced isosymmetric phase transitions can be classified into the following five types (Fig. 6): (I) layer shift; (II) tilting and rotation of SiO_4 tetrahedra; (III) charge transfer; (IV) coordination number increase; and (V) spin crossover transition. Previous research indicates that types I and II only trigger isosymmetric first-order phase transitions (Dera et al. 2003; Gatta et al. 2011; Ke et al. 2014; Liang et al. 2020). While type V typically causes isosymmetric second-order phase transitions (Lin et al. 2005;

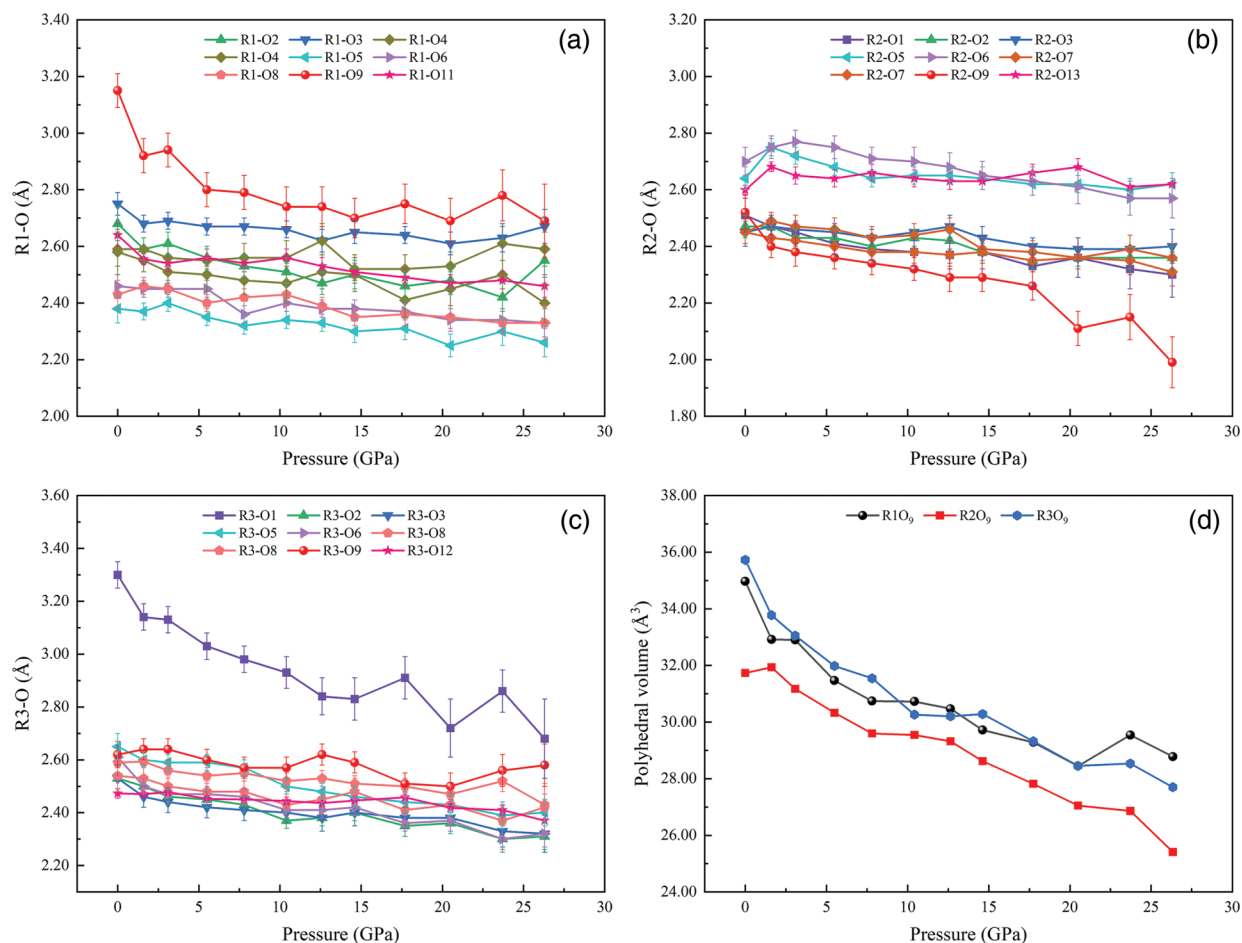


FIGURE 5. REE-O interatomic distance (a–c) and polyhedral volume (d) as a function of pressure. (Color online.)

Merlini et al. 2010; Chen et al. 2012). Although there has been a report of first-order phase transitions, i.e., an isostructural volume may collapse due to spin crossover in ϵ -FeOOH (Thompson et al. 2020), it is only a conjecture that this phase transition is isosymmetric, and there is no direct evidence. On the other hand, types III and IV are capable of triggering both isosymmetric first- (Louie and Cohen 1974; Haines et al. 1998; Liu et al. 2011) and second-order phase transitions (Xu et al. 2017; Liang et al. 2020; Tao et al. 2024). In this study, we demonstrate that the isosymmetric second-order phase transition in cerite is triggered by pressure-induced coordination number increase.

The occurrence of isosymmetric phase transitions resulting from pressure-induced coordination number increases has received limited attention. An isosymmetric first-order phase transition caused by coordination number increases was observed in lead fluoride (PbF_2) (Haines et al. 1998). In this case, the cationic coordination number increases from 9 to 10 during the transition from the cotunnite-structured α phase (α - PbCl_2 -type, $Pnam$, $Z=4$) to an orthorhombic γ phase (Co_2Si -related, $Pnam$, $Z=4$). The transition is accompanied by a 2% volumetric change. Similarly, Xu et al. (2017) demonstrated the occurrence of pressure-induced coordination number increase in Na-pyroxene (aegirine; $\text{NaFeSi}_2\text{O}_6$). They observed

an increase in the coordination number of Na^+ from 6 at ambient pressure to 8 at ~ 24 GPa. This coordination number increase also does not alter the crystal symmetry or cause any discontinuity in the P - V curve but leads to a discontinuity in the P - K curve, indicating a second-order phase transition.

A study by Pakhomovsky et al. (2002) on cerite-(La) revealed that all three RO_9 polyhedra are ninefold coordinated at ambient pressure. In their cerite structure, $d_{\text{R1-O}} = 2.408(9)$ – $2.813(9)$ Å and $d_{\text{R2-O}} = 2.473(8)$ – $2.802(9)$ Å. Interestingly, $d_{\text{R3-O1}} = 3.00(1)$ Å, which is significantly larger than the other eight $d_{\text{R3-O}}$ distances [$2.485(4)$ – $2.762(9)$ Å]. In our study, $d_{\text{R2-O}} = 2.45(5)$ – $2.70(5)$ Å (Fig. 5; Online Materials¹ Table S2). However, $d_{\text{R1-O9}} = 3.15(6)$ Å (Fig. 5a), which is considerably larger than the other $d_{\text{R1-O}}$ distances [$2.38(5)$ – $2.75(4)$ Å]. Similarly, in the R3O_9 polyhedron (Fig. 5c), $d_{\text{R3-O1}}$ [$3.30(5)$ Å] is larger than the other $d_{\text{R3-O}}$ [$2.473(18)$ – $2.65(5)$ Å]. Consequently, in our cerite structure, in contrast to the findings of Pakhomovsky et al. (2002), only R2 is ninefold coordinated, whereas R1 and R3 are eightfold coordinated at ambient pressure.

As the pressure increases, the $d_{\text{R1-O9}}$ distance exhibits a rapid decrease until reaching 5.5 GPa, reducing from $3.15(6)$ to $2.80(6)$ Å, which corresponds to an 11.1% decrease (Fig. 5a). However, above 5.5 GPa and up to 26.3 GPa, the decrease is

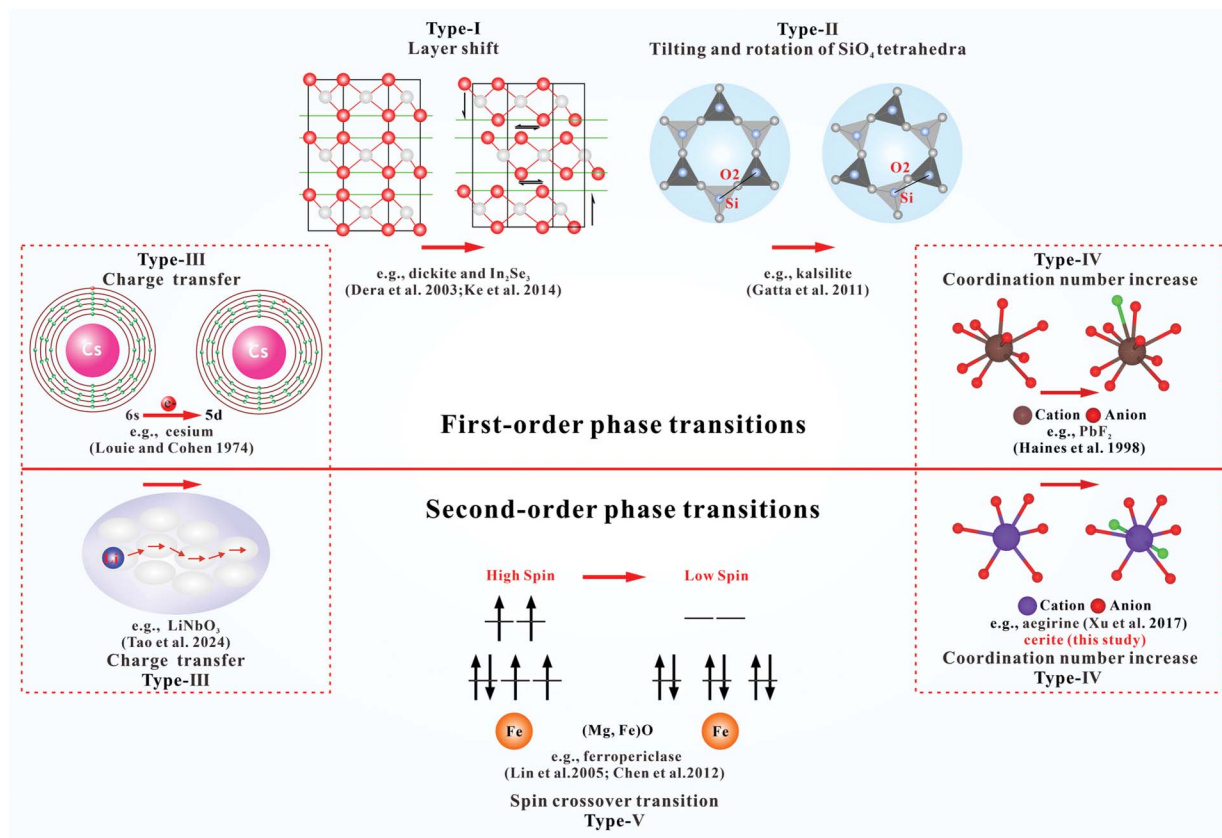


FIGURE 6. The main types of pressure-induced isosymmetric phase transitions. The upper part is the isosymmetric first-order phase transitions, encompassing type I (layer shift), type II (tilting and rotation of SiO_4), type III (charge transfer), and type IV (coordination number increase). The lower part is the isosymmetric second-order phase transitions, including type III (charge transfer), type IV (coordination number increase), and type V (spin crossover transition). (Color online.)

only 3.9%. This suggests that the interaction between the R1 and O9 undergoes a significant increase beyond 5.5 GPa, resulting in a reduced rate of distance reduction between them. We speculate that the formation of an R1-O9 bond occurs near 5.5 GPa, leading to a change in the compression mechanism and triggering the second-order phase transition. In contrast, the decreasing rate of $d_{\text{R3-O1}}$ remains relatively consistent as the pressure increases but is considerably higher compared to the other $d_{\text{R3-O}}$ distances in the R3O_9 polyhedron (Fig. 5c). This indicates a relatively weak interaction between R3 and O1 across the pressure range investigated. Therefore, the isosymmetric second-order phase transition in cerite may be attributed to the pressure-induced coordination number increase, specifically the formation of the R1-O9 bond at 5.5 GPa, which alters the compression mechanism of cerite. These findings suggest that the pressure-induced coordination number increase leading to the isosymmetric second-order phase transition is not limited to monoclinic minerals but can also occur in other crystal systems. However, further explanation is needed as to why the pressure-induced coordination number increase manifests as a first-order phase transition in certain crystalline phases while appearing as a second-order phase transition in others.

It is worth noting that isosymmetric phase transitions involve minor changes in the crystal structure. In the case of simple

compounds like PbF_2 , as mentioned earlier, the structure consists of a single fundamental building unit (PbF_9 polyhedron). When subjected to the pressure that triggers the isosymmetric phase transition, the formation of new chemical bonds leads to a contraction in the polyhedral volume. This contraction effect is observed throughout the structure due to the presence of only one type of building unit. As a result, the unit-cell volume experiences a sudden decrease, exhibiting the characteristics of a first-order phase transition. However, in the case of more complex compounds such as Na-pyroxene and cerite, the structure comprises multiple building units, including NaO_8 , SiO_4 , and FeO_6 polyhedra in Na-pyroxene, and three types of RO_9 , SiO_4 , and MO_6 polyhedra in cerite. The structures of these compounds are much more flexible under high pressure. During the phase transition induced by pressure, the formation of new chemical bonds occurs only in one of the building units, while the other units do not undergo significant changes. Additionally, the volume reduction resulting from the contraction of one building unit can be compensated by the dilation of the other building units. As demonstrated in Figure 5 and Online Materials¹ Figure S2, the shortening of $d_{\text{R1-O9}}$ is accompanied by the elongation of $d_{\text{Si3-O9}}$. Therefore, the impact of the formation of new chemical bonds on volume contraction is diminished. Consequently, the phase transition exhibits the characteristics of a second-order

transition. In summary, the nature of pressure-induced isosymmetric phase transitions, whether first-order or second-order, depends on the complexity of the building units in the structures of various crystalline phases.

IMPLICATIONS

Pressure-induced polymorphic phase transitions play a pivotal role in fundamental physics and chemistry. In this study, we have observed an isosymmetric second-order phase transition of cerite at 5.5 GPa, which is triggered by the pressure-induced formation of R1-O9 chemical bonds. Furthermore, given the intricate compositions of natural cerite, the mixed sites within the cerite studied here might play an important role in the second-order phase transition. Hence, investigating whether synthetic pure end-member cerite demonstrates similar properties in future studies would be intriguing.

It is worth noting that pressure-induced coordination number increase leading to isosymmetric phase transitions may be prevalent in various minerals, particularly REE minerals. For instance, Wu et al. (2024) investigated the structural evolution of a rare earth hydroxyhalide [$\text{YCl}(\text{OH})_2$] up to 9.4 GPa and observed an increase in the coordination number of Y^{3+} from 8 to 9 at ~6 GPa without altering the crystal symmetry. However, they did not observe a phase transition. This could potentially be attributed to the limited pressure range of their experiment, which may have hindered the detection of anomalies in their EoS analysis. Therefore, further investigation with a broader experimental pressure range is warranted to determine whether the coordination number increase triggers a second-order phase transition in $\text{YCl}(\text{OH})_2$.

Moreover, pressure-induced phase transitions can lead to significant changes in material properties (e.g., Li et al. 2018, 2022; Pei et al. 2021). However, there is limited research on the physical property changes resulting from pressure-induced isosymmetric phase transitions. Only a few studies have explored superconducting critical temperature (Liu et al. 2011) and elastic properties (Liang et al. 2020). In this study, we observed a discontinuity in the bulk modulus accompanying the second-order phase transition as in previous studies (Louie and Cohen 1974; Dera et al. 2003; Lin et al. 2005; Chen et al. 2012; Xu et al. 2017). This finding suggests the presence of a corresponding discontinuity in the compressional wave velocity, as predicted by the approximation of the Newton-Laplace equation. Further research is needed to determine whether isosymmetric second-order phase transitions also influence other physical properties, such as electrical and thermal conductivity.

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