Pressure-induced volume collapse and structural phase transitions in SrRuO₃

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Abstract

We report on the low temperature (6 K) structural properties of SrRuO₃ under quasi-hydrostatic pressure studied by synchrotron X-ray powder diffraction in a diamond anvil cell. First principle calculations predict a first-order perovskite (Pv) to post-perovskite (pPv) phase transition at ~40 GPa accompanied by a 1.9% volume collapse. Our results rule out the occurrence of a pPv phase to 54 GPa. Instead, we find a Pv to monoclinic to triclinic sequence of phase transitions. The monoclinic to triclinic phase transition at ~38 GPa is accompanied by a 3.5% volume collapse. X-ray absorption spectroscopy indicates that this volume collapse is not accompanied by a change in Ru valence state. Our results should help guide improvements to theoretical treatments of this and other correlated d-electron systems based on density functional theory.

1. Introduction

During the past few decades, significant efforts have been devoted to the study of 3d transition metal oxides (TMOs), which are host to myriad phenomena of potential technological relevance such as high temperature superconductivity, colossal magneto-resistance, and multiferroicity [1–3]. The richness of phase diagrams that characterize these materials is tied to the ability to control the relative strength of on-site Coulomb interactions and electronic bandwidth in the quasi-localized 3d states. On the other hand, 4d orbitals of transition metals are more extended than their 3d counterparts, the quasi-delocalized states usually resulting in the absence of local moments or even itinerant magnetism [4]. SrRuO₃ stands out against other 4d TMOs as being the only ferromagnetic perovskite ABO₃ compound displaying a relatively high Curie temperature $T_c$ ~ 163 K [5]. It is a good electrical conductor, which is indicative of “band” or itinerant ferromagnetism of the 4d electrons. Due to its unique properties, SrRuO₃ is widely used as a metallic perovskite electrode in oxide based electronic and spintronic devices [6] and has been discussed as a candidate material to display exotic quantum critical phenomena, such as unconventional superconductivity and non-Fermi-liquid behavior [7,8]. The latter can be triggered by a small perturbation of the ground state; e.g., by the application of external hydrostatic pressure, magnetic fields or chemical doping [9].

According to recent theoretical calculations [10–12], SrRuO₃ was predicted to provide an example of the long sought-after perovskite to post-perovskite (Pv-to-pPv) phase transition under high pressure with a concomitant collapse of the ferromagnetic ground state. However, despite significant efforts neither the Pv-to-pPv phase transition nor the collapse of magnetism has been observed in SrRuO₃. Prior high-pressure studies reported that no structural transition occurs up to 34 GPa [13,14]. More recently, first-principles calculations based on density functional theory (DFT) predicted that SrRuO₃ will undergo a first order, ferromagnetic-Pv to non-magnetic pPv, phase transition with related volume collapse under hydrostatic pressure of about 40 GPa [15].

In this article we report a previously unknown structural transition in SrRuO₃ to triclinic P phase at ~38 GPa accompanied by a volume collapse of 3.5%. This transition is preceded by small monoclinic distortions of the initial Pv (Pbnm) phase within the pressure range of 21–38 GPa. The triclinic phase persists up to at least 54 GPa. While a volume collapse is indeed observed near 40 GPa as predicted by density functional theory [15], the lowest energy (experimental) structure is found to be triclinic instead of the predicted pPV structure [15].
2. Experimental

2.1. Synthesis

Polycrystalline SrRuO$_3$ was prepared by solid-state reaction of stoichiometric ratios of SrCO$_3$ (99.994%) and RuO$_2$ (99.99%). The as-received severely hygroscopic RuO$_2$ powder was heated to 600 °C in a stream of nitrogen to remove water. The final product was made by firing in the following sequence: 900 °C/12 h in nitrogen, followed by subsequent firings in air at 700 °C, 750 °C, and 800 °C for 5 h each with intermediate grindings. Choice of the firing atmosphere was based on a detailed study of oxygen and Ru nonstoichiometry in SrRuO$_3$ published by Dabrowski et al. [16]. The reaction was deemed complete when no further change to the powder X-ray diffraction pattern was observed. DC magnetization revealed a sharp ferromagnetic transition at ~162 K, indicative of a high quality stoichiometric SrRuO$_3$ phase (see Fig. 1). SrRuO$_3$ has an orthorhombically distorted perovskite structure with Pbnm space group (No. 62) at ambient pressure. Hereafter the non-standard space group Pbnm is used to be consistent with the published literature. Space group Pmnma has a doubled $b$ axis with respect to the cubic perovskite structure whereas Pbnm has a doubled $c$ axis and the transformation from Pmnma to Pbnm is obtained by $a_1 \rightarrow b_2$, $b_1 \rightarrow c_2$, and $c_1 \rightarrow b_2$.

2.2. High pressure XRD experiment

High-pressure X-ray diffraction (XRD) experiments were performed in a Mao-type symmetric diamond anvil cell (DAC) in combination with cubic boron nitride seats on a polycrystalline SrRuO$_3$ sample, at HP-CAT beam line 16-BM-D of the Advanced Photon Source (APS), Argonne National Laboratory. In this study, two different pressure media, namely neon and helium, were used in order to discriminate against non-hydrostatic stress effects [17]. The powder SrRuO$_3$ sample was loaded in DACs with a full diamond anvil opposite a partially perforated diamond anvil with $300 \mu$m (DAC loaded with neon) and 180 $\mu$m (DAC loaded with helium) together with small ruby spheres and gold culet sizes of 300 $\mu$m in diameter made at the center of the BN insert. A pair of Kirkpatrick–Baez (KB) mirrors was used to focus the beam to $\sim 10 \times 10 \mu$m$^2$. Incident and transmitted beams were measured using a N$_2$ filled ion chamber and a Si photodiode, respectively.

3. Results and discussion

3.1. XRD data

The SrRuO$_3$ sample was initially measured at room temperature and low pressures (2.5 GPa with He, and 5 GPa with Ne pressure media, Fig. 1). The lattice parameters obtained from the Rietveld refinements at 2.5 GPa $[a=5.5516(4) \, \text{Å}, \ b=5.5130(9) \, \text{Å}, \ c=7.8220(1) \, \text{Å}]$ and 5 GPa $[a=5.5340(5) \, \text{Å}, \ b=5.4855(6) \, \text{Å}, \ c=7.7955(7) \, \text{Å}]$ for the orthorhombic Pbnm (No. 62) structure are in good agreement with the results of Hamlin et al. [13]. Subsequently, the DACs were cooled to a base temperature of 6 K and XRD patterns were collected at different pressures up to 54 GPa. Pressure was adjusted in-situ without removing the DACs from the cryostat and each pressure point was stabilized for about 15 min prior to data collection. XRD patterns collected at pressures from 10 GPa to 54 GPa are shown in Fig. 2 with expanded views of the data in the regions near the dashed lines shown in Figs. 3 and 4.

A full Rietveld refinement of the structure has been performed using data collected at 10 GPa. Data measured at 21 GPa and higher pressures were fit using the Le Bail method [22] since typical Rietveld refinements are hampered by severe pressure-induced peak broadening and overlap. Fits using the the LeBail method yield information on the best possible space group symmetry and the corresponding lattice parameters but no useful information can be obtained for the fractional atomic coordinates. Analysis of the diffraction data shows the expected systematic shift with pressure of the peaks to smaller $d$-spacing values. In addition, splitting of the diffraction peaks at 21 GPa indicates the occurrence of a structural change from orthorhombic Pbnm.
(No. 62) to a lower monoclinic symmetry of space group $P2_1/n$ (No. 14). The derivation of the space group symmetry is discussed below. In the orthorhombic $Pbnm$ phase, a major peak group at $d$-spacing of $\sim 2.74$ Å (10 GPa) actually consists of three peaks: (2 0 0) at 2.7467 Å, (1 1 2) at 2.7293 Å, and (0 2 0) at 2.7082 Å. In the monoclinic phase at 21 GPa, the (1 1 2) peak splits into two peaks (1 1 2 and 1 1 2). The peaks are now positioned as (1 1 2) at 2.7307 Å, (1 1 2) at 2.700 Å, (0 2 0) at 2.6840 Å, and (2 0 0) at 2.6804 Å. Further at 23 GPa, the peak positions evolve to: (1 1 2) at 2.7281 Å, (0 2 0) at 2.7015 Å, (1 1 2) at 2.6807 Å, and (2 0 0) at 2.6498 Å. The split 1 1 2 peaks (1 1 2 and 1 1 2) are only consistent with a lower than orthorhombic symmetry; thus, giving firm evidence for the appearance of the monoclinic phase. In addition, a feeble splitting of (2 2 0) and (0 0 4) peaks (positioned at 1.9284 Å and 1.9314 Å, respectively) at 10 GPa in $Pbnm$ phase dramatically enhances at pressures above 21 GPa (Fig. 3). For comparison, had the data at 21 GPa been fitted with the $Pbnm$ symmetry, the resulting $\chi^2$ – a measure of goodness of fit [23] – would deteriorate by about 57% and the prominent (2 2 0) and (0 0 4) peaks splitting could not be reproduced. Therefore, the data taken at 21 GPa cannot be described with the $Pbnm$ structure. The monoclinic $P2_1/n$ phase with a monoclinic angle 90.9° $< \beta <$ 91.5° persisted up to 36 GPa.

The observed orthorhombic to monoclinic phase transition is consistent with theoretical analysis carried out using the online software ISOTROPY developed by Campbell and Stokes [24]. The fact that no superstructure reflections appear under pressure implies that $\Gamma$ must be the k-point vector to be investigated. All other k-points allowed by the symmetry of the parent $Pbnm$ structure require the doubling or rotation of one or more unit cell parameters. With this in mind, the only possible continuous distortions can be accommodated by the orthorhombic $Pbnm$, $P2_1$2121, $Pmc2_1$, $Pna2_1$, and the monoclinic $P2_1/m$ and $P2_1/n$ (standard $P2_1/c$) space groups. However, since the split peaks cannot be indexed using any orthorhombic space groups we are only left with $P2_1/m$ and $P2_1/n$ space groups as possible solutions. The difference between these two solutions is mainly related to the distortion pattern of the oxygen atoms which cannot be resolved satisfactorily with X-rays. Nonetheless and despite the small X-ray scattering length of oxygen, best-fit LeBail refinements were obtained using the $P2_1/n$ symmetry as shown in Fig. 3. Additionally, we also note that both the $Pbnm$ and $P2_1/n$ symmetries belong to the same $a \cdot a \cdot c^*$ octahedral tilt system as described by Woodward et al. and Glazer’s notation [25–27] while $P2_1/m$ is not. We also note that the original Glazer tilt systems only considered the continuous distortions from cubic $Pm3m$ to pseudocubic superstructures of a similar unit cell size. Woodward and his coworkers [27] expanded this idea to include ordered superstructures or larger supercells similar to ours (with

![Fig. 2. XRD patterns measured at 6 K in the pressure range of 10–54 GPa with two different pressure media (He and Ne, indicated near each curve). Flat curve regions between 2.0 Å and 2.3 Å in the data measured with He correspond to the exclusions of Re gasket diffraction peaks. Dashed lines serve as guide to the eye highlighting the peaks shift.](image)

![Fig. 3. Pressure-dependent XRD data for selected Bragg peaks measured with He and Ne pressure media for pressure range 10–36 GPa, together with their Rietveld (10 GPa) and Le Bail (P > 10 GPa) refinements.](image)
\(a \sim \sqrt{2a_p}\) and \(c \sim 2a_p\) where \(a_p\) is the cubic perovskite unit cell dimension). There are many examples in the literature showing similar transitions taking place between the same two space groups (e.g., GdFeO\(_3\) and similar ferrites [28], Y\(_{1-x}\)Ca\(_x\)TiO\(_3\) [29], nickelates and manganites, etc. [30]).

A complete set of unit cell parameters, including angles and volume as a function of pressure is given in Table 1. The pressure-dependent volume data in Table 1 was fitted with a second-order Birch–Murnaghan (\(B-M\)) equation of state (EOS) [31] below 36 GPa (Fig. 5) since the limited number of data points and pressure range up to the volume collapse prevents us from accurately determining both the bulk modulus and its pressure derivative. The corresponding fitted curve (lower dashed line in Fig. 5) yielded values of \(V_0=237(1)\) Å\(^3\) for the unit cell volume at ambient pressure and \(B_0=323(18)\) GPa for the bulk modulus. As expected, this bulk modulus measured at 6 K is larger than its value at 300 K (\(B_0=192\) GPa; Ref. [13]). We also carried out a fit to the \(B-M\) equation including the ambient pressure data point measured by neutron diffraction in Ref. [26] (241.5 Å\(^3\) at \(T=1.5\) K). The corresponding fit (upper dashed line in Fig. 5) yielded values of \(V_0=240.1(1)\) Å\(^3\) and \(B_0=260(25)\) GPa for the bulk modulus. This last fit is consistent, within errors, with both the X-ray data and the ambient pressure neutron data [32]. Note that forcing a third-order \(B-M\) EOS with a pressure derivative of the bulk modulus \(B_0'\)=5 from Ref. [13] returns \(B_0=246(22)\) GPa, which is within one to two standard deviations from the values obtained by the second order \(B-M\) EOS fits. We do not have enough knowledge of the exact cationic or anionic stoichiometry of the sample used in Ref. [32]. Hence, inclusion of the neutron results from Ref. [32] in our fits may not be fully warranted and an accurate determination of \(B_0\) would become difficult to achieve. We note that our sample is inferred to be stoichiometric based on its sharp magnetic transition with 162 K ordering temperature, as reported in the systematic study of \(T_c\) vs. stoichiometry in SrRuO\(_3\) [16]. Nevertheless, the main focus of this paper is not providing an exact measurement of the bulk modulus of SrRuO\(_3\) but rather testing the theoretical

![Fig. 4. Pressure-dependent XRD data for selected Bragg peaks measured with He and Ne pressure media for pressure range 36–54 GPa, together with their Le Bail refinements.](image)

<table>
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<th>(P) (GPa)</th>
<th>(a) (Å)</th>
<th>(b) (Å)</th>
<th>(c) (Å)</th>
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<td>5.3803(10)</td>
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As the pressure increases beyond 36 GPa, the XRD patterns (Fig. 2) can no longer be indexed using the $P2_1/n$ monoclinic space group and the broadened peak shape profiles (Fig. 4) cannot be reproduced. Instead, using the LeBail fit procedure we observed a second phase transition to a lower $P$-type triclinic symmetry. The transition features a dramatic change in peak shape profiles especially at the $d$-space positions of ≈2.65 Å and ≈1.87 Å (Fig. 4), as seen by comparing the data measured at 36 GPa and 38 GPa with Ne pressure medium. For these two data sets, the LeBail fit revealed a concomitant volume collapse of 3.5%. The angles $\alpha$ and $\gamma$ in the triclinic phase do not exceed 90.4° and 91°, respectively (Table 1). For comparison, had the data above 36 GPa been poorly fit with the $P2_1/n$ structural model, the resulting $\chi^2$ would have increased by a factor of 2.7 (54 GPa data), 9 (48 GPa data), and 16 (44 GPa data). Evidently, data taken above 36 GPa cannot be described by a monoclinic structure. Note, that the small diffraction peak around 2.25 Å in the 36 GPa and 48 GPa data (Ne data sets, Fig. 2) is the Au (1 1 1) peak from the Au pressure calibrant.

Theoretical analysis using ISOTROPY shows that continuous distortions from both the monoclinic $P2_1/n$ or $P2_1/n$ space groups can only lead to the triclinic $P\overline{1}$ (No. 2) space group. The lower $P1$ (No. 1) triclinic symmetry would have been possible if superstructures were to be observed or possibly with first-order structural transitions. While we can rule out the formation of superstructures, our data does indicate a first-order like phase transition and consequently $P1$ (No. 1) cannot be excluded at this stage. Nonetheless, at these extreme pressures, to distinguish between $P1$ from $P\overline{1}$ would require the precise determination of all oxygen positions and therefore it cannot be reliably done. Neutron diffraction would be the ideal tool to determine the oxygen positions and the exact effects of pressure on the structure. However, such experiments would be extremely challenging because of the large pressures needed to drive the structural transitions with the related constraints on beam collimation and sample size. The best fit to our data using the $P\overline{1}$ (No. 2) space group is shown in Fig. 4.

As noted in the introduction, previous DFT calculations [15] predicted a phase transition from P–SrRuO$_3$ to P–SrRuO$_3$ with a Cmcm crystal structure and a volume collapse of 1.9% at a pressure of 40 GPa. Instead, in the present study we observe a monoclinic to triclinic phase transition at similar pressures, but no signature of the P–Pv phase can be seen in the diffraction patterns. The comparison of the data measured at 38 GPa and the simulated theoretical pV diffusion pattern for the predicted SrRuO$_3$ Cmcm crystal structure [15] at 40 GPa using the same Cagliotti parameters (GU, GV, GW, LX, LY [21]) are shown in Fig. 6. The absence of two major groups of diffraction peaks with $d$-spacings in the 2.1–2.3 Å and 2.8–3.0 Å range in the bottom panel of Fig. 6 clearly rules out the formation of a high-pressure, post-perovskite orthorhombic structure in SrRuO$_3$.

### 3.2. XANES data

Finally, Ru K-edge XANES measurements were performed at room temperature in order to probe for possible Ru valence changes that may take place at the high-pressure volume collapse transition. XANES provides element specific formal valence and information on the chemical and electronic structures including coordination environment (number and local symmetry). The sequence of XANES spectra measured at different pressures, together with their energy derivatives, is shown in Fig. 7. The spectra were normalized to a unit edge jump in order to account for possible variations in the sample thickness as the pressure increased. We found no evidence of a shift in the absorption edge of Ru as a function of applied pressure. This indicates that no
significant charge transfer or a change in Ru valence takes place across the full sequence of phase transitions. Furthermore, we conclude that the volume collapse is not electronically driven by a valence transition of the Ru ions.

4. Conclusions

In summary, we probed both the crystal structure and electronic structure of SrRuO₃ under high pressures up to 45 GPa. We observed a previously unpredicted sequence of structural phase transitions, namely perovskite orthorhombic Pbnm to monoclinic P₂₁/n between 10 GPa and 21 GPa to triclinic P at ~38 GPa. The latter transition is accompanied by a volume collapse of 3.5%. The observed phase transitions are sequenced according to the valence transition of the Ru ions.

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References

[18] Yongmao Cai, Yingjin Wei, Xing Ming, Fei Du, Yang Ding, Changyong Park, Dmitri Popov, and Curtis Kenney-Benson for their help during experiments at HP-CAT and Yang Ding for his valuable advice regarding the use of Beryllium gaskets in the diamond anvil cell.

Fig. 6. (top) Simulated diffraction pattern from pPV-SrRuO₃ Cmcm crystal structure using atomic coordinates from Ref. 15; (bottom) data measured in this study at 38 GPa with corresponding Le Bail fit.

Fig. 7. Ru K-edge XANES spectra measured at different pressures using transmission geometry through a Be gasket. The inset is an expanded view of the energy derivative of the XANES spectra, showing the absence of any detectable Ru valence transition in this pressure range.