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Synthesis and characterization of $Sr_2Ir_{1-x}M_xO_4$ (M=Ti, Fe, Co) solid solutions

Alvin J. Gatimu, Romain Berthelot, Sean Muir, Arthur W. Sleight, M.A. Subramanian *

Department of Chemistry, Oregon State University, Corvallis, OR 97331, USA

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ABSTRACT

The effects of Ti, Fe and Co substitutions for Ir on the structure and on the physical properties of Sr_2IrO_4 are investigated. A complete solid solution $Sr_2Ir_{1-x}Ti_xO_4$ is obtained while both Fe and Co doping are relatively limited. In each case however, the c-axis cell parameter and the initial IrO_6 octahedra tilting decreases with substitution. Doping with Ti, Fe and Co results in a decrease of the magnetic susceptibility and in an increase in the paramagnetic effective moment for Co and Fe doped samples and a suppression of the weak ferromagnetic ordering observed for Sr_2IrO_4.

1. Introduction

Transition metal oxides display a wide variety of structural and physical properties and continue to be of great interest to researchers. Oxides with a K_2NiF_4-type structure have been intensively investigated following the discovery of superconductivity in $La_{2-x}Ba_xCuO_4$ compositions [1]. Soon after researchers identified Sr_2IrO_4 as another intriguing composition due to its structural and electronic similarities with La_2CuO_4 [2,3,4]. Both are Mott insulators at room temperature and contain a transition metal with spin 1/2 and a half filled d-band. These similarities have led some researchers to theorize that doped Sr_2IrO_4 compounds can exhibit interesting behaviors including high temperature superconductivity, as in the case of doped cuprates [5].

Numerous studies have therefore explored the influence of electron and hole doping in Sr_2IrO_4, as well as aliovalent substitution, in search of superconductivity and other interesting phenomena. Electron doping can be achieved by La^{3+} substitution on the Sr site; however, the doping limit differs from one study to another with less than 5% according to Klein and Terasaki [6] and up to 20% for Cosio-Castaneda et al. [7]. This substitution led to a notable decrease of the resistivity although keeping a semiconducting dependence. Introduction of very dilute oxygen vacancies can also lead to electron doping; single-crystals of $Sr_2IrO_{4-\delta}$ with $\delta \leq 0.04$ demonstrated reduced lattice parameters and an insulator-to-metal transition at 105 K [8–10]. As Sr_2RuO_4 also adopts the K_2NiF_4-type structure, Ir substitution by Ru (hole doping for small Ru fractions) has been also investigated through the complete solid solution $Sr_2Ir_{1-x}Ru_xO_4$ [4]. These compositions exhibit an interesting insulator-to-metal transition for $x \sim 0.6$–0.8 coinciding with a maximum in the effective paramagnetic moment observed. It is also reported that Ca^{2+} and Ba^{2+} can be substituted for Sr^{2+} in small fractions with little influence on magnetic and transport properties [11].

Structurally, Sr_2IrO_4 was first assumed to adopt the ideal K_2NiF_4-type structure, i.e. a perovskite framework of IrO_6 corner-shared octahedra forming IrO_2 planes and separated by a SrO double layer [12] (Fig. 1a and b). However, further electron and neutron diffraction studies on polycrystalline samples revealed some superstructure peaks and indicated a modified crystal structure due to a low rotation of IrO_6 octahedra of about $\theta = 11^\circ$ about the crystallographic c-axis (Fig. 1c) [2,13]. This structural change results in a less symmetric space group $I4_1/acd$ compared to the initial $I4/mmm$, and the larger modified unit cell with the dimensions $a = 5.4979(2)$ Å $= \sqrt{2}a_0$ and $c = 25.798(1)$ Å $= 2c_0$, where a_0 and c_0 stand for the cell parameters of the initial unit cell. Note that a similar structural distortion has been observed in Sr_2RhO_4 [3] and Ca_2MnO_4 [14,15]. To our knowledge Sr_2IrO_4 is the only K_2NiF_4-type transition metal oxide containing a 5d cation.

Here we report on our investigation of Ir substitution by three different 3d transition metals (Ti, Fe and Co). These metals were chosen as Sr_2TiO_4, Sr_2FeO_4 and Sr_2CoO_4 compounds all adopt the ideal K_2NiF_4-type structure [16–18] and we are interested in investigating the evolution of structure–property relationships as the transition metal coordination moves back towards ideality. These solid-state substitutions are studied by X-ray diffraction, magnetism and electrical measurements.

2. Experimental

Polycrystalline samples were prepared by conventional solid-state method using strontium carbonate $SrCO_3$ (Alfa 99.9%),

* Corresponding author. Fax: +1 541 737 2062.
E-mail address: mas.subramanian@oregonstate.edu (M.A. Subramanian).

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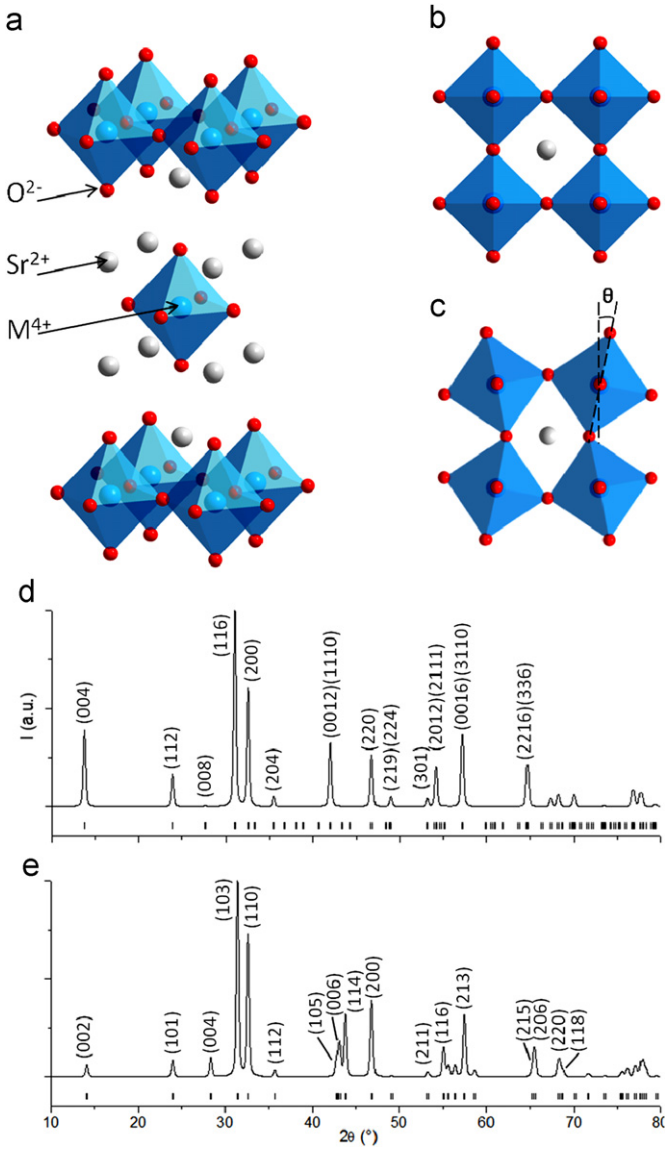

Fig. 1. Representation of the K_2NiF_4-type structure for Sr_2MO_4 (M=Ti, Fe, Co) in a perspective view: (a) and in projection in the (a, b) plane (b). In case of Sr_2IrO_4, the same latter projection (c) evidences the octahedra tilting $\theta \sim 11^\circ$ around the c-axis. Simulated XRD patterns of Sr_2IrO_4 (d) from [2] and Sr_2TiO_4 (e) from [16] are shown for comparison.

iridium oxide IrO_2 (obtained by heating hydrated iridium chloride $IrCl_3 \cdot xH_2O$ (JMC 99.9%) two times for 12 h at 700 °C under air) with either titanium oxide TiO_2 (JMC 99.99%), iron oxide Fe_2O_3 (Alfa 99.99%) or cobalt oxide Co_3O_4 (Alfa 99.7%). $SrCO_3$ was dried overnight at 120 °C before use to avoid moisture contamination. Precursors were mixed thoroughly in the stoichiometric proportions, pelletized, and heated in air on a platinum tray in an alumina crucible. Typical heating treatments were 12 h at 1050 °C with heating and cooling rates set to +5 and −5 °C/min respectively.

Each powder sample was firstly characterized by X-Ray Diffraction (XRD) using a Rigaku Miniflex II diffractometer for the 2θ range from 10° to 80°. Cu$K\alpha$ radiation was selected with a graphite monochromated diffracted beam. Room temperature cell parameters were refined using GSAS and Fullprof softwares. Magnetic and electronic properties were carried out using a Quantum Design Physical Properties Measurement System (PPMS). Magnetic susceptibility measurements were done on encapsulated powder samples in a magnetic field of 1 T, from 5 to 300–325 K (zero-field-cooled). Magnetization versus magnetic field data was collected at 5 K from 0 to 5 T. Samples were reground, pelleted, and sintered for an additional 12 h in order to perform four-probe resistivity measurements from 5 to 300 K.

3. Results and discussion

3.1. XRD characterization

3.1.1. $Sr_2Ir_{1-x}Ti_xO_4$ complete solid solution

XRD patterns obtained from the nominal compositions $Sr_2Ir_{1-x}Ti_xO_4$ ($0 \le x \le 1$) are shown in Fig. 2a. Single phase patterns were obtained at all values of x, indicating a complete solid solution from Sr_2IrO_4 to Sr_2TiO_4.

From a structural point, the interest of this complete solid solution is the transition from the tilted ($I4_1/acd$) to the ideal ($I4/mmm$) structure. The octahedral tilting (θ) should disappear with Ti substitution as the structure adopts the ideal K_2NiF_4-type structure. An initial close comparison of the simulated XRD patterns of both Sr_2IrO_4 from [2] and Sr_2TiO_4 from [16] highlights some clear differences between them (Fig. 1d and e). For example at ~8 ° in 2θ, the (0,0,4) peak becomes (0,0,2) while its intensity dramatically decreases. On the contrary at ~28°, the weak (0,0,8) peak observed for Sr_2IrO_4 becomes more intense as it transitions to the (0,0,4) for Sr_2TiO_4. As it is sometimes difficult to correctly track the evolution of diffraction peak intensity, it is more reasonable to focus on the 40–48° 2θ range, where the indistinguishable (0,0,12) and (1,1,10) peaks observed for Sr_2IrO_4 are replaced by the three distinct peaks (1,0,5), (0,0,6) and (1,1,4) in the case of Sr_2TiO_4 (Fig. 2b). However, these initial observations can be misleading as it is important to also consider symmetry and scattering factor effects in these XRD patterns. The Ir end member has a larger unit cell and lower symmetry and thus an XRD pattern with more peaks is expected. In addition, Ir and Ti possess different scattering powers and thus some peak intensities may vary from Sr_2IrO_4 to Sr_2TiO_4. XRD simulations show that this is actually the case for the (1,1,4) peak of Sr_2TiO_4 which becomes very weak in theoretical Sr_2IrO_4 with no IrO_6 tilting. Neutron diffraction experiments can overcome this problem. However, the high cost of iridium precursors and the large mass of samples required for neutron diffraction hindered us in performing such an analysis. Therefore, we tried to clarify the Sr_2IrO_4 to Sr_2TiO_4 transition by focusing on the evolution of cell parameters.

From Sr_2IrO_4 to Sr_2TiO_4, the c parameter significantly decreases (Fig. 2c) which is as expected considering the ionic radii of Ir^{4+} and Ti^{4+} (respectively 0.625 and 0.605 Å in a 6-fold coordination [19]). Two distinct linear trends are noticed on either side of x=0.4. The change in the a cell parameter with changing x is much less than the c parameter change. This is due to the presence of two competing processes, which tend to cancel each other. The smaller size of Ti will contribute to a decrease in a, but the expected decrease in octahedral tilting will contribute to an increase in a. Clearly, the decreased tilting dominates the change in a as Ti is first introduced (Fig. 2c). However, there is then a change from a positive to a negative slope (highlighted by the two dotted lines) at the same Ti content where there is a change in slope for the c cell parameter (highlighted by the dashed lines). The solid line indicates the expected change in the a cell parameter if the octahedral tilting did not occur. This line is based on the assumption that the M–O distance will be a simple weighted average of the values observed for the end members. In the case on the ideal Sr_2TiO_4 structure the a cell parameter is simply twice the Ti–O distance in the ab plane. (For ease of comparison the values in the figures for a are multiplied by $\sqrt{2}$ for the high x compositions.) Essentially all values of a fall below the ideal value based on no tilting of