



Structural, magnetic and electrical transport properties of Co doping in LaKFeMoO₆ double perovskite

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ABSTRACT

The structural, magnetic and transport properties of La_{1+x}K_{1-x}Fe_{1-y}Co_yMoO₆ (0.0 ≤ x ≤ 0.1 and 0.1 ≤ y ≤ 0.2) series are studied. At room temperature, the crystal structure is a monoclinic system with space group P2₁/n. The antisite defect lowers with Co doping in LaKFe_{1-y}Co_yMoO₆ series. However, it increases with the substitution of K by La. Magnetizations increase with the increase in Co content (x=0) and with the La substitution for K, respectively. All compounds demonstrate semiconducting behavior. Their electrical resistivities increase with Co content for LaKFe_{1-y}Co_yMoO₆ and also increase with La for La_{1+x}K_{1-x}Fe_{1-y}Co_yMoO₆. For the LaKFe_{1-y}Co_yMoO₆ the electrical transport behavior can be described by Mott variable range hopping model in the studied temperature range, whereas for the La_{1+x}K_{1-x}Fe_{1-y}Co_yMoO₆ (x ≠ 0 and y ≠ 0) the electrical transport behavior follows the Mott and ES variable range hopping model in high and low temperature ranges, respectively. Each sample exhibits a large magnetoresistance effect.

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1. Introduction

Recently, half-metallic transition metal oxides with ordered double perovskite (DP) structure A₂B'B''O₆ (A is an alkaline-earth element, B' and B'' are transition metal elements) appear to be promising candidates for magnetoresistive devices owing to their remarkable tunneling and intergrain magnetoresistance (MR) around room temperature [1–3]. Among the DP compounds synthesized so far, Sr₂FeMoO₆ is the most extensively studied compound, due to the reported substantial low-field magnetoresistance at room temperature and high Curie temperature T_C ≈ 400 K. The ideal structure of Sr₂FeMoO₆ can be viewed as a regular arrangement of corner-sharing FeO₆ and MoO₆ octahedra, alternating along the three directions of the crystal, with the voluminous Sr cations occupying the voids in between the octahedra. In a simple picture, the ferrimagnetic structure can be described as an ordered array of parallel Fe³⁺ (S=5/2) magnetic moments, antiferromagnetically coupled with Mo⁵⁺ (S=1/2) spins [4]. In this ideal model, the saturation magnetization, at low temperature, would be 4 μ_B per formula unit (fu). In the real world, such a large magnetization value has not been obtained for bulk Sr₂FeMoO₆ till date; instead smaller value below 3.7 μ_B/fu have been reported [1,5,6]. The origin of this difference with theoretical magnetization can be found in the so-called antisite B-cation disorder, implying that some Mo⁵⁺ cations occupy the positions of Fe³⁺ cations, and vice versa.

The actual degree of order depends on, on the one hand, the synthesis conditions; on the other hand, the charge and size differences between B-site cations [7].

In recent years, much effort has been devoted to the tuning and optimization of the MR properties of Sr₂FeMoO₆-related perovskites, by chemical substitution at both Sr and (Fe,Mo) sublattices. Sr atoms have been replaced completely by Ca or Ba atoms, leading to different modifications of the physical properties [8,9]. Perhaps the most significant changes have been described for the LaKFeMoO₆, in which MR increases to nearly 80% at 80 K [10]. However, unwanted antisite magnetic frustration and/or disordering effect are promoted, in such a way that the saturation magnetization dramatically decreases. In order to improve the magnetization we investigate the effect of Co substitution for Fe on the structure, magnetization and electrical behavior of LaKFeMoO₆ double perovskite by means of X-ray diffraction, magnetization and electrical resistivity.

2. Experimental

The polycrystalline La_{1+x}K_{1-x}Fe_{1-y}Co_yMoO₆ (0.0 ≤ x ≤ 0.1 and 0.1 ≤ y ≤ 0.2) series have been synthesized by standard solid state reaction technique. The raw materials, La₂O₃ (preheated at 800 °C for 8 h), K₂CO₃ (preheated at 300 °C for 3 h), Fe₂O₃, Co₃O₄ and (NH₄)₆Mo₇O₂₄·4H₂O, of high purity (more than 99.95%) were mixed by hand in an agate mortar for at least 40 min. Then it was pressed into pellets under 10 MPa pressure for 1 min, following preheating in air at 800 °C for 8 h. The calcined mixture was

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pulverized and pressed into pellets. The pellets were sintered at 850 °C for 8 h in a steam of 6% H₂/Ar. Following this, sintered samples were ground and pressed into pellets, which were heated at 1000 °C for 10 h in a steam of 5% H₂/Ar. Samples annealing at 1000 °C were cooled down to 500 °C at 5 °C/min, then naturally cooled to room temperature in a furnace. Phase analysis and characterization were carried out by X-ray diffraction (XRD) using CuK α radiation in a X'TRA model X-ray diffractometer. The estimation of cations in the sample was determined by atomic adsorption spectroscopic analysis. The oxygen content was determined by redox titration method. Cobalt oxidation state was characterized by X-ray photoelectron spectroscopy (XPS).

Temperature dependence of magnetization curves was measured by a vibrating-sample magnetometer in the field of 0.5 T over the temperature range of 80–300 K. Transport properties were determined by a standard four-probe DC method in the temperature range of 80–300 K.

3. Results and discussion

XRD was performed on powdered samples, i.e. La_{1+x}K_{1-x}Fe_{1-y}Co_yMoO₆ (0.0 ≤ x ≤ 0.1 and 0.1 ≤ y ≤ 0.2), over the 2 θ range from 18° to 80° at room temperature. All samples were identified to be single phase based on XRD. The superstructure peaks present around 2 θ ~ 19.5° and ~ 37.5° arise from alternate ordering of Fe (Co) and Mo atoms in the B-sublattice. These are clearly visible in Fig. 1 and no impurities were detected based on XRD patterns. The diffraction peaks of all samples could be indexed in a monoclinic system with space group P2₁/n. However, the tolerance factors are 1.0135, 1.0123, 1.0156, 1.0131, 1.0065 and 1.0016 for LaKFe_{0.9}Co_{0.1}MoO₆ (Co³⁺ intermediate spin state), LaKFe_{0.9}Co_{0.1}MoO₆ (Co³⁺ high spin state), LaKFe_{0.8}Co_{0.2}MoO₆ (Co³⁺ intermediate spin state), LaKFe_{0.8}Co_{0.2}MoO₆ (Co³⁺ high spin state), La_{1.05}K_{0.95}Fe_{0.9}Co_{0.1}MoO₆ and La_{1.1}K_{0.9}Fe_{0.8}Co_{0.2}MoO₆, respectively ($r_{\text{La}^{3+}} = 0.136$ nm for CN=12, $r_{\text{K}^+} = 0.164$ nm for CN=12, $r_{\text{Fe}^{3+}} = 0.0645$ nm for CN=6, $r_{\text{Co}^{2+}} = 0.0745$ nm for CN=6, $r_{\text{Co}^{3+}} = 0.056$ nm (intermediate spin state) for CN=6, $r_{\text{Co}^{3+}} = 0.061$ nm for CN=6, $r_{\text{Mo}^{5+}} = 0.061$ nm for CN=6 and $r_{\text{O}^{2-}} = 0.140$ nm for CN=6), indicating that the average ionic radii of La³⁺ and K⁺ ions are slightly large to fit in the cavity formed by the Fe(Co)O₆ and MoO₆ octahedra. The structure should be a cubic system based on the tolerance factors. The tolerance factor of Ba₂FeMoO₆ double perovskite is 1.050 and its crystal structure belongs to a cubic system [11]. In order to illustrate the correction of the structure the Rietveld refinement was carried out in several space groups P4/mmm, P4/m, P4₂/n, Pn $\bar{3}$ and P2₁/n and the space group P2₁/n is the most reasonable in these space groups. Fig. 1 shows the result of Fullpro suite refinement with space group P2₁/n. The lattice parameters and the final atomic coordinates of the different compounds are reported in Table 1. The interatomic distances and some selected bond angles are also listed in Table 2. It can be seen from Tables 1 and 2 that the lattice parameters of LaKFe_{1-y}Co_yMoO₆ series decrease with Co doping, while the angle β slightly increases and that the interatomic distances and the bond angles also reduce with Co substitution for Fe. As the radius of Co²⁺ ($r_{\text{Co}^{2+}} = 0.0745$ nm) is larger than that of Fe³⁺ ($r_{\text{Fe}^{3+}} = 0.0645$ nm), the lattice parameters should increase with Co doping if the Co ion takes a +2 valence state (3d⁷ configuration). However, the experimental results are contrary to that assumption. Therefore, we conjecture that the Co-ion oxidation state is +3 in the LaKFe_{1-y}Co_yMoO₆ series agreed with literature [12]. The decrease in the bond angles of Fe(Co)–O–Mo for LaKFe_{1-y}Co_yMoO₆ (y = 0.1 and 0.2) with Co substitution for Fe is due to the increasing mismatch between A- and B-sites. One can see from Tables 1 and 2 that the lattice parameters, a and V, of the other samples decrease with La substitution for K from 0.05 to 0.10; however, the parameters, c and β , slightly increase and the interatomic distances decrease with the replacement of K by La, while the bond angles increase and the lattice

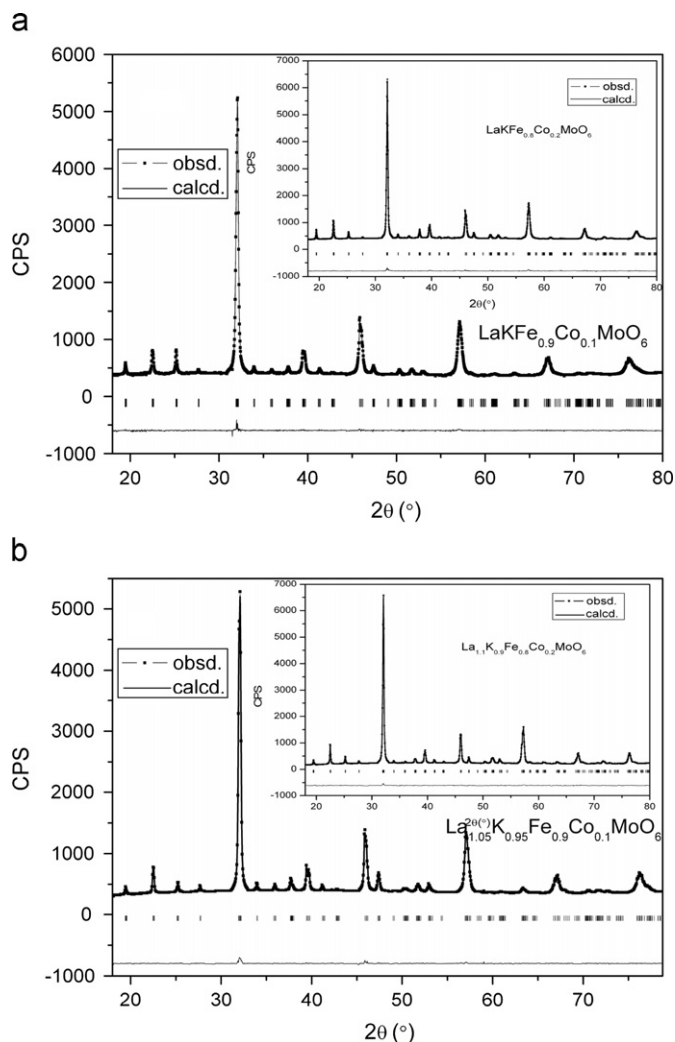


Fig. 1. (a and b) XRD patterns of La_{1+x}K_{1-x}Fe_{1-y}Co_yMoO₆ compounds.

parameter, b, is nearly unchanged. Based on the change in these parameters and ionic sizes of La³⁺, K⁺, Co²⁺ and Co³⁺ we expect that Co ions take +2 oxidation states. The elongation along the c-axis has a large influence on the electronic structure since it lifts the three-fold degeneracy of Co t_{2g} levels and splits them into a lower-energy doublet (xz/yz) and a higher-energy singlet (xy) [13]. One can see from Fig. 1 that the intensities of superstructure peaks slightly increase with y, whereas, slightly decrease with x. These changes indicate that the degree of alternating order of Fe(Co) and Mo ions in the B-sublattice increases with the substitution of Fe by Co and decreases with the replacement of K⁺ by La³⁺. These results agree with the refinement results, the antisite percentages are 0.30, 0.22, 0.36 and 39 for y=0.1, 0.2, x=0.05 and y=0.1, x=0.1 and y=0.2, respectively.

The cation content in the specimens and oxygen were determined by atomic adsorption spectroscopic analysis and redox titration, respectively. The constitution of these compounds is consistent with normal composition.

The oxidation state of cobalt in selected samples, LaKFe_{0.8}Co_{0.2}MoO₆ and La_{1.1}K_{0.9}Fe_{0.8}Co_{0.2}MoO₆, was determined by XPS. Fig. 2 shows spectra of the selected samples. It can be seen from Fig. 2 that the oxidation states of cobalt take +3 and +2 in these selected samples, LaKFe_{0.8}Co_{0.2}MoO₆ and La_{1.1}K_{0.9}Fe_{0.8}Co_{0.2}MoO₆, respectively. This supports our conjecture mentioned above.

The temperature dependence of the magnetization was measured in the warming run under the magnetic field of 0.5 T in the temperature range of 80–300 K. Fig. 3 shows the thermal magnetic

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