

Pressure Dependence of Structural Behavior and Electronic Properties in Double Perovskite Ba₂SmSbO₆

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phase transition, the light absorption, and the bandgap of double perovskite Ba_2SmSbO_6 investigated by using *in situ* high-pressure synchrotron X-ray diffraction and Raman and ultraviolet-visible (UV-vis) absorption spectroscopy measurements up to 40 GPa. We found that pressure induces the phase transition from a cubic *Fm-3m* to a tetragonal *I*4/*m* at 8.6–12.8 GPa, as accompanied by the splitting and broadening of the diffraction peaks. The evolution of various modes in the Raman spectra and the enthalpy calculations support the phase transition of Ba_2SmSbO_6 under compression. The



analysis of UV-vis absorption spectroscopy reveals that the bandgap as a pressure of function is closely related to the phase transition. Calculation results demonstrate that the pressure-induced variation of the electronic structure mainly stems from the contribution of conduction states in Ba_2SmSbO_6 . Our investigations provide a fundamental understanding of the structure-property modulation in Ba_2SmSbO_6 under high pressure and will functionalize a new application-pressure sensor.

1. INTRODUCTION

Double perovskite $(A_2B'B''O_6)$ represents a unique class of materials for electrode materials in batteries, sensors, and fuel cells.¹⁻⁶ These ternary compounds exhibit a wide range of physical and chemical properties, i.e., intersite charge transfer,⁷ disproportionation,⁸ and phase transformation.⁹⁻¹¹ When the difference of charge or ionic radii between B' and B" cations are greater, double perovskites have ordered structures.^{12,13} $A_2B'B''O_6$ with rare-earth B' and B'' cations attracts widespread attention, due to geometric magnetic frustration¹⁴ and high-quality superconducting thick films.¹⁵ Recently, reports of double perovskites continue to exhibit significant progress in magnetic order^{16,17} and photoluminescence properties.^{41,42} For example, the antiferromagnetic order of Ni²⁺ ion moments is determined by Ln = La, Pr, Nd, Sm, Eu, Gd, and Tb in double perovskite NaLnNiWO₆ in the range of 23-30 K.¹⁶ The ferrimagnetic order of Er₂CoMnO₆ stems from the longrange order of Er³⁺ moments below 10 K.¹⁷ Furthermore, when Eu^{3+} ions are doped into the $Sr_2YTaO_6^{41}$ and $La_2CaSnO_{64}^{42}$ the phosphors emit high purity red light.

A crystal structure can regulate the arrangement of A- and Btype cations in double perovskites, turning their microscopic interactions, resulting in the transformation of macroscopic properties.^{18–21} Practically speaking, choosing the B-site cations is a critical element for controlling the electronic properties in double perovskites. The electron-electron interactions and the spatial orbital overlap of 3d, 4d, and 5d transition elements lanthanide and actinium with different valent states at the B-sites determine the electronic bandgap of a double perovskite.²⁰⁻²² Typically, the bandgap of double perovskites with 3d transition elements at B sites is narrow because the interelectronic repulsion in 3d transition elements is relatively strong and the overlap between 3d orbitals and O 2p orbitals is less.^{20,21} Inversely, the 4d or 5d orbitals are more extended than 3d orbitals, leading to a wider bandgap in double perovskites with 4d or 5d transition metals.² However, very few reported compounds are metallic or halfmetallic.^{22,24-26} Most conductions in double perovskites depend on the thermally excited small-polaron hopping, but a few cases are governed by Mott variable-range hopping. Generally speaking, the structural distortions, oxygen vacancies, and cation disorder can induce the localization electrons in the impurity band near the Fermi energy, causing the

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Figure 1. (a) Fm-3m structure of Ba₂SmSbO₆. (b) Structural evolution of Ba₂SmSbO₆ probed by high-pressure synchrotron XRD at ambient temperature. (c) I4/m structure of Ba₂SmSbO₆. (d) Pressure-dependent diffraction peak (400).

isolator-metal transitions in double perovskites, such as $Sr_2MnRu{O_{6\prime}}^{22}$ $Sr_2CoIr{O_{6\prime}}^{25}$ and $Sr_2CrMo{O_{6\prime}}^{26}$

Previous studies indicate that pressure as an external variable has a similar effect to carrier doping by changing the electronic and magnetic properties.^{27,28} Therefore, pressure provides an opportunity to regulate the relations between structure and property for semiconductor and insulator compounds, especially for materials with new high-pressure phases. Most of the double perovskite compounds undergo a phase transition to the lower symmetry structures under compression. For example, Ba₂BiSbO₆ experiences the structural phase transition from *R*-3 to $I2/m_{\star}^{29}$ Ba₂YTaO₆ from *Fm*-3*m* to $I4/m_{\star}^{30}$ Sr₂ZnWO₆ from $P2_1/n$ to *P*-1,³¹ and Ba₂SmBiO₆ *Fm*-3*m* from *Pnma*³¹ under compression accompanied by remarkable optimization of their physical properties. In this paper, we conducted a systematic study to investigate the crystal structures and electronic properties of Ba₂SmSbO₆ at high pressure using in situ synchrotron X-ray diffraction (XRD), Raman spectroscopy, and UV-vis absorption spectroscopy. The possible paths and electronic properties of the structural phase transition in the compressed double perovskite Ba₂SmSbO₆ are discussed with the aid of the first-principles calculations.

2. METHODS

2.1. Experimental Details. Ba_2SmSbO_6 powder samples were synthesized by solid-state reaction. $BaCO_3$ (99.99% in purity), Sm_2O_3 (99.99%), and Sb_2O_3 (99.99%) as initial materials were prepared by the molar ratio of 4:1:1. These mixtures were pressed into pellets and then heated at 1500 K for 24 h. As the pellets were quenched to room temperature, the white Ba_2SmSbO_6 was obtained.

In situ high-pressure XRD ($\lambda = 0.4340$ Å) measurement was conducted by an angle dispersive synchrotron XRD mode at

beamline 13-BM-C of the Advanced Photon Source (APS), Argonne National Laboratory as well as beamline 14B1 and beamline15U1 of the Shanghai Synchrotron Radiation Facility (SSRF). LaB₆ powders were used to calibrate the instrumental parameters. Liquid argon as a pressure-transmitting medium was loaded into a gasket in a diamond anvil cell (DAC). A monochromatic beam (~26 \times 28 μ m²) was focused on the sample, and two-dimensional Debye-Scherrer rings were recorded by the image plate Mar345 with a resolution of 100 μ m/pixel. The two-dimensional Debye–Scherrer rings were integrated by DIOPTAS software³² and then exported to powder diffraction patterns. These powder diffraction patterns were fitted by the general structure analysis system (GSAS) program.³³ The in situ high-pressure Raman spectrum was measured by a Nd:YAG 532 nm laser with an optical grating of 2400 g/mm at the Center for High-Pressure Science and Technology Advanced Research. The focal spot size of the Nd:YAG 532 nm laser was $1 \times 1 \ \mu m^2$, and the corresponding Rayleigh filter was an edge filter. These Raman spectra were collected over a wavenumber range of 100-1200 cm⁻¹. The pressure was calibrated by the ruby luminescence method in the high-pressure experiments.

For the *in situ* high-pressure ultraviolet–visible (UV–vis) absorption spectroscopy experiment, a deuterium–halogen light source and a pair of type II diamonds with IR-transmitting low fluorescence were used in the measurement. The UV–vis absorption data were collected by an optical fiber spectrometer with a response time of 1 s in the wavelength range from 200 to 800 nm. The bandgap of Ba_2SmSbO_6 under compression was deduced by analyzing UV–vis absorption data.

2.2. Computational Details. The enthalpy value, band structures, and density of states (DOS) of $Ba_2SmSbO_6(Fm-3m and I4/m structures)$ at different pressure were obtained by

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Figure 2. (a) Representative refinements of the patterns for the cubic and tetragonal structures of Ba_2SmSbO_6 at 7.0, 21.5, and 36.6 GPa. (b) Calculated enthalpies per formula unit for the *Fm*-3*m* and *I*4/*m* structures of Ba_2SmSbO_6 in the pressure range of 40 GPa. The enthalpies of the *Fm*-3*m* structure are taken as the reference enthalpies. (c) Pressure-dependent unit cell volume for the *Fm*-3*m* and *I*4/*m* structures of Ba_2SmSbO_6 . (d) Various lattice constants *a*, *b*, and *c* of Ba_2SmSbO_6 were obtained from the Rietveld-refined XRD pattern under compression.

density-functional theory (DFT) in the CASTEP code.³⁴ The ultrasoft pseudopotentials of Ba, Sm, Sb, and O were used for the calculations.³⁵ The exchange–correlation energy was described using the local-density approximation (LDA)³⁶ parametrized by the Ceperley–Alder–Perdew–Zunger (CA-PZ) function.³⁷ To obtain a highly accurate result, a Monkhorst–Pack k-point mesh sampling more than $6 \times 6 \times 6$ of the Brillouin zone and a basic set of plane waves with a kinetic energy cutoff of 380 eV were used for expanding the wave functions. $2s^22p^4$, $5s^25p^3$, $5s^25p^66s^2$, and $4f^65s^25p^66s^2$ were selected as the valence electrons in the atomic electronic states of O, Sb, Ba, and Sm atoms, respectively.

3. RESULTS AND DISCUSSION

3.1. Phase Transition under High Pressure. Ba₂SmSbO₆ crystallizes in a cubic *Fm-3m* space group (Z = 4) with lattice parameters (a = b = c = 8.50 Å) as shown in Figure 1a, which is in good agreement with a previous report.³⁸⁻⁴⁰ The XRD patterns of polycrystalline Ba₂SmSbO₆ at various pressure up to ~40 GPa are shown in Figure 1b. The low-pressure XRD patterns of Ba₂SmSbO₆ can be indexed and fitted to the cubic *Fm-3m* structure as expected. However, the (400) diffraction peak begins to broaden above 8.6 GPa. The broadening of the (400) diffraction peak is followed by a peak splitting at 18.6 GPa and becomes more pronounced with increasing pressure as observed in Figure 1c, indicating that Ba₂SmSbO₆ experiences a phase transition. However, we note that the strongest (220) diffraction peak remains unchanged up to 40 GPa, suggesting that the high pressure has the lattice parameters of a = b and $a \neq c$, which can be either a tetragonal or hexagonal system. On the basis of the crystallography analysis of the hexagonal system (h + k + l = 3m, m = 1, 2, 3, m = 1, 2, 3)...), new diffraction peaks should appear if the high-pressure phase had a hexagonal structure. During the phase-transition process, no new diffraction peaks are observed in the highpressure XRD patterns of Ba2SmSbO6. Therefore, the highpressure structures of Ba2SmSbO6 should belong to the tetragonal system. On the basis of the stoichiometric ratio of Ba2SmSbO6, we finally deduced the high-pressure structure with space group I4/m (Z = 2), which belongs to the tetragonal system as shown in Figure 1c. The phase-transition path of Ba₂SmSbO₆ under compression is consistent with that of Ba₂YTaO₆.³⁰ It is reported that Ba₂SmBiO₆ experiences phase transition from cubic (Fm-3m) to orthorhombic (Pnma) at high pressure.³¹ Compared with Ba₂SmSbO₆, the p-d electron interaction in Ba₂SmBiO₆ is stronger, leading to the lower crystal symmetry at high pressure.

Representative diffraction patterns are indexed and fitted well (Rietveld refinement) with the *Fm*-3*m* at 7.0 GPa, *I*4/*m* at 36.6 GPa, and two-phase coexistence at 21.5 GPa, as shown in Figure 2a. The refining parameters $w_{\rm Rp}$ are 5.9%, 3.5%, and 5.8% at 7.0 GPa, 36.6 GPa, and 21.5 GPa, respectively. To obtain a high-pressure structure accurately, the enthalpy values of the possible structures at high pressure were calculated by the first-principles method. The lattice parameters and atomic coordinates of the *Fm*-3*m* and *I*4/*m* structures at an ambition environment can be found in Tables S1 and S2. On the basis of the enthalpy calculations under high pressure, Ba₂SmSbO₆ experiences a phase transition from the *Fm*-3*m* to the *I*4/*m*



Figure 3. (a) In situ high-pressure Raman spectra of Ba_2SmSbO_6 from 0.8 to 35.2 GPa at ambient temperature. Green T, L, v_1 , v_2 , v_5 represent the Raman modes of the I4/m structure. (b) Pressure-dependent Raman frequency shifts of the Fm-3m and I4/m structures.

structure at 7.8 GPa as shown in Figure 2b, which is close to the phase transition pressure observed experimentally.

Figure 2c shows the pressure-dependent unit-cell volumes of the *Fm*-3*m* and I4/m structures. It can be seen that the unit cell volumes can be a third-order Birch-Murnaghan equation of state (EOS), respectively. The EOS fitting gives the zeropressure volume $V_0 = 155.4(1)$ Å³ and bulk modulus $B_0 =$ 205.6(4) GPa (pressure derivative $B_0' = 4.2$) for the Fm-3m structure and $V_0 = 150.8(2)$ Å³ and $B_0 = 239.5(9)$ GPa ($B_0' =$ 2.5) for the I4/m structure. The lattice constants a and c as a function of pressure are shown in Figure 2d. The red and black solid lines represent the linear fitting lattice constants under pressure. The decreasing lattice constants a and c during compression lead to a decreasing unit-cell volume, as shown in Figure 2c. We observe a clear volume reduction of about 2.1% across the structural transition, suggesting that the phase transition in Ba₂SmSbO₆ is a first-order phase transition. Above 28.9 GPa, the I4/m structure fully dominates the crystal structure of Ba₂SmSbO₆ as seen in Figure 1b, indicating the completion of the phase transition. Under decompression, the I4/m structure is not recovered to ambient pressure, but the Fm-3m structure recovers back as shown in Figure S1, indicating the reversible nature of the phase transformation of Ba₂SmSbO₆.

In situ high-pressure Raman measurements were carried out to understand the phonon behavior across the phase transition of Ba₂SmSbO_{6.} The representative Raman spectra of Ba₂SmSbO₆ at various pressures are shown in Figure 3a. On the basis of the group theory analysis, Ba₂SmSbO₆ with the Fm-3m structure has four Raman active modes A1g, Eg, and 2F₂₀.⁹ These Raman active modes center at around 760, 566, 374, and 102 cm^{-1} at ambient conditions, and all these Raman modes exhibit blue shifts with increasing pressure as observed in Figure 3b. The solid lines in Figure 3b represent the linear fitting of Raman frequency under pressure. Through the P-wrelation $(w = w_0 + aP)$ and bulk modulus (B_0) deduced from P-V data in the XRD measurement,⁴³ the Grüneisen parameter γ of each Raman mode is obtained, and these parameters w_0 , a, γ are summarized in Table S3. The Grüneisen parameters γ and a are positive in the Fm-3m

structure below 24.0 GPa, due to the hardening of chemical bonding under compression. Compared with Ba₂SmBiO₆,³¹ the pressure coefficients of Ba₂SmSbO₆ are larger, indicating that Ba₂SmSbO₆ is easier to compress than Ba₂SmBiO₆. Furthermore, the Grüneisen parameter of Ba₂SmSbO₆ is larger than Ba₂SmBiO₆, demonstrating that the Sb–O bond has a stronger ionic character than Bi–O under compression.

Under compression, the intensities of the A_{1g} , Eg, and $2F_{2g}$ modes gradually decrease and several new Raman modes are observed above 24.0 GPa as denoted by T, L, v_2 , v_5 , and v_1 , which signals the pressure-induced phase transition of Ba₂SmSbO₆ observed from the XRD experiments in Figure 3a. The Raman signals of the high-pressure phase are relatively weaker than the Fm-3m structure under compression. The Raman signals of the new phase are only visible when the ratio of the new phase is larger than the Fm-3m structure. As a result, the critical pressure of the Ba₂SmSbO₆ phase-transition in Raman measurements can depend on the full-width-halfmaximum (fwhm) of the vibration modes. Above 7.2 GPa, the fwhm of the Eg mode exhibits an obvious broadening phenomenon with increasing pressure (Figure S3). Therefore, the critical pressure of the phase transition in Raman measurements is 7.2 GPa. This result is consistent with XRD data and DFT calculations. However, the vibration modes of the new phase are difficult to index because the Raman signals of the new phase are so weak under high pressure, as shown in Figure 3a. According to the XRD data, Ba₂SmSbO₆ completely transforms to the I4/m phase above 28.9 GPa. On the basis of the group theory analysis, the I4/m structure has 9 Raman active modes (3Ag, 3Bg, and 3Eg). The Raman modes of Ba₂SmSbO₆ can be deduced by comparing its spectrum with that of $Sr_2ZnTeO_6^{44}$ and $Sr_2CoWO_6^{45}$ with I4/m structure, as shown in Figure 3b. The translational (T) and rotational (L) modes of the SbO₆ octahedra are assigned to the wavenumbers below 300 cm⁻¹, while in the region of \sim 300-500 cm⁻¹, Raman modes are attributed to the antisymmetric stretching (v_2) and symmetric stretching (v_5) of the SbO₆ octahedra. Above wavenumber 600 cm⁻¹, the v_1 Raman mode exhibits the symmetric bending of SbO₆. The pressure coefficient *a* (in Table S4) of the I4/m phase is smaller than that of the *Fm*-3m

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Figure 4. (a) Representative UV-vis absorption spectra of Ba_2SmSbO_6 under compression. (b) Evolution of the bandgap with pressure at 0-40.6 GPa. The arrows represent the shift tendency of absorption peaks.



Figure 5. Energy-band structures for the Fm-3m at 0 GPa (a) and 5 GPa (b). Energy-band structures for the I4/m at 20 GPa (c) and (d) 40 GPa. Density of states (DOS) for the Fm-3m at 0 GPa (e) and (f) I4/m at 40 GPa.

phase, demonstrating that the compressibility of Ba_2SmBaO_6 is lower above 24.0 GPa. This result is consistent with the XRD data. Indeed, the ~8.9% reduction in volume is for the *Fm-3m* structure below 24.0 GPa, while the 8.0% decrease in volume corresponds to the *I4/m* structure from 24.0 to 40.0 GPa in XRD measurements. The Grüneisen parameter of the *I4/m* phase (in Table S4) is less than 2, indicating that the Sb–O bonds approach the properties of covalent bonds above 24.0 GPa.⁴³ **3.2. UV–Visible Absorption Spectrum and Electronic Structure.** To understand the electronic properties, *in situ* high-pressure UV–vis absorption spectroscopy of Ba_2SmSbO_6 was measured, as shown in Figure 4a. The band structure of Ba_2SmSbO_6 can be inferred from the shape of the absorption edge. The absorption edge of Ba_2SmSbO_6 (Figure 4a) exhibits a smooth slope under compression, indicating that Ba_2SmSbO_6 has an indirect bandgap up to 40 GPa. The absorption peak shows a gradual blueshift as the pressure increases to ~8.0

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GPa. Inversely, a redshift is observed from 8.0 to 16.7 GPa, followed by a stable peak position with pressure up to 40.6 GPa. This result is consistent with the band structure of the DFT calculation at high pressure (Figure 5). The bandgap of Ba₂SmSbO₆ is fitted by the linearized Tauc coordinates $(\alpha hv)^{1/2} - hv$ in Figure 4b. The obtained bandgap exhibits an obvious change around 8.0 GPa, agreeing with the results in our XRD experiments and enthalpy calculations, indicating the pressure-induced phase transition causes the bandgap changes. Furthermore, the band structures of Ba2SmSbO6 with stable high-pressure phases were calculated under compression. As the pressure increases, the bandgap of the Fm-3m structure decreases from 3.4 (0 GPa) to 1.0 eV (8.0 GPa) as shown in Figure S4. Compared with Figure 5a and Figure 5b, pressure adjusts the localized electrons of the Fm-3m structure near the Fermi energy and finally causes the reduction of the bandgap in the *Fm*-3*m* structure. Indeed, the Sm-4f electrons occupy the valence bands, and the electrons of Ba-4d, Ba-4s, and O-2p take over the conduction bands near Fermi energy at 0 GPa (Figure 5e). Meanwhile, the localized electrons at the conduction and valence bands near Fermi energy are predominated by the Sm-4f electrons at 5 GPa (in Figure S7a). The density of states (DOS) of the *Fm-3m* structure at 0 and 5 GPa (Figures 5e and S7a) demonstrate that pressure adjusts the position of the localized electrons near the Fermi energy. That is, the pressure pushes the localized electrons at the valence bands toward the conduction bands in the Fm-3m structure under compression. The electron interactions of the p-4f orbitals are weaker than of the p-d orbitals in double perovskites.⁴⁰ As a result, the bandgap of Ba₂SmSbO₆ in the Fm-3m structure exhibits a dramatic reduction between 0 and 8.0 GPa. Above 8.0 GPa, our DFT calculations reveal that the bandgap of the I4/m structure at high pressure (Figure 5c and Figure 5d) is larger than that of the Fm-3m structure (Figure 5b). As a result, the ratio of the new phase I4/m gradually increases with increasing pressure, leading to an incremental increase of the bandgap of Ba₂SmSbO₆ from 8.0 to 16.7 GPa as shown in Figure 4b.

Under further compression, the bandgap remains almost steady as large as 3.0 eV at \sim 16.7–40.0 GPa (Figure 4b). The DOS of the Fm-3m structure at 0 GPa and that of I4/mstructure at 40 GPa are calculated to elucidate the electronic properties of Ba₂SmSbO₆ under compression. Figure 5f exhibits that the conduction bands near the Fermi energy of the I4/m structure are mainly composed of the Sm-5d and Ba-4d states, while the conduction bands near the Fermi energy of the *Fm*-3*m* structure are mainly dominated by the O-2p, Ba-4d, and Ba-6s contributions as shown in Figure 5e. The partial densities of state (PDOS) of O, Sb, Ba, and Sm for the Fm-3m at 0 GPa and I4/m at 40 GPa are calculated in Figures S5 and S6. As a result, the pressure-induced structure transition in Ba₂SmSbO₆ causes an increase of d electrons at the conduction bands, eventually leading to the enhancement of the p-d electron interactions. Although pressure can adjust the band structure and resemble carrier doping, the strengthened p-d electron interactions in Ba_2SmSbO_6 suppressed the reduction of the bandgap.^{18–23} Therefore, pressure as an external condition can control the bandgap variation in the lanthanide oxides Ba₂RESbO₆, but metallic or half-metallic phenomena are difficult to observe at high pressure. Furthermore, the valence bands near the Fermi energy of two phases originate from the Sm-4f state. Compared to the valence bands and conduction bands of different structures, pressure more easily

regulates the localized electrons at conduction bands than that of valence bands in the I4/m structure.

4. CONCLUSIONS

In summary, we investigated the phase transition and electronic structure of Ba₂SmSbO₆ with in situ high-pressure XRD, Raman spectroscopy, UV-vis absorption spectroscopy, and the first-principles calculations up to 40 GPa. The splitting and broadening of the diffraction peak (400) indicate that pressure induces a phase transition from Fm-3m to I4/m at 8.6-12.8 GPa. The phase transition of Ba₂SmSbO₆ is reversible. The enthalpy calculations indicate the I4/mstructure replaces the Fm-3m structure above 7.8 GPa, consistent with our experimental observation. The appearance of new Raman peaks above 24 GPa further confirms the nucleation of the new phase during compression. The enthalpy, bandgap, and DOS were calculated to elucidate the possible phase paths and the relationship between the crystal structure and electronic properties under compression. Below 8.0 GPa, the dramatic change of the bandgap of Ba_2SmSbO_6 with pressure is attributed to the variation of the localized electrons near Fermi energy. Above 8.0 GPa, the increase of d electrons at the conduction bands restrains the regulatory effect of pressure on the bandgap, due to the phase transition. Our results give insight into the structural behavior and electronic properties of double perovskite Ba₂SmSbO₆, whose I4/m phase is stable until 28.9 GPa. Further magnetic explorations of the high-pressure phase are desirable in the future.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c07153.

Lattice parameter and atomic coordinates of the *Fm*-3*m* and *I*4/*m* structures, Raman data, X-ray diffraction patterns of Ba_2SmSbO_6 under decompression, and partial densities of state (PDOS) of O, Sb, Ba, and Sm in the *Fm*-3*m* at 0 and 5 GPa and the *I*4/*m* at 40 GPa (PDF)

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Notes

The authors declare no competing financial interest.

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