Journal of Solid State Chemistry 238 (2016) 74–82

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

High pressure structure studies of 6H-$SrIrO_3$ and the octahedral tilting in 3C-$SrIrO_3$ towards a post-perovskite

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ARTICLE INFO

Article history:
Received 2 February 2016
Received in revised form
24 February 2016
Accepted 4 March 2016
Available online 8 March 2016

Keywords:
$SrIrO_3$
High pressure
Perovskite
Polymorphism
Post-perovskite

ABSTRACT

The high pressure behaviors of the two perovskite structures (hexagonal 6H-$SrIrO_3$ and orthorhombic 3C-$SrIrO_3$) have been studied in diamond anvil cells to 43 and 60 GPa, respectively, using synchrotron powder X-ray diffraction. 6H-$SrIrO_3$ was first synthesized at ambient pressure and subsequently transformed into 3C-$SrIrO_3$ in a large volume press at 8.8 GPa and 1000 °C. Both polymorphs were found to retain the initial symmetry up to the highest pressures measured, but in the case of 6H-$SrIrO_3$, two anomalies were identified: a change in the axial compressibilities at 24 GPa and a change in both the axial and volume compressibilities at 32 GPa. Fitting a 3rd order Birch-Murnaghan equation of state to the obtained *P-V* data yielded bulk moduli of $K_0=151.5(12)$ GPa (fitted range $0<P<30$ GPa) for 6H-$SrIrO_3$ and $K_0=187.1(9)$ GPa for 3C-$SrIrO_3$. Analysis of the structural parameters for 6H-$SrIrO_3$ aided by *F-f* plots suggests the anomalies are caused by changes in the compression mechanism. Comparison of the two polymorphs reveals that 6H-$SrIrO_3$ becomes less compressible than 3C-$SrIrO_3$ above 32 GPa as a result of the mechanistic change, and a crossing of their *P-V* curves is avoided. For 3C-$SrIrO_3$, analysis of the octahedral tilt angles shows that these increase monotonically from the ambient value of 7.23(6) to 23.0(2)° at 60 GPa suggesting that a transition to a post-perovskite is approached.

1. Introduction

Ternary metal oxides containing 4*d* and 5*d* transition metals that adopt the perovskite and perovskite-related structures have received growing attention in recent years. This is driven by their magnetic and electronic properties, which arise from the interplay of crystal field, electronic correlations as a result of extended *d*-orbitals and strong spin orbit coupling (SOC) [1–6]. The alkaline-earth iridates, $AIrO_3$ (A=Ca, Sr or Ba), contain Ir^{4+} with $5d^5$ orbital configuration. These iridates crystallize in three different structures at ambient conditions and show rich polymorphism when treated with high pressure and high temperature [7]. The thermodynamically stable phase of $SrIrO_3$ is a distorted variant of the hexagonal 6H-$BaTiO_3$-type perovskite. 6H-$SrIrO_3$ is metallic, but deviates from Fermi-liquid behavior at low temperatures suggesting proximity to a quantum critical point [8,9]. High pressure and high temperature synthesis stabilizes an orthorhombic perovskite, 3C-$SrIrO_3$, which was first reported by Longo et al. and more recently by Zhao et al. [8,10]. 3C-$SrIrO_3$ is a semimetal and calculations suggests a $J_{\mathrm{eff}}=½$ band near the Fermi level and proximity to a Mott instability [2]. Epitaxial stabilization of 3C-$SrIrO_3$ in thin films and super-lattices has also been demonstrated which allows for tuning of the electronic and magnetic properties [11–16], and makes 3C-$SrIrO_3$ a potential candidate for realization of novel electronic states and applications [11,16]. The physical properties are very sensitive to the structural arrangements in these iridates and high pressure is an efficient approach to explore their structure-property relationships [4]. Foroozani et al. studied the properties of single crystal 6H-$SrIrO_3$ to a modest pressure of 0.9 GPa and observed decreasing resistivity, but speculated that superconductivity could be induced at higher pressure [17]. Experimental studies of thin films grown on top of different substrates show that compressive strain applied to 3C-$SrIrO_3$ increases the resistivity [10]. High pressure structure studies of the $SrIrO_3$ polymorphs have not been reported to date.

For perovskites, mismatching of ionic sizes and bond covalence favor distortion from the ideal cubic structure, the most common distortion being the orthorhombic $GdFeO_3$-type perovskite (3C, space group *Pnma*, #62). The distortion occurs when the size of the A-site cation is too small for the 12-coordinate site and is achieved by coupled tilting of the corner-linked BO_6 octahedra, which stabilizes the structure. As a rule of thumb, the structure of ABO_3

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http://dx.doi.org/10.1016/j.jssc.2016.03.012
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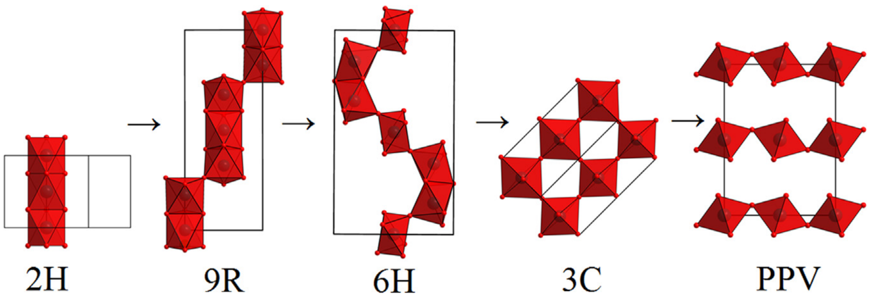

Fig. 1. General structures of the perovskite polymorphs and the post-perovskite (PPV) observed in $AIrO_3$ compounds, where A is an alkali earth metal. In the 2H structure all the BO_3 layers are hexagonal closed packed. In the 9R structure the packing sequence is *chhchhchh*. In the 6H structure the packing sequence is *cchcch*. In the 3C structure all BO_3 layers are cubic closed packed. (c=cubic and h=hexagonal).

compounds can to some extent be predicted from the ionic radii by the Goldschmidt tolerance factor, $t=(r_A+r_O)/\sqrt{2}(r_B+r_O)$. When the tolerance factor is close to 1, cubic structures occur and distortions to tetragonal, orthorhombic and monoclinic symmetries are expected for lower values. For tolerance factors above 1, hexagonal perovskites are expected [18]. Hexagonal perovskites have both corner- and face-sharing octahedra, and can accommodate larger A cations and shorter B-B distances between the face-sharing octahedra. Since the A-cations are usually more compressible relative to the B and O ions, high pressure phase transitions generally follow a trend with decreasing hexagonal character: $2H \rightarrow 9R \rightarrow 4H \rightarrow 6H \rightarrow 3C$ [7,19–21]. This series of structure types are shown in Fig. 1.

The pressure behavior of $BaIrO_3$, with the large and compressible Ba^{2+} ion ($t=1.060$, calculated using ionic radii reported by Shannon et al. [22]), is well suited to illustrate the pressure dependence on the polymorphism in $AIrO_3$ structures. Synthesis at ambient pressure produces 9R-$BaIrO_3$, which is in agreement with the prediction of the tolerance factor. Gradual increase of the synthesis pressure leads to the series $9R \rightarrow 5H \rightarrow 6H \rightarrow 3C$ [7]. The series follows the expected trend, except that the 4H polymorph has not yet been observed in this system [21]. The smaller A-site cation in $CaIrO_3$ ($t=0.880$) leads to a distorted orthorhombic structure (3C), but a post-perovskite (PPV) structure can also be synthesized at ambient pressure [23,24]. Although pressures of 1–3 GPa favor the 3C-$CaIrO_3$ structure, higher pressures stabilize the post-perovskite structure [25,26].

The tolerance factor for $SrIrO_3$, $t=0.992$, suggests that a cubic or pseudo-cubic symmetry is to be expected. However, the ambient phase of $SrIrO_3$ is a monoclinic distortion of the 6H polymorph, and has been previously referred to as “6H”-$SrIrO_3$ (space group $C2/c$, #15) [8,10]. It is highly unusual for ABO_3 compounds with $t<1$ to crystallize as hexagonal perovskites and demonstrates that a simple ionic size model is insufficient to describe the crystal chemistry of $SrIrO_3$. Furthermore, the monoclinic distortion ($\beta=93.2°$) indicates that bond covalence is significant. In analogy to the high pressure transformation, it has also been shown that the face-sharing IrO_6 octahedra of the 6H structure can be destabilized by partial Ir substitution with larger and less electronegative cations, resulting in the 3C polymorph [27–29].

The size of the SrO_3 layer that separates the Ir^{4+} ions decreases when the 6H-$SrIrO_3$ phase is subjected to pressure. This creates interionic repulsions between the Ir^{4+} ions and destabilizes the face-sharing octahedra, which has also been observed for similar 6H structures [30]. The transition to a denser packing with only corner-sharing octahedra is therefore favorable under high pressure. The transition from the ambient 6H-to the 3C-$SrIrO_3$ polymorph is the last step in the series and it is not expected that other hexagonal polymorphs can be stabilized by pressure. However, as in the case of $CaIrO_3$, some perovskite compounds distort further when subjected to high pressure and transform into the post-perovskite structure [31]. The post-perovskite structure has layers of edge-sharing and corner-sharing BO_6 octahedra separated by the A cations [32,33]. This structure type has been of high interest since the discovery that $MgSiO_3$ (a major component of our Earth's lower mantle) undergoes this transition at 125 GPa [34]. Since then, several other ABO_3 compounds have been found to undergo this perovskite to post-perovskite phase transformation [31,35–41].

Despite the great interest in $SrIrO_3$ there have been no structure investigations concerning the compression of the 6H and 3C polymorphs. In this study the first order phase transformation from 6H- to 3C-$SrIrO_3$ was found to require heating. By carrying out measurements at room temperature, we have compared the compression behavior of the two polymorphs to pressures of more than an order of magnitude above that required to synthesize the 3C polymorph. The results from the two pressure studies indicate a change in compression mechanism for 6H-$SrIrO_3$ and that a transition to the post-perovskite is possibly approached for 3C-$SrIrO_3$.

2. Experimental methods

6H-$SrIrO_3$ was synthesized by the conventional solid state reaction reported by Zhao et al. [10]. Stoichiometric quantities of $SrCO_3$ and Ir were mixed and ground thoroughly and then pressed to a pellet. The pellet was heated at a rate of 100 °C/h in air to 800 °C for 10 h. The pellet was ground, re-pelleted and heated again for 24 h at 1000 °C and then furnace cooled. To achieve high crystallinity, the last step was repeated twice.

The high pressure synthesis of 3C-$SrIrO_3$ was performed in a large volume multi-anvil press equipped with a Walker-type module with 32 mm tungsten carbide cubes. The synthesis was performed using 14/8 COMPRES octahedral assemblies [42]. Presynthesized 6H-$SrIrO_3$ was used as precursor and was contained in a gold foil capsule to avoid contamination. The pressure was ramped to 8.8 GPa at room temperature (using the calibration by Leinenweber et al. [42], press load 220 tons). The sample was heated at a rate of 50 °C/min to 1000 °C, and quenched to room temperature after 30 min by switching off power to the furnace.

6H- and 3C-$SrIrO_3$ were characterized at ambient conditions by powder X-ray diffraction (PXRD) on a Rigaku SmartLab diffractometer equipped with a rotating Cu-anode in Bragg-Brentano geometry using monochromatic Cu $K\alpha_1$ radiation ($\lambda=1.54056$ Å). The Rietveld method was employed to conduct refinements of the structural model describing the collected PXRD data. 6H-$SrIrO_3$ was refined using the starting model ICSD#187813 and 3C-$SrIrO_3$ was refined using cell parameters and atomic positions reported by Zhao et al. [10], using the FullProf program [43].

High pressure PXRD measurements of 6H-$SrIrO_3$ and 3C-$SrIrO_3$ were carried out at room temperature in Le Toullec-type