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Journal of Solid State Chemistry 178 (2005) 2282–2291
JOURNAL OF SOLID STATE CHEMISTRY
www.elsevier.com/locate/jssc

Temperature and pressure dependent structural studies of the ordered double perovskites $Sr_2TbRu_{1-x}Ir_xO_6$

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Received 21 February 2005; accepted 6 April 2005
Available online 9 June 2005

Abstract

High resolution powder diffraction studies are reported for the series of mixed RuIr perovskites $Sr_2TbRu_{1-x}Ir_xO_6$. Using a combination of synchrotron X-ray and neutron powder diffraction precise structures are established for the two end-member oxides, where the Tb oxidation state changes from +3 in the Ru oxide to +4 in the Ir containing oxide. The structures of both oxides are monoclinic. Composition dependent studies show that this valence transition is first order. Variable temperature diffraction show no evidence for any structural or valence state transitions. However, upon application of pressure $Sr_2TbRu_{0.3}Ir_{0.7}O_6$ undergoes a valence state transition at low pressures.

Keywords: Perovskite; Valence state; Crystal structure; Phase transition

1. Introduction

Oxides of the double perovskite family $A_2BB'O_6$ (where A is an alkaline earth cation and B and B' are transition metals or lanthanides) are of considerable interest as a consequence of their remarkable magnetic and electrical properties [1–3]. There is ample evidence that partial replacement of one of the B-site cations can have a dramatic effect on the observed magnetic and electrical properties, e.g., colossal magnetoresistance and superconductivity, especially when the B-site cation is a transition metal [4–8]. Altering the number of metal-ion d-electrons, and the energy of the d-levels relative to the oxygen $2p$ levels, can have significant impact on the electronic properties of transition metal oxides [9]. Small chemical substitutions can lead to a distortion of the structures of the double perovskites that are correlated with their electronic properties.

The series $Ba_2PrRu_{1-x}Ir_xO_6$ is an example in point. Magnetic measurements have shown that the pure Ru compound contains pentavalent Ru, whereas the pure Ir compound contains tetravalent Ir, thereby forming the two oxides $Ba_2Pr^{3+}Ru^{5+}O_6$ and $Ba_2Pr^{4+}Ir^{4+}O_6$ [10]. Solid solutions of the type $Ba_2PrRu_{1-x}Ir_xO_6$ can be prepared and detailed structural and magnetic studies show these oxides undergo a first-order valence state transition [10], accompanied by a monoclinic to tetragonal structural phase transition [11]. The valence state and structural transition can be induced by changes in either temperature [10,11] or pressure [12], with high pressure or low temperatures favoring the lower valence Pr^{4+}-containing tetragonal structures.

Recently, Doi and co-workers [13] reported a similar dependence of the valence state on the composition in the solid solutions $Sr_2TbRu_{1-x}Ir_xO_6$, although they did not consider the possibility that the valence state

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doi:10.1016/j.jssc.2005.04.030

transition was accompanied by a structural phase transition. Their published monoclinic lattice parameters for Sr_2TbIrO_6, obtained using powder X-ray diffraction measurements, are close to being metrically cubic $a' = a/\sqrt{2} = 4.067 \approx b' = b/\sqrt{2} = 4.073 \approx c' = c/2 = 4.069\,\text{Å}$ and the possibility that this has a higher symmetry structure cannot be discounted. Importantly, they did not consider the influence of temperature and/or pressure on the structures and valence states of the oxides.

Given the complex temperature and pressure dependence of the structure of the analogous $Ba_2PrRu_{1-x}Ir_xO_6$ series [10–12], coupled with the paucity of well characterized valence state transitions in transition metal oxides [14,15], we have re-investigated the structures of the series $Sr_2TbRu_{1-x}Ir_xO_6$ using high-resolution powder diffraction. We find that the application of moderate pressures can induce a valence state transition but surprisingly find no evidence for any temperature induced structural phase transitions.

2. Experimental

Polycrystalline samples of 10 members in the series of solid solutions $Sr_2TbRu_{1-x}Ir_xO_6$ were prepared by the reaction of the appropriate stoichiometric mixture of $SrCO_3$, Tb_4O_7, Ru and Ir. The reactants were intimately mixed in an agate mortar under acetone, placed in an alumina crucible and heated at temperatures of up to 1200 °C for 3 days with intermediate grindings.

The sample purity was established by powder X-ray diffraction measurements using Cu$K\alpha$ radiation on a Shimadzu D-6000 Diffractometer. Synchrotron X-ray powder diffraction patterns were collected on the high resolution Debye-Scherrer diffractometer at beamline 20B, the Australian National Beamline Facility, at the Photon Factory, Japan [16]. The samples were finely ground and loaded into 0.3-mm glass capillaries that were rotated during the measurements. All measurements were performed under vacuum to minimize air scattering. Data were recorded using two Fuji image plates. Each image plate is 20×40 cm and covers 40° in 2θ. The data were collected at a wavelength of 0.80282 Å (calibrated with a NIST Si 640c standard) over the 2θ range of 5–85° with step size of 0.01°. High temperature measurements were recorded in the same manner using a custom built furnace.

Neutron powder diffraction data were collected at the HIFAR facility operated by the Australian Nuclear Science and Technology Organisation (ANSTO) using the High Resolution Powder Diffractometer at a wavelength of 1.4928 Å [17]. Each sample was held in an aluminum capped vanadium sample holder and was rotated throughout the measurements. The diffractometer is equipped with 24 ^{3}He detectors individually separated by 5°. The patterns were collected at room temperature over the 2θ range 0–150° with step size of 0.05°.

A modified Merrill–Bassett diamond-anvil cell was used for the X-ray studies in the pressure range 0.0–6.0 GPa. The powdered sample together with a few small ruby chips was loaded into a 200 μm hole in a steel gasket. A methanol–ethanol–water (16:3:1) mixture was used as the hydrostatic pressure-transmitting medium. The pressure was calibrated by measuring the shift of the R_1 fluorescence line of ruby before and after each run. The variable pressure X-ray diffraction data were collected using synchrotron radiation at the bending magnet beamline, X7A, of the National Synchrotron Light Source at Brookhaven National Laboratory [18]. A wavelength of 0.69385 Å was selected using a channel cut Ge 1 1 1 monochromator.

Structural parameters were refined by the Rietveld method using the program RIETICA [19]. A pseudo-Voigt function was used to model the peaks. The background in the synchrotron diffraction measurements was fitted by linear interpolation between regions where there were no Bragg peaks. A polynomial function was used to estimate the background in the neutron diffraction profiles.

3. Results and discussion

3.1. Crystal structures of Sr_2TbRuO_6 and Sr_2TbIrO_6

The neutron diffraction data for the end-member ($x = 0$) compound Sr_2TbRuO_6, is shown in Fig. 1, and agrees with the previously published structure [20,21]. It is worth noting that the neutron scattering lengths of Tb and Ru are approximately equal, (0.721 and 0.738 fm, respectively) and as such it was not possible to distinguish these in the neutron diffraction measurements. Nevertheless, the pattern contained a number of reflections that could be indexed to an R-point mode. Usually this is taken as evidence for cation ordering [22,23] however, it should be stressed that an R-point mode is also associated with out-of-phase tilting of the BO_6 octahedra in successive layers [24]. The observation of these reflections in the neutron diffraction data shows that cation ordering and/or out-of-phase tilting is present. These structural features cannot be distinguished by extinction rules. This problem does not exist for the synchrotron X-ray diffraction data (Fig. 2), since the contribution to the intensity of the R-point reflections from the octahedra tilting is much less than that from the difference in scattering power of Tb and Ru. Furthermore, both the neutron and X-ray diffraction pattern show some X-point reflections that arise from a coupling of the M-point modes (responsible for the in-phase octahedral tilting) and the