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Crystal structural, magnetic and electrical transport properties of $CeKFeMoO_6$ double perovskite

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ABSTRACT

The crystal structural, magnetic and electrical transport properties of double perovskite $CeKFeMoO_6$ have been investigated. The crystal structure of the compound is assigned to the monoclinic system with space group $P2_1/n$ and its lattice parameters are a=0.55345(3) nm, b=0.56068(2) nm, c=0.78390(1) nm, β=89.874(2). The divergence between zero-field-cooling and field-cooling M–T curves demonstrates the anisotropic behavior. The Curie temperature measured from C_p–T curve is about 340 K. Isothermal magnetization curve shows that the saturation and spontaneous magnetization are 1.90 and 1.43 μ_B/f.u. at 300 K, respectively. The electrical behavior of the sample shows a semiconductor. The electrical transport behavior can be described by variable range hopping model. Large magnetoresistance, -0.88 and -0.18, can be observed under low magnetic field, 0.5 T, at low and room temperature, respectively.

1. Introduction

The recent discovery of large low-field magnetoresistance effect at room temperature (RT) in polycrystalline sample Sr_2FeMoO_6 by Kobayashi et al. [1] has stimulated research on the properties of double perovskite (DP) oxides. The magnetic structure of Sr_2FeMoO_6 is attributed to an ordered arrangement of parallel Fe^{3+} ($3d^5$, $S=\frac{5}{2}$) magnetic moments, antiferromagnetically coupled with Mo^{5+} ($4d^1$, $S=\frac{1}{2}$) spins. A large number of compounds with DP structure $A_2B'B''O_6$ have been synthesized [2]. Among them A_2FeMoO_6 (where A=Ca, Sr and Ba) are known to be ferrimagnetic with critical temperatures T_C in the range 330–420 K [3], which are higher than those of doped manganites. Many researchers [4–7] have reported structural, magnetic and electrical transport properties of the DP transition-metal oxides, especially for the Fe-based compounds. The Fermi level exists within the down-spin band, which is composed of Fe t_{2g} and Mo t_{2g} electrons. As an intuitive picture for the electronic state, the electrons of Fe and Mo cations may be considered as localized and itinerant, respectively. Taking the magnetic interaction (interatomic antiferromagnetic exchange) between Fe and Mo into account, a ferrimagnetic half-metallic state [8] is expected for this ordered DP with localized up-spins of Fe^{3+} and itinerant down-spin electron of Mo^{5+}. $CeKFeMoO_6$ also assigns to the class of DP compounds with general formula $A'A''B'B''O_6$ where A′ and A″ are alkaline or alkaline-earth and rare-earth elements, respectively and B′ and B″ are two different transition metal elements. Recently, it has been reported that substitution of La^{3+} for Sr^{2+} in Sr_2FeMoO_6 promotes an increase in T_C and a decrease in M_s as doping level increases [9]. Kim et al. [10] reported that replacement of Ba^{2+} by K^+ in Ba_2FeMoO_6 reduces T_C as K^+ content increases. With La^{3+} or K^+ doping in DP A_2FeMoO_6 compounds (where A is the alkaline-earth metal) carrier doping is inevitable in these materials. In order to figure out some effects without changing ionic valence states of B′ and B″ sites by A-site doping, we have studied the structural, magnetic and electrical transport properties and magnetoresistance of $LaKFeMoO_6$ compound and it shows low magnetic moment, large resistivity and magnetoresistance [11]. In order to improve the magnetic moment of $LaKFeMoO_6$, the La^{3+} is replaced by magnetic Ce^{3+} ion in compound $LaKFeMoO_6$. In this paper, we investigate the crystal structure, magnetic and transport of DP $CeKFeMoO_6$ polycrystalline sample.

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2. Experimental

The polycrystalline sample of $CeKFeMoO_6$ has been synthesized by standard solid-state reaction technique. The raw materials, CeO_2, K_2CO_3, Fe_2O_3 and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, of high purity (more than 99.99%) were mixed and ground in an agate mortar for at least 45 min. Then it was pressed into pellets under 10 MPa pressure for 1 min following preheating in air at 800 °C for 10 h. The calcined mixture was pulverized and pressed into pellets. The pellets were sintered at 900 °C for 21 h in a stream of 6% H_2/Ar with intermediate grindings. Phase analysis and characterization were carried out by X-ray diffraction (XRD) using CuKα radiation on an X'TRA model X-ray diffractometer. Temperature dependence of magnetization was measured by a vibrating-sample magnetometer (VSM) in a field of 0.5 T over the temperature range 80–300 K. Transport properties were measured by standard four-probe DC method in the temperature range 80–300 K. Temperature dependence of heat capacity curve was carried out by differential scanning calorimetry (DSC) in the temperature range 220–400 K. The estimation of cations in the sample was measured by atomic adsorption spectroscopic analysis. The oxygen content was determined by redox titration method in an argon atmosphere.

3. Results and discussion

The XRD data of powdered sample were collected at RT and the XRD pattern is displayed in Fig. 1, which shows that the sample is single phase. No impurities were detected based on XRD pattern. The diffraction peaks could be indexed in monoclinic system with space group $P2_1/n$. However, the tolerance factor is 1.008 ($r_{Ce^{3+}}=134$ Å for CN=12, $r_{K^+}=1.64$ Å for CN=12, $r_{Fe^{3+}}=0.645$ Å for CN=6, $r_{Mo^{5+}}=0.61$ Å for CN=6 and $r_{O^{2-}}=1.40$ Å for CN=6), indicating that the average ionic radii of Ce^{3+} and K^+ ions are slightly large to fit in the cavity formed by the FeO_6 and MoO_6 octahedra. The structure should be a cubic system based on the tolerance factor. Therefore, we carefully examined the diffraction lines and found some of them splitting, indicating that the symmetry of structure is less than that of the cubic system. For example, at 76.8° the line (6 2 0) in cubic system is asymmetrically split in intensity (inset of Fig. 1). In order to illustrate the correction of the structure the Rietveld refinement was carried out in several space groups $I4/m$, $P4_2/n$, $Pn\bar{3}$ and $P2_1/n$ and the space group $P2_1/n$ is the most reasonable in these space groups. Fig. 1 shows the result of Fullpro_suite refinement with space group $P2_1/n$. The lattice parameters were obtained from the refinement and are: $a=0.55345(3)$ nm, $b=0.56068(2)$ nm, $c=0.78390(1)$ nm, $\beta=89.874(2)$. The refinement results are detailed in Table 1. The monoclinic distortion [12] can be described by the space group $P2_1/n$ (Glazer tilt system $a^+b^-b^-$), corresponding to a "classic" *Pnma* structure of simple perovskites without cationic ordering. However, the presence of the cationic ordering in $CeKFeMoO_6$ can clearly be seen from substantial intensity of the supperlattice diffraction at about 37.7° in Fig. 1. According to report [13], this supperlattice diffraction peak could be explained as due to the anti-phase tilting of the octahedral around the two-fold $[1\,1\,0]_P$-axis.

The infrared spectrum was measured in the range 1000–300 cm^{-1} at RT and its pattern is shown in inset of Fig. 2. Three absorption bands were observed (inset of Fig. 1). The strong band 560 cm^{-1} is involving the asymmetric stretching mode of the BO_6 octahedra, whilst shoulder observed at 470 cm^{-1} can be assigned

Table 1
Refined atomic positions, temperature factors, bond distances and angle of Fe–O–Mo at room temperature.

	x	*y*	*z*	*B* (nm^2)
Ce (K)	0.994	0.0377	0.255	–
Fe	0.5	0	0	–
Mo	0.5	0	0.5	–
O1	0.738	0.349	0.464	–
O2	0.796	0.288	0.007	–
O3	0.304	0.394	0.035	–

$d_{\text{Mo-O}\langle\text{average}\rangle}$ 0.196(nm); $d_{\text{Fe-O}\langle\text{average}\rangle}$ 0.201(nm); average angle$_{\text{(Fe-O-Mo)}}$ 156.86(°).

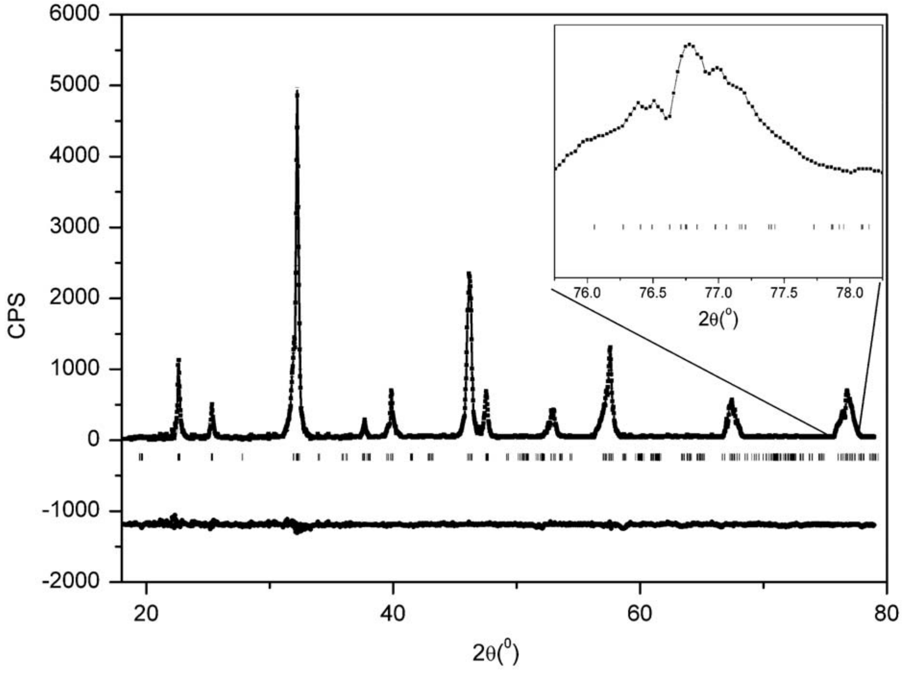

Fig. 1. X-ray diffraction pattern of $CeKFeMoO_6$ sample; inset: the expanded view of reflections in the range 76–78°.