



Cationic ordering and role of the B-site lanthanide(III) and molybdenum(V) cations on the structure and magnetism of double perovskites $\text{Sr}_2\text{LnMoO}_6$



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ARTICLE INFO

Article history:

Received 13 June 2014

Received in revised form 12 December 2014

Accepted 17 February 2015

Available online 19 February 2015

Keywords:

- A. Inorganic compounds
- C. X-ray diffraction
- C. Neutron diffraction
- D. Crystal structure
- D. Magnetic properties

ABSTRACT

We describe the preparation, crystal structure determination and magnetic properties of a new series of ordered double perovskite oxides $\text{Sr}_2\text{LnMoO}_6$ (Ln = Eu, Gd, Dy, Ho, Er, Yb) with Mo^{5+} and Ln^{3+} electronic configurations. These compounds have been obtained by solid state reaction under reducing conditions in order to stabilize Mo^{5+} cations. Structural characterization by XRPD and NPD was performed when Ln = Ho, Er, Yb and just XRPD for absorbing Ln = Eu, Gd, Dy. At room temperature, an excellent Rietveld fit was obtained for all the samples in a monoclinic symmetry, space group $P2_1/n$, with long-range ordering of Ln and Mo atoms. Magnetic susceptibility measurements show that some of these materials present magnetic ordering below 25 K and the determined effective magnetic moments are consistent with those expected for the pair $\text{Ln}^{3+}\text{--Mo}^{5+}$. All the phases have negative values of the Weiss temperature indicating dominance of antiferromagnetic interactions.

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1. Introduction

In recent years, interesting electronic and magnetic properties have been observed in ordered double perovskites with $\text{A}_2\text{B}'\text{B}''\text{O}_6$ stoichiometry. The coexistence of electron itinerancy and ferrimagnetism in a selected number of compounds has given rise to room-temperature magnetoresistance, as described in the ordered double perovskites $\text{Sr}_2\text{FeMoO}_6$ [1] and $\text{Sr}_2\text{FeReO}_6$ [2]. The properties of $\text{Sr}_2\text{FeMoO}_6$ have been rationalized in terms of superexchange between Fe^{3+} and Mo^{5+} , leading to an antiparallel alignment of their magnetic moments with an incomplete spin cancellation and ferrimagnetic order below 420 K. The potentially useful magnetoresistive effect arises due to the fully polarized electron density contributed from Mo^{5+} occupying a delocalized band while the electrons arising from Fe^{3+} are fully localized in a $t_{2g}^3e_g^2$ configuration.

The structure of $\text{A}_2\text{B}'\text{B}''\text{O}_6$ double perovskites presents a tridimensional framework of corner-sharing octahedra $\text{B}'\text{O}_6$ and $\text{B}''\text{O}_6$ with the A cations occupying the voids between every eight octahedra, in an ideal AO_{12} coordination. Whereas the ideal perovskite is cubic, a large number of examples correspond to distorted perovskites [3]. The main cause of such distortions is the octahedral tilting, which may happen along one, two or the three crystalline axes in order to optimize the A–O bond lengths. The presence or absence of tilting can be assessed by the Goldschmidt's tolerance factor defined as follows for double perovskites:

$$t = \frac{r_A + r_O}{\sqrt{2} \times [r(\text{B}' + \text{B}''/2) + r_O]} \quad (1)$$

For an ideal cubic perovskite this factor takes the value of 1 and, when t becomes smaller than unity because A ions are too small, tilting distortions are expected.

The incorporation of lanthanide cations in double perovskites is most frequently carried out at the A site, for instance in compounds of $\text{Ln}_2\text{B}'\text{B}''\text{O}_6$ stoichiometry (e.g., $\text{La}_2\text{ZnTiO}_6$ [4], $\text{La}_2\text{NiMnO}_6$ [5], etc. However, despite the large ionic size of Ln^{3+} , it is also possible to

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incorporate them into the octahedral B sublattice. A few reports are devoted to compounds with A_2LnMoO_6 stoichiometry. A magnetic, electronic and structural study of the double perovskites Ba_2LnMoO_6 ($Ln=Sm, Eu, Gd, Dy$) was reported by McLaughlin [6]. On the other hand, a perovskite with $A=Sr$ and $Ln=Er$ was originally synthesized by Cussen [7] as the end member of a solid solution of Sr and Ba at the A sublattice of a double perovskite, although a full structural investigation of materials belonging to this family has not yet been completed.

In an attempt to learn more about the structure and magnetic properties of $Ln^{3+}-Mo^{5+}$ based oxides and the behavior of these cations when located at the octahedral sites we have synthesized the double perovskites Sr_2LnMoO_6 ($Ln=Eu, Gd, Dy, Ho, Er, Yb$). In the present report we describe the preparation and crystal structures, magnetic and electronic properties from X-ray powder diffraction (XRPD) and neutron powder diffraction (NPD) (for the non-absorbing $Ln=Ho, Er, Yb$ atoms), in complement with magnetic susceptibility measurements.

2. Experimental

Sr_2LnMoO_6 double perovskites with $Ln=Eu, Gd, Dy, Ho, Er, Yb$ were obtained as well-crystallized powders under reducing conditions by the standard ceramic method. Stoichiometric amounts of analytical grade $SrCO_3$, Ln_2O_3 and MoO_3 were mixed, ground, placed in platinum crucibles and treated at 800–1000 °C in air during 24 h. After that, the samples were reground and fired at 1200 and 1400 °C during 12 h in reducing atmosphere (1% $H_2/99\%$ N_2) in order to stabilize Mo^{5+} cations.

The identification and characterization of the final products were carried out by laboratory XRPD ($Cu K\alpha = 1.5418 \text{ \AA}$) for $Ln=Eu, Gd, Dy, Ho, Er, Yb$. The data were obtained between 10 and 120° in steps of 0.05°. For the samples with $Ln=Ho, Er$ and Yb NPD data were collected at the HRPT diffractometer of SINQ spallation source (Paul Scherrer Institute, Villigen, Switzerland) with a wavelength of 1.494 Å at 295 K. The refinements of the crystal structures were performed by the Rietveld method [8] using the Fullprof program [9]. The peak profiles were modeled by a pseudo-Voigt function. The following parameters were refined in the final run: scale factors, background coefficients, zero point error, pseudo Voigt-corrected for asymmetry parameters, positional coordinates, isotropic thermal factors and occupancy factors for oxygen atoms. For the Eu, Gd, and Dy-containing samples the structures were refined from XRPD data, collected between 10 and 120° with a step of 0.02° and a counting time of 10 s per step, in order to increase the statistics of the pattern. By this way, in the refinement, we have analyzed the same structural parameters than the samples studied by NPD excepting isotropic thermal and occupancy factors for oxygen atoms.

The magnetic measurements were performed in a commercial superconducting quantum interference device magnetometer (SQUID) from Quantum Design. The magnetic susceptibility data, ZFC and FC curves, were collected in the $4 < T < 300 \text{ K}$ range under an applied magnetic field of 0.1 T. For the samples with a irreversibility between ZFC and FC magnetization curves, additional measurements were performed at 0.01 T between 2 and 40 K. Isothermal magnetization curves were obtained with magnetic fields up to 5 T at $T=4 \text{ K}$.

3. Results and discussion

3.1. Crystal structure: X-ray and neutron powder diffraction studies

All the samples were obtained as black polycrystalline powders, with a highly insulating behavior at room temperature ($\rho > 10^6 \Omega \text{ cm}$). Fig. 1a displays the XRPD patterns obtained for all the samples

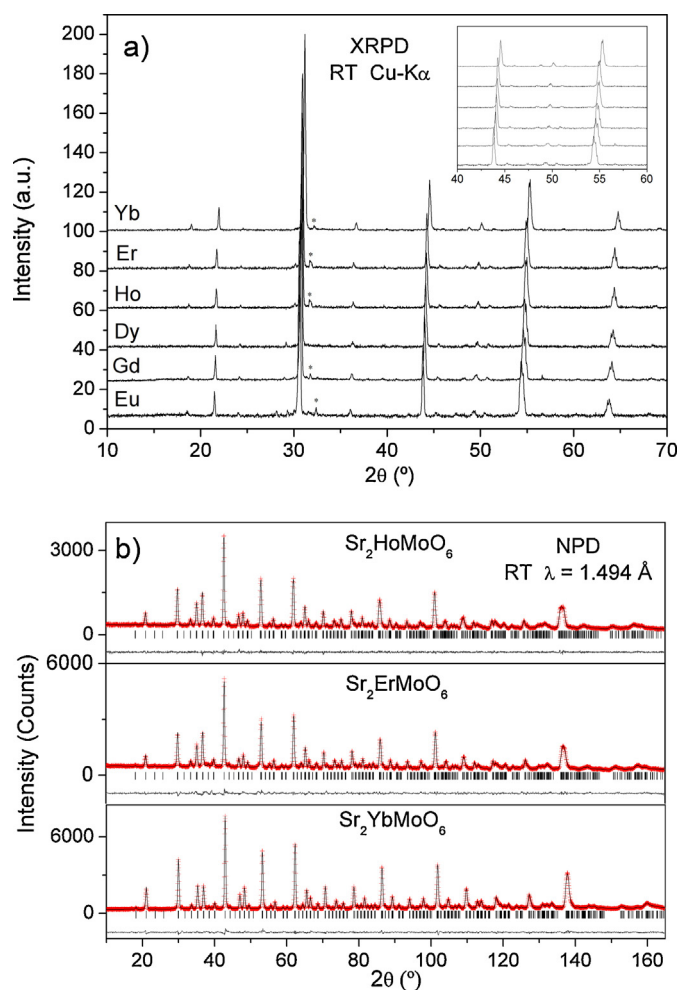


Fig. 1. a) Room temperature X-ray powder diffraction data obtained for all the studied double perovskites. The inset shows the offset of the patterns for the different lanthanide ions. The asterisks indicate the diffractions of the impurity phases. b) Observed (red circles), calculated (solid line) and difference (bottom) profiles after the Rietveld refinements of the NPD data collected in HRPT ($\lambda = 1.494 \text{ \AA}$) for the samples with $Ln=Ho, Er$ and Yb . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

studied in this work, showing minor impurities of the lanthanide oxide in each pattern. These impurities were included in the refinement and from the scale factors of the main and secondary phases less than 1% in weight were found for the different refinements. Fig. 1b shows the NPD data refinements for $Ln=Ho, Er$ and Yb collected at 295 K.

In all cases the crystal structure for Sr_2LnMoO_6 ($Ln=Eu, Gd, Dy, Ho, Er$ and Yb), was refined following the model previously described for Sr_2ErMoO_6 [7] in the monoclinic $P2_1/n$ space group $N^\circ 14, Z=4$. Sr atoms were located at the $4e (x, y, z)$ positions; Ln and Mo situated at $2b$ and $2c (1/2, 0, 0)$ and $(0, 1/2, 0)$ sites, respectively, and oxygen atoms at the $4e (x, y, z)$ positions. Ln_2O_3 were included in the refinements as secondary phases. The Rietveld plots after the refinements of the crystal structures show excellent fits between observed and calculated profiles (Fig. 1b). The unit-cell parameters, reliability factors and the most important structural parameters after the refinements are listed in Table 1. Table 2 shows some selected bond distances, angles and the bond-valence sums.

These double perovskites exhibit a long range ordering between $Ln(III)$ and $Mo(V)$ cations over the octahedral sites: trials to refine an antisite disordering converged to full $Ln-Mo$ ordering. Fig. 2a

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