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

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ABSTRACT: Understanding the structural behavior of double perovskites plays a pivotal role in optimizing their optical, electrical, and magnetic properties, especially when the effects of external parameters are considered. In this work, we report the high-pressure phase transition, the light absorption, and the bandgap of double perovskite Ba2SmSbO6 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 I4/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 Ba2SmSbO6 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 Ba2SmSbO6. Our investigations provide a fundamental understanding of the structure−property modulation in Ba2SmSbO6 under high pressure and will functionalize a new application—pressure sensor.

1. INTRODUCTION

Double perovskite (A2B′B″O6) 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 A2B′B″O6 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 order16,17 and photoluminescence properties.18,19 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 long-range order of Er3+ moments below 10 K.17 Furthermore, when Eu3+ ions are doped into the Sr2YTaO641 and La2CaSnO6,42 the phosphors emit high purity red light.

A crystal structure can regulate the arrangement of A- and B-type 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.20,21 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.22−26 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
isolator-metal transitions in double perovskites, such as Sr$_2$MnRuO$_6$, Sr$_2$CoIrO$_6$, and Sr$_2$CrMoO$_6$.

Previous studies indicate that pressure as an external variable has a similar effect to carrier doping by changing the electronic and magnetic properties. 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, Ba$_2$BiSbO$_6$ experiences the structural phase transition from $R$-3 to $I2/m_n$; Ba$_2$YTaO$_6$ from $Fm-3m$ to $I4/m$; Sr$_2$ZnWO$_6$ from $P21/n$ to $P-1$; and Ba$_2$SmBiO$_6$ $Fm-3m$ 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 Ba$_2$SmSbO$_6$ 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 Ba$_2$SmSbO$_6$ are discussed with the aid of the first-principles calculations.

2. METHODS

2.1. Experimental Details. Ba$_2$SmSbO$_6$ powder samples were synthesized by solid-state reaction. BaCO$_3$ (99.99% in purity), Sm$_2$O$_3$ (99.99%), and Sb$_2$O$_3$ (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$_2$SmSbO$_6$ 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 beamline 15U1 of the Shanghai Synchrotron Radiation Facility (SSRF). LaB$_6$ 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 ($\sim 26 \times 28 \mu$m$^2$) was focused on the sample, and two-dimensional Debye–Scherrer rings were recorded by the image plate Mar345 with a resolution of 100 μm/pixel. The two-dimensional Debye–Scherrer rings were integrated by DIOPTAS software and then exported to powder diffraction patterns. These powder diffraction patterns were fitted by the general structure analysis system (GSAS) program. 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$_2$SmSbO$_6$ 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$_2$SmSbO$_6$($Fm-3m$ and $I4/m$ structures) at different pressure were obtained by...
Ba$_2$SmSbO$_6$ experiences a phase transition. However, we note increasing pressure as observed in Figure 1c, indicating that splitting at 18.6 GPa and becomes more pronounced with parameters of up to 40 GPa, suggesting that the high pressure has the lattice environment can be found in Tables S1 and S2. On the basis of the enthalpy calculations under high pressure, Ba$_2$SmSbO$_6$ experiences a phase transition from the cubic (Fm-3m) to orthorhombic (Pmna) at high pressure. Compared with Ba$_2$SmBiO$_6$, the p–d electron interaction in Ba$_2$SmBiO$_6$ is stronger, leading to the lower crystal symmetry at high pressure. Representative diffraction patterns are indexed and fitted well (Rietveld refinement) with the Fm-3m at 7.0 GPa, I4/m at 36.6 GPa, and two-phase coexistence at 21.5 GPa, as shown in Figure 2a. The refining parameters $R_w$ 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-3m and I4/m structures at an ambition environment can be found in Tables S1 and S2. On the basis of the enthalpy calculations under high pressure, Ba$_2$SmSbO$_6$ experiences a phase transition from the Fm-3m to the I4/m 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 Ba$_2$SmSbO$_6$ 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 ($h + k + l = 3m, m = 1, 2, 3, \ldots$), 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 high-pressure XRD patterns of Ba$_2$SmSbO$_6$. Therefore, the high-pressure structures of Ba$_2$SmSbO$_6$ should belong to the tetragonal system. On the basis of the stoichiometric ratio of Ba$_2$SmSbO$_6$, 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 Ba$_2$SmSbO$_6$ under compression is consistent with that of Ba$_2$YTaO$_6$. It is reported that Ba$_2$SmBiO$_6$ experiences phase transition from cubic (Fm-3m) to orthorhombic (Pmna) at high pressure.

3. RESULTS AND DISCUSSION

3.1. Phase Transition under High Pressure. Ba$_2$SmSbO$_6$ 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. The XRD patterns of polycrystalline Ba$_2$SmSbO$_6$ at various pressure up to ~40 GPa are shown in Figure 1b. The low-pressure XRD patterns of Ba$_2$SmSbO$_6$ 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 Ba$_2$SmSbO$_6$ 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
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 \( \text{Fm}-3m \) and \( \text{I}4/\text{m} \) 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 zero-pressure volume \( V_0 = 155.4(1) \) \( \text{Å}^3 \) and bulk modulus \( B_0 = 205.6(4) \) GPa (pressure derivative \( B'_0 = 4.2 \)) for the \( \text{Fm}-3m \) structure and \( V_0 = 150.8(2) \) \( \text{Å}^3 \) and \( B_0 = 239.5(9) \) GPa (\( B'_0 = 2.5 \)) for the \( \text{I}4/\text{m} \) 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 \( \text{Ba}_2\text{SmSbO}_6 \) is a first-order phase transition. Above 28.9 GPa, the \( \text{I}4/\text{m} \) structure fully dominates the crystal structure of \( \text{Ba}_2\text{SmSbO}_6 \) as seen in Figure 1b, indicating the completion of the phase transition. Under decompression, the \( \text{I}4/\text{m} \) structure is not recovered to ambient pressure, but the \( \text{Fm}-3m \) structure recovers back as shown in Figure S1, indicating the reversible nature of the phase transformation of \( \text{Ba}_2\text{SmSbO}_6 \).

**In situ** high-pressure Raman measurements were carried out to understand the phonon behavior across the phase transition of \( \text{Ba}_2\text{SmSbO}_6 \). The representative Raman spectra of \( \text{Ba}_2\text{SmSbO}_6 \) at various pressures are shown in Figure 3a. On the basis of the group theory analysis, \( \text{Ba}_2\text{SmSbO}_6 \) with the \( \text{Fm}-3m \) structure has four Raman active modes \( A_{1g}, E_g, \) and \( 2F_{2g} \). 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 \( P \sim \omega \) relation \( (\omega = \omega_0 + aP) \) and bulk modulus \( (B_0) \) deduced from \( P \sim V \) data in the XRD measurement,\(^43\) the Grüneisen parameter \( \gamma \) of each Raman mode is obtained, and these parameters \( \omega_0, a, \gamma \) are summarized in Table S3. The Grüneisen parameters \( \gamma \) and \( a \) are positive in the \( \text{Fm}-3m \) structure below 24.0 GPa, due to the hardening of chemical bonding under compression. Compared with \( \text{Ba}_2\text{SmBiO}_6 \),\(^31\) the pressure coefficients of \( \text{Ba}_2\text{SmSbO}_6 \) are larger, indicating that \( \text{Ba}_2\text{SmSbO}_6 \) is easier to compress than \( \text{Ba}_2\text{SmBiO}_6 \). Furthermore, the Grüneisen parameter of \( \text{Ba}_2\text{SmSbO}_6 \) is larger than \( \text{Ba}_2\text{SmBiO}_6 \), demonstrating that the Sb–O bond has a stronger ionic character than Bi–O under compression.

Under compression, the intensities of the \( A_{1g}, E_g, \) and \( 2F_{2g} \) modes gradually decrease and several new Raman modes are observed above 24.0 GPa as denoted by \( T, L, v_4, v_5, \) and \( v_1 \), which signals the pressure-induced phase transition of \( \text{Ba}_2\text{SmSbO}_6 \) observed from the XRD experiments in Figure 3a. The Raman signals of the high-pressure phase are relatively weaker than the \( \text{Fm}-3m \) structure under compression. The Raman signals of the new phase are only visible when the ratio of the new phase is larger than the \( \text{Fm}-3m \) structure. As a result, the critical pressure of the \( \text{Ba}_2\text{SmSbO}_6 \) phase transition in Raman measurements can depend on the full-width-half-maximum (fwhm) of the vibration modes. Above 7.2 GPa, the fwhm of the \( E_g \) 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, \( \text{Ba}_2\text{SmSbO}_6 \) completely transforms to the \( \text{I}4/\text{m} \) phase above 28.9 GPa. On the basis of the group theory analysis, the \( \text{I}4/\text{m} \) structure has 9 Raman active modes \( (3A_g, 3B_g, \) and \( 3E_g \)). The Raman modes of \( \text{Ba}_2\text{SmSbO}_6 \) can be deduced by comparing its spectrum with that of \( \text{Sr}_2\text{ZnTeO}_6 \)\(^44\) and \( \text{Sr}_2\text{CoWO}_6 \)\(^45\) with \( \text{I}4/\text{m} \) structure, as shown in Figure 3b. The translational (\( T \)) and rotational (\( L \)) modes of the \( \text{Sb}_6 \) octahedra are assigned to the wavenumbers below 300 cm\(^{-1} \), while in the region of \( \sim300–500 \) cm\(^{-1} \), Raman modes are attributed to the antisymmetric stretching \( (v_4 \) and symmetric stretching \( (v_5 \) of the \( \text{Sb}_6 \) octahedra. Above wavenumber 600 cm\(^{-1} \), the \( v_1 \) Raman mode exhibits the symmetric bending of \( \text{Sb}_6 \). The pressure coefficient \( a \) (in Table S4) of the \( \text{I}4/\text{m} \) phase is smaller than that of the \( \text{Fm}-3m \)
phase, demonstrating that the compressibility of Ba$_2$SmBaO$_6$ is lower above 24.0 GPa. This result is consistent with the XRD data. Indeed, the $\sim$8.9% reduction in volume is for the $Fm\overline{3}m$ structure below 24.0 GPa, while the 8.0% decrease in volume corresponds to the $I\overline{4}/m$ structure from 24.0 to 40.0 GPa in XRD measurements. The Grüneisen parameter of the $I\overline{4}/m$ 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, \textit{in situ} high-pressure UV–vis absorption spectroscopy of Ba$_2$SmSbO$_6$ was measured, as shown in Figure 4a. The band structure of Ba$_2$SmSbO$_6$ can be inferred from the shape of the absorption edge. The absorption edge of Ba$_2$SmSbO$_6$ (Figure 4a) exhibits a smooth slope under compression, indicating that Ba$_2$SmSbO$_6$ has an indirect bandgap up to 40 GPa. The absorption peak shows a gradual blueshift as the pressure increases to $\sim$8.0
Ba$_2$SmSbO$_6$ causes an increase of d electrons at the conduction bands near the Fermi energy. As a result, the pressure-induced structure transition at 0 GPa and 8.6 GPa is reversible. The enthalpy calculations indicate the 14/m structure 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$_2$SmSbO$_6$ 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 Ba$_2$SmSbO$_6$ whose 14/m phase is stable until 28.9 GPa. Further magnetic explorations of the high-pressure phase are desirable in the future.

4. CONCLUSIONS

In summary, we investigated the phase transition and electronic structure of Ba$_2$SmSbO$_6$ 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 Ba$_2$SmSbO$_6$ is reversible. The enthalpy calculations indicate the I4/m structure 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$_2$SmSbO$_6$ 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 Ba$_2$SmSbO$_6$ whose 14/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.

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Notes
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