Pressure-Induced Structural and Electronic Transition in \( \text{Sr}_2\text{ZnWO}_6 \) Double Perovskite

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ABSTRACT: High-pressure structural and electrical properties of \( \text{Sr}_2\text{ZnWO}_6 \) double perovskite were investigated using in situ angle-dispersive synchrotron X-ray diffraction (XRD), Raman, and alternating current (AC) impedance spectroscopy. A structural transition from monoclinic (\( P2_1/n \)) to triclinic (\( P\overline{1} \)) phase around 9 GPa was observed due to the pressure-induced distortion of (W, Zn)O\(_6\) octahedron. In situ high-pressure Raman spectroscopy showed the increasing interaction among O–W–O in WO\(_6\) octahedron with pressure and a transition pressure consistent with the XRD results. From the AC impedance spectroscopy measurements, the resistivity increased steeply by \( \sim 1 \) order of magnitude around 11 GPa, indicating an electronic transition accompanying the symmetry change. The increase in the interaction among O–W–O enhances the attraction of O\(^{2–}\) electrons toward W\(^{6+}\), thus increasing the covalence, which in turn lowers the charge transfer energy between O\(^{2–}\) and W\(^{6+}\) and induces the resistivity increase under high pressure.

INTRODUCTION

As new theoretical challenges arise and potential impacts of new technological applications are explored intensively, perovskite and double perovskite were widely investigated in recent decades because of their interesting physical properties and potential applications, such as the room-temperature magnetoresistance in \( \text{Sr}_2\text{FeMoO}_6 \) and \( \text{Sr}_2\text{FeReO}_6 \), the temperature-induced insulator–metal transition in \( \text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3 \), and the superconducting behavior in \( \text{Sr}_2\text{YRu}_{0.95}\text{Cu}_{0.05}\text{O}_6 \) at ambient pressure. Pressure is an alternative way to tune the crystallographic and electronic structure, which provides an effective approach to explore new physical mechanisms and search for new materials with tailored properties. For instance, a sharp drop in electrical resistivity is linked to the heavily buckled Co–O–Co bonds in the high-pressure phase of BiCo\(_2\). REFeO\(_3\) (RE = La, Pr) and \( \text{Sr}_2\text{FeMoO}_6 \) also show a pressure-induced metallization at 120 and 2.1 GPa, respectively. However, the opposite electric transport effect under high pressure has been reported in simple metals. Sodium and lithium transform from metal to insulator and semiconductor
under high pressure, respectively, due to pressure-induced pairing of alkali atoms. It would be interesting to know if also in the complex systems like perovskites or double perovskites such unusual electrical properties could be induced by high pressure and thus affect their applications. In this report, we applied pressure to Sr2ZnWO6 double perovskite, and observed the resistivity increasing sharply with pressure until 8.7 GPa, where a structural phase transition was triggered. For Sr2ZnWO6, W6+ is a d0 transition metal, and the distortion of the d0 cation from the center of its WO6 octahedron may give origin to a variety of technologically important properties such as piezoelectricity, ferroelectricity, pyroelectricity, and nonlinear optical phenomena. Here we focus on its structural and electronic evolution studies under high pressure with in situ high-pressure synchrotron X-ray diffraction (XRD), Raman spectroscopy, and resistivity measurements.

**EXPERIMENTAL DETAILS**

For the preparation of the sample, the standard method of solid-state chemical reaction was used. Stoichiometric amounts of the reacting compounds were mixed according to the following chemical reaction:

\[
2\text{SrCO}_3 + \text{ZnO} + \text{WO}_3 \rightarrow \text{Sr}_2\text{ZnWO}_6 + 2\text{CO}_2
\]

The reacting compounds (all supplied by Sigma-Aldrich) had the following purities: SrCO3 99.995%; WO3 99.995%; ZnO and 99.995%. All compounds were used as received. The starting materials were mixed and ground in an agate mortar and heated in air in alumina crucibles. The following heat treatment was used: 24 h at 900 °C; 24 h at 1000 °C; and 48 h at 1100 °C. After each heating, the sample was cooled slowly (3 °C/min); and reground (remixed) to improve homogeneity.

The in situ high-pressure XRD measurements were performed in an angle-dispersive mode at the beamline 16-BMD of the Advanced Photon Source (APS), Argonne National Laboratory. Symmetric diamond anvil cells (DAC) with 400 μm culet sized anvils were used with neon pressure medium. Rhenium thin foils were precompressed to 40 μm thick and drilled with a 150 μm diameter hole for sample chambers. Pressure was calibrated by the ruby luminescence method.22 Rietveld refinements were performed using the General Structure Analysis System (GSAS) and graphical user interface EXPGUI package.23 The high-pressure Raman spectra were measured by a Raman spectrometer using a 532 nm excitation laser with 3 mW of power at HPSynC. The preparation of sample and DAC for the Raman study was the same as for the XRD measurement.

AC impedance spectroscopy in the frequency range from 0.01 Hz to 10 MHz under high pressure was conducted by using Solartron 1260 impedance analyzer equipped with Solartron 1296 dielectric interface. The applied AC voltage was 0.2 V. Van der Pauw electrodes were used on one facet of DAC. The fabrication process of the detecting microcircuit has been reported in previous publications.24 No pressure medium was used in the resistivity measurements.

**RESULTS AND DISCUSSIONS**

**High-Pressure X-ray Diffraction Studies of Sr2ZnWO6.**

Sr2ZnWO6 has the monoclinic symmetry (space group P21/n, Z = 2) at the ambient conditions.21,25 This monoclinic structure of Sr2ZnWO6 can be presented as a three-dimensional network of interstitial spaces. At ambient pressure, when heated, Sr2ZnWO6 transforms from monoclinic (P21/n) to tetragonal (I4) phase around 340 K and cubic (Fm3m) phase at 770 K.26 To study its structural evolution under high pressure, angle-dispersive XRD measurements were performed up to 18.1 GPa at room temperature. Figure 1a shows the XRD patterns at different pressures. At 2.8 GPa, the Bragg peaks around 10.8° and 17.1° started to split. This splitting is due to the different compressibility of a, b, and c axes without symmetry break. At 8.7 GPa, a new peak marked by the dotted line emerged among the rest low angle peaks split clearly, indicating a structural transition occurred from the high symmetry to a low symmetry. The Rietveld refinement results shown in Figure 1b,c confirm that Sr2ZnWO6 transformed from the monoclinic (P21/n) phase to the triclinic (P1) phase. The detailed structural information is shown in Table S1 in the Supporting Information.

From the structural point of view, the atomic positions in the unit cell of the ideal cubic structure of the perovskite-type oxide ABO3 have two features: tilting of the BO6 octahedron and the cation displacement at the A site. In general, the change in any of these two features can lead to the structural instability and phase transition. For example, BiFeO3 transfers from rhombohedrally distorted perovskite to a distorted monoclinic structure at 3 GPa due to pressure-induced simultaneous FeO6 octahedron tilting and Bi cation displacement. At 10 GPa, a...
second phase transition occurs from distorted monoclinic structure to nonpolar orthorhombic \( Pnma \) structure as characterized by the cation displacements.\textsuperscript{27–29} LaAlO\(_3\) undergoes a rhombohedral-to-cubic phase transition around 14 GPa due to the tilts of AlO\(_6\) octahedra.\textsuperscript{30} In the current study of \( \text{Sr}_2\text{ZnWO}_6 \), we performed the Rietveld refinements for all the XRD patterns below 8.7 GPa using \( P2_1/n \) space group and obtained \((\text{Zn}, \text{W})\)–O bond length and \((\text{Zn}, \text{W})\)–O–(W, Zn) bond angle under high pressure as shown in Figure 2a–c. The rotation of the \((\text{W}, \text{Zn})\)O\(_6\) octahedron produces three \((\text{Zn}, \text{W})\)–O bond angles, two in the \( ab \) plane and one along the \( c \) direction as shown in Figure 2c. As shown in Figure 2ab, the difference between the three pairs \((\text{W}, \text{Zn})\)–O of bond lengths increased with increasing pressure. Zhao et al. introduced a standard infinitesimal strain tensor to describe the distortion of the octahedral in NaMgF\(_3\) perovskites.\textsuperscript{31} Here, we took one of octahedron strain tensor parameters: a structure parameter \( \delta = \sqrt[3]{\frac{1}{6}}\sum_{i=1,6} \left( d_{iB-O} - d_{iB-O}' \right)^2 \) of \((\text{W}, \text{Zn})\)O\(_6\) octahedron to characterize the degree of distortion away from the regular octahedron (\( \delta = 0 \)). The larger \( \delta \), the more distortion of the \((\text{W}, \text{Zn})\)O\(_6\) octahedron. As shown in Figure 2d, \( \delta \) increases with pressure until the structural phase transition occurs at 8.7 GPa. Figure 2e shows the schematic of the crystal structure change for \( \text{Sr}_2\text{ZnWO}_6 \) under high pressure.

The pressure dependences of the lattice parameters and unit cell volume up to 18.1 GPa are shown in Figure 3. The unit cell volume decreases monotonically, and a small volume collapse (\( \sim 0.3\% \)) occurs at the transition pressure of 8.7 GPa. The fittings of the \( P-V \) curve with a third-order Birch–Murnaghan equation of state:

\[
P = \frac{3}{2} B_0 \left[ \frac{V_0}{V} \right]^{7/3} - \frac{3}{2} \left( \frac{V_0}{V} \right)^{5/3} \times \left\{ 1 + \frac{3}{4} (B'_0 - 4) \right\} \left[ \frac{V_0}{V} \right]^{2/3} - 1
\]

at low and high pressure regions yield the bulk modulus, \( B_0 = 139(3) \) GPa and its derivative \( B'_0 = 6.5 \) for the low-pressure monoclinic \((P2_1/n)\) phase, and \( B_0 = 166(9) \) GPa and \( B'_0 = 4.3 \) for the high-pressure triclinic \((P\bar{T})\) phase.

**High-Pressure Raman Spectroscopy Studies of \( \text{Sr}_2\text{ZnWO}_6 \).** For \( \text{Sr}_2\text{ZnWO}_6 \) with \( P2_1/n \) space group, there are 24 Raman-active modes, represented as \( M = 12A_g + 12B_g \). However, only a small number of modes can be observed because of the accidental degeneracy.\textsuperscript{27} In our study, five strong bands can be observed at 141, 149, 448, 868, and 1006 cm\(^{-1}\), named as \( A_1, A_2, A_3, A_4, \) and \( A_5 \) respectively. Figure 4a shows the Raman spectra at different pressures up to 40 GPa. From 8.7 GPa, two new bands began to appear at 873 and 376 cm\(^{-1}\) labeled as modes \( A_6 \) and \( A_7 \), respectively, indicating a structural phase transition. This is consistent with our XRD results. Figure 4b summarizes the frequency changes of Raman bands with pressure. These Raman modes can be categorized into three types according to refs 32–35: below 200 cm\(^{-1}\), the modes are related to the \( \text{Sr}^{2+} \) translation, and translational and rotational modes in WO\(_6\) octahedron; between 200 and 500 cm\(^{-1}\), the modes are associated with the O–W–O bending vibrations; over 500 cm\(^{-1}\), the modes are related to W–O stretching modes. Therefore, the new bonding \( A_6 \) at 376 cm\(^{-1}\) and \( A_7 \) at 873 cm\(^{-1}\) originate from degenerations of the O–W–O \( A_3 \) bending and W–O \( A_4 \) stretching modes, respectively, upon the structural phase transition from the monoclinic to the triclinic phase occurred at \( \sim 8.7 \) GPa.

**Alternating Current Impedance Spectroscopy Measurement at High Pressure.** From the luminescence spectroscopy study reported in refs 35 and 36, there is an O → W charge transfer (CT) band in \( \text{Sr}_2\text{ZnWO}_6 \). This CT is attributed...
Figure 4. Raman spectra at different pressures recorded during increasing pressure (a) and Raman mode frequencies (b).

Figure 5. Nyquist plots of impedance spectroscopy of Sr2ZnWO6 up to 29.0 GPa. With increasing pressure, the arc semicircles move fast toward higher resistance.
Sr2ZnWO6 showed an abnormal electronic behavior due to electric conductivity and eventually metallization. Here, broadening the energy levels, so the material exhibits a higher makes atomic distance shorter and closes the band gap by Sr2ZnWO6 under high pressure. It can be seen that the arcs conducted up to 29 GPa.

Figure 5 shows the typical Nyquist plots for polycrystalline Sr2ZnWO6 under high pressure. It is seen that the arcs diameter increases with increasing pressure. The impedance data are modeled by two equivalent series circuits consisting of resistor (R) and constant phase element (CPE). The CPE is expressed by the following equation and defined by two values T and P.

\[ Z = \frac{1}{T(j\omega)^{nP}} \]

Here T is expressed in unit of capacitance components; \( \omega \) and \( j \) are the frequency and the imaginary unit, respectively. A CPE is placed in parallel to a resistance, so it produces a Cole element (depressed semicircle). With two series Cole circuits, it separates each of the parallel RC elements and measures their component R and C values. The total impedance has contributions of grains and grain boundaries. By fitting the data using the ZView impedance analysis software, we obtain the low frequency, which originates from grain contribution as shown in Figure 6. The grain resistivity increased in the low pressure phase region (below 10 GPa), followed by a sharp change in the phase transition region (between 10 and 14 GPa) and relative constant value at high pressure region (above 14 GPa).

As discussed in the Introduction section, normally pressure makes atomic distance shorter and closes the band gap by broadening the energy levels, so the material exhibits a higher electric conductivity and eventually metallization. Here, Sr2ZnWO6 showed an abnormal electronic behavior due to the pressure-enhanced CT between the ligand (O2−) and the metal (W6+) in WO6 octahedron. From the XRD analysis, the distortion parameter \( \delta \) of WO6 increases with pressure and reaches plateau at the phase transition. The Raman results also confirmed that the O=W−O bending vibrations and the W−O stretching increase with pressure. All of these evidence lead to enhancing the attraction between O2− and W6+, that is, increasing the covalence strength and thus reducing the conductivity. When the structural phase transition occurred, the interaction among O=W−O showed up as a sharp increase in the A6 and A1 Raman modes. This, in turn, triggers the electronic phase transition with an order of magnitude resistivity increase.

CONCLUSIONS

The high-pressure structural and electronic transport properties of Sr2ZnWO6 double perovskite have been investigated using angle-dispersive synchrotron XRD, Raman spectroscopy, and AC impedance spectroscopy at room temperature. Sr2ZnWO6 upon compression underwent a structural transition from a monoclinic phase (P21/n) to a triclinic phase (P1) around pressure of 9 GPa, accompanied by more than 1 order of magnitude increase in resistivity. Comparing to pressure-induced enhanced conductivity in most inorganic compounds, the abnormal conductivity behavior in Sr2ZnWO6 is attributed to the increase of the distortion in (W, Zn)O6 octahedron and the enhanced covalence bonding among O=W−O in the WO6 octahedron. Our combined study on the structural evolution by the XRD, Raman spectroscopy, and electrical transport measurements under high pressure provides a comprehensive understanding of this type of double perovskite from the lattice, bond strength, and electronic configuration points of view. We expect that the pressure-induced abnormal electric transport property and mechanism uncovered here will provide a useful guidance for the practical novel material design and synthesis under high pressure.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b01091.

The detail structural information on Sr2ZnWO6 at 0.7 GPa. (CIF)
The detail structural information on Sr2ZnWO6 at 10.7 GPa. (CIF)
Crystal structural information on Sr2ZnWO6 at 0.7 and 10.7 GPa. (PDF)

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Notes

The authors declare no competing financial interest.

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