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Ceramics International 39 (2013) S233–S237

CERAMICS INTERNATIONAL

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Structural and magnetic studies of *A* site doped $LaRh_{1-x}Cu_xO_3$($A = Ca^{2+}$, Sr^{2+}, Pb^{2+} and Bi^{3+})

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Available online 22 October 2012

Abstract

A site doped Rh perovskites with general formula $La_{0.75}A_{0.25}Rh_{0.7}Cu_{0.3}O_3$ and $La_{0.75}A_{0.25}Rh_{0.5}Cu_{0.5}O_3$ ($A = Ca^{2+}$, Sr^{2+}, $Pb^{2+}$and Bi^{3+}) were synthesized by solid-state methods and their crystallographic, magnetic, and electric properties investigated. Doping by divalent cations resulted in much lower cell volumes and octahedral distortions than doping with a trivalent oxide. The Pb^{2+} and Bi^{3+} ($6s^2$) doped oxides exhibited the lowest magnetic moments and the highest activation energies. Magnetization curves are indicative of antiferromagnetic behavior. The addition of Ca^{2+}, Sr^{2+}, $Pb^{2+}$and Bi^{3+}cations to the *A*-site decreases the conductivity.

Keywords: C. Magnetic properties; D. Perovskites; *A*-site doping

1. Introduction

The magnetic properties of many double perovskite oxides remain controversial, and enormous efforts have been deployed searching for improved understanding. One extensively studied system is the alkaline earth 3*d*-4*d* mixed metal perovskites oxides Sr_2FeMoO_6. The effect of the variation of the *A* site doping on the ferromagnetism is still open to discussion, but it appears that charge delocalization between the 3*d* (Fe) and 4*d* (Mo) cations is important [1,2].

In the present work, we address the influence of the *A* site doping on the structure, electrical and magnetic properties of some related oxides, $La_{0.75}A_{0.25}Rh_{1-x}Cu_xO_3$ where $A = Ca^{2+}$, Sr^{2+}, Pb^{2+} and Bi^{3+}. The partial substitution at the *A* site is expected to influence the extent of electron delocalization between the two *B* site transition metals similar to that described in $LaRh_{0.5}Cu_{0.5}O_3$ which has $Rh^{3.5+}$ and $Cu^{+2.5}$ [3], leading to changes in the physical properties. These changes could be influenced, not only by the differences in the effective charges, but also by differences in the ionic radii and the electron configurations of both the *A* and *B*-site cations. The $Pb^{2+}$and Bi^{3+} doped oxides are found to exhibit electrical and magnetic behavior different to that of the alkaline earth doped oxides. This is believed to be a consequence of the sterochemical influence of the $6s^2$ lone pair electrons.

2. Experimental

Commercially available materials La_2O_3, CuO, Bi_2O_3, PbO, $CaCO_3$ and $SrCO_3$ (Aldrich ≥ 99.9%), Rh (Althaca 99.95%) were utilized in the synthesis. The appropriate stoichiometric amounts were mixed, using a mortar and pestle, and then heated in several steps with intermittent regrinding. Samples were initially heated for 24 h at 850 °C followed by reheating at 950 °C for 24 h, and then 1000 °C for 48 h and 1050 °C for 48 h. The samples were finally annealed at 1100 °C for 48 h, until the X-ray diffraction pattern no longer changed.

Neutron powder diffraction data were measured using the high resolution powder diffractometer, Echidna, at the OPAL facility (Australian Nuclear Science and Technology Organization) at a wavelength of 2.4395 Å. Synchrotron X-ray powder diffraction data were collected over the angular range $5 < 2\theta < 85°$, using X-rays of wavelength 0.82554 Å on the powder diffractometer at the Australian Synchrotron.

The magnetic measurements were carried out using a Quantum Design PPMS. The temperature dependence of

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http://dx.doi.org/10.1016/j.ceramint.2012.10.068

the magnetic susceptibilities was measured under both zero-field cooled (ZFC) and field cooled (FC) conditions in an applied field of 5 kOe over the temperature range 4–300 K. The temperature dependence of the resistivity was measured using a DC four probe technique with the same measurement system.

3. Result and discussion

3.1. Crystal structure

Initially, our synthetic attempts focused on $La_{0.75}A_{0.25}Rh_{0.5}Cu_{0.5}O_3$ oxides where $A=Ca^{2+}$ Sr^{2+}, $Pb^{2+}$and Bi^{3+}, however only for Pb^{2+} and Bi^{3+} were single phase samples obtained. Subsequently, the pure members of the series $La_{0.75}A_{0.25}Rh_{0.7}Cu_{0.3}O_3$ were prepared. X-ray diffraction measurements showed these are isostructural with undoped $LaRhO_3$ [4] and have an orthorhombic (*Pbnm*) crystal structure. The structural refinements, from the synchrotron diffraction data, provided precise lattice parameters, however the presence of the very heavy La, Pb and Bi cations limited the accuracy of the refined structures. Consequently, and as illustrated in Fig. 1, neutron diffraction data were also collected for a representative example, $La_{0.75}Pb_{0.25}Rh_{0.5}Cu_{0.5}O_3$. The refined structure parameters are given in Table 1. The structural refinement provides no evidence for any anion vacancies. The tilting of the corner sharing MO_6 octahedra for the pervoskite $La_{0.75}Pb_{0.25}Rh_{0.5}Cu_{0.5}O_3$ (151.3(3)°and 150.16(1)°) is similar to that reported for $LaRhO_3$ (150.5°and 149.1°).

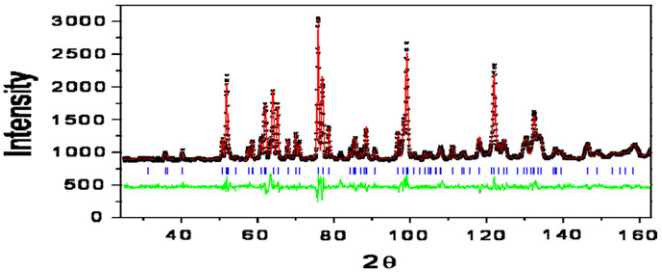

Fig. 1. Neutron diffraction profiles for the $La_{0.75}Pb_{0.25}Rh_{0.5}Cu_{0.5}O_3$. The data are represented by the crosses and the solid lines are the calculated and difference profiles. The positions of the space group allowed reflections are shown by the vertical markers immediately below the observed profile.

Table 1
Results of the structural refinements $La_{0.75}Pb_{0.25}Rh_{0.5}Cu_{0.5}O_3$ using neutron powder diffraction data. The lattice parameters $a=5.5483(4)$, $b=5.6929(3)$ and $c=7.8447(3)$ Å; The reliablity factors $R_p=7.07$, $R_{wp}=9.11$, $\chi^2=2.09$.

Atom	x	y	z	B_{iso} (Å^2)
La/Pb	0.4900 (5)	−0.0499 (4)	0.25	1.66 (10)
Cu/Rh	0	0	0	1.61 (9)
O(1)	0.5875 (6)	0.5222 (6)	0.25	0.85 (13)
O(2)	0.2992 (4)	0.2014 (4)	0.0443 (3)	1.73 (7)

3.2. Unit cell volume

The composition dependence of the unit cell volumes estimated from the synchrotron diffraction data for $La_{0.75}A_{0.25}Rh_{0.7}Cu_{0.3}O_3$ and $La_{0.75}A_{0.25}Rh_{0.5}Cu_{0.5}O_3$ is illustrated in Fig. 2. Doping with divalent metals, such as Ca and Sr, significantly reduces the cell volume. This is likely driven by the partial oxidation of the Rh^{3+} (6 coordinate ionic radius (IR), 0.67 Å) to Rh^{4+} (0.60 Å) [5] necessary to maintain charge neutrality. Despite the impact of such oxidation, the Pb doped oxide exhibits an increase in the cell volume due to the large ionic size of the Pb^{2+} cation (8 coordinate IR, 1.29 Å). Doping with trivalent metals such as Bi is expected to have little impact on the charge delocalization in the system. The similarity in formal valency of La^{3+} and Bi^{3+} results in no change in the overall charge of the perovskite system. The small increase in cell volume of $La_{0.75}Bi_{0.25}Rh_{0.7}Cu_{0.3}O_3$ is consistent with the relative ionic size of the Bi^{3+} (8 coordinate IR, 1.17 Å) and La^{3+} (1.16 Å) cations [5]. The $La_{0.75}A_{0.25}Rh_{0.5}Cu_{0.5}O_3$ oxides have lower cell volumes than the corresponding $La_{0.75}A_{0.25}Rh_{0.7}Cu_{0.3}O_3$ oxides, presumably due to charge delocalization between the Rh and Cu cations. As described above, partial change transfer involving Rh^{4+} to Rh^{3+} and Cu^{2+} (6 coordinate IR, 0.73 Å) to Cu^{3+} (0.53 Å) is possible [3]. $La_{0.75}A_{0.25}Rh_{0.5}Cu_{0.5}O_3$ has the lowest cell volume in the series, possibly as a consequence of local order effects. It is postulated that both the balance between the long range Coulomb energy and the short range ionic repulsion in the lattice, and A site cation displacements are either modified or enhanced by local ordering or covelency effects of the A site cations resulting in a decrease in the average cell volume [6]. The contraction in the cell volume was seen in the compound $La_{0.75}A_{0.25}Rh_{0.5}Cu_{0.5}O_3$ rather than in $La_{0.75}Bi_{0.25}Rh_{0.7}Cu_{0.3}O_3$, possibly reflects the solubility limit of Cu ions in the compound with $x=0.5$. It is thought that local clustering of the doped ions is more likely to occur near the solubility limit. It was not possible to prepare single phase samples with $x>0.5$.

3.3. Octahedral distortion

The diffraction studies demonstrate that both Cu and Rh cations were disordered at the octahedral sites of the perovskite structure. This distortion can be quantified by Eq. (1), where d_i is the individual bond distance between the B site cations and the oxygen anions, and d_{av} is the average of these distances. Δd was estimated to be 1.67×10^{-4} for $La_{0.75}Pb_{0.25}Rh_{0.5}Cu_{0.5}O_3$. This value is higher than found for $LaRhO_3$ ($\Delta d=0.25\times10^{-4}$) [7].

$$\Delta d=\sum_i (d_i-d_{av})^2/(d_{av})^2 \quad (1)$$

Examination of the oxides structures, refined from synchrotron X-ray diffraction data, show that increasing the Cu content from 0.3 to 0.5 significantly increases the