Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

$La_{1-x}Sr_xFeO_3$ solid solutions in magnetic field

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ARTICLE INFO

Keywords:
Charge disproportionation
Lattice distortion
Dopant
Magnetic transition

ABSTRACT

Magnetic properties of $La_{1-x}Sr_xFeO_3$ (x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5) have been investigated in a wide magnetic field range from 0 to 35 T using pulsed high magnetic field magnetization and electron spin resonance measurements. Experimental results show that both the non-magnetic Sr^{2+} dopant and high magnetic fields affect the stability of the robust antiferromagnetic coupling between Fe ions and induce new phase transitions. Especially the phase transition temperatures and hysteresis behavior show a high sensitivity on the Sr dopant and its doping level. On the other hand, a nonlinear Sr doping level dependence of the transition temperatures and hysteresis behavior were observed, indicating that the charge disproportionation is not the sole influence. Thus, in the series Sr doping $La_{1-x}Sr_xFeO_3$ samples, the dopant induced FeO_6 octahedron distortion and charge disproportionation are coexistence and competition, which leads to a complicated and Sr doping level nonlinearly dependent magnetization behavior.

1. Introduction

The perovskite structure having general formula ABO_3 (A = La + 3 and B = Fe, Mn, Cr), have been shown remarkable attention due to their interesting electrical, magnetic, and catalytic properties [1]. In which the perovskite materials, $LaFeO_3$ is one of most common orthorhombic perovskite materials which is potential candidates for multiferroic materials with large magnetoelectric (ME) coupling [1,2] and ultrafast optical control of spins [3,4]. The correlation between physical properties, especially magnetic properties and their electronic structures was one of the historically interesting topics in solid state physics, in which the crystal structure of the $La_{1-x}A_xFeO_3$ (A = Sr and Ca) has been investigated in the past [5–8]. For the Sr dopant induced mixed-valence system $La_{1-x}Sr_xFeO_3$, the most interesting phenomena are the charge disproportionation, charge ordering (CO) and the interplay between the CO and the magnetism [9]. The presence of complex CO phenomena in $La_{1-x}Sr_xFeO_3$ has been revealed by transmission electron microscopy at low temperatures [10], in which the distortion of structural and valence states of Fe ion depend on the Sr doping level. Mössbauer spectroscopy investigation shows, in a lower Sr-doping level $x < 0.4$, the valence states of Fe ions are +3 or +4, and Gallagher et al. stated to have observed the resolution into the distinct valence states of Fe^{3+} and Fe^{4+} at ~ 4 K [11]. In order to interpret the existence of CO states, in which there are almost as many Fe^{4+} ions as Fe^{3+} ones in the charge rich areas (or streaks) was suggested, and in the other Fe^{4+} poor areas, the Fe ions are almost Fe^{3+} states, the average ratio of Fe^{3+} and Fe^{4+} maintains 2:1. According to the high resolution electron micrographs obtained at low temperatures, a novel charge segregation phenomenon was observed in $La_{0.7}Sr_{0.3}FeO_3$, in which the presence of structural modulation related to CO in the sequence of . . . $Fe^{3+}Fe^{3+}Fe^{5+}Fe^{3+}Fe^{3+}Fe^{5+}$ . . . along the [111] axis [2,12–14].

In the magnetism investigation of the $La_{1-x}Sr_xFeO_3$, the superexchange interaction is expected to be stronger due to the nearly 180° Fe–O–Fe bond angle and the intersite Coulomb interaction is better screened due to the longer metal-metal distance than in the spinel-type structure [15]. Both Fe^{3+} and Fe^{5+} have no orbital degrees of freedom, and according to the investigation, in $La_{1-x}Sr_xFeO_3$, there is no detectable lattice distortion in the CO state [1,2,16], it indicates that the superexchange coupling is much more important than the electron-lattice coupling. On the other hand, due to the mixed valence of Fe ions, the systems can possess Fe^{4+}-O-Fe^{4+} and Fe^{3+}-O-Fe^{3+} superexchange interactions with an antiferromagnetic and the Fe^{3+}-O-Fe^{4+} coupling giving rise to ferromagnetic interactions, thus, the different magnetic couplings lead to the competing interactions. This is manifested in a number of the kinds of system as unidirectional anisotropy leading the phenomenon of exchange bias, which is also the origin of polarization [17].

The substitution of a Sr^{2+} ion for La^{3+} provides hole doping, and it yields the formation of ferromagnetic clusters that show superparamagnetic and spin glass properties in the lower doping range

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http://dx.doi.org/10.1016/j.ceramint.2017.09.150
Received 6 July 2017; Received in revised form 12 September 2017; Accepted 19 September 2017
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$0.05 < x < 0.2$ [18]. Surprisingly Yamaguchi et al. [19] have found that very small doping levels ($x = 0.002$) give rise to an unexpectedly large magnetic susceptibility at low temperatures that cannot be explained by the occurrence of a small amount of individual magnetic Fe^{4+} ions due to charge compensation. Experimental results show that a doped hole forms a magnetic polaron with a huge local magnetic moment, though its nature has remained unclear. In addition to charge compensation mechanisms, structural distortions can also affect the Neel temperature and magnetic hysteresis. In this present paper, the magnetization behavior of a series Sr doped $La_{1-x}Sr_xFeO_3$ compounds have been investigated, and the Sr doping level dependence of antiferromagnetic (AFM) ordering temperatures, the Fe–O–Fe bond length and angle have been investigated. The cooperation and competition between charge disproportionation and lattice (octahedron) distortion were assumed, it hope to give a reasonable interprets on the nonlinear Sr doping level dependent on the observed complicated magnetization behavior.

2. Experimental

The polycrystalline samples of $La_{1-x}Sr_xFeO_3$ ($x = 0$, 0.1, 0.2, 0.3, 0.4 and 0.5) were prepared by a conventional solid-state reaction. The starting materials La_2O_3 (99.99%), $SrCO_3$ (99.95%) and Fe_2O_3 (99.9%) powders were taken in stoichiometric proportion and sintered at 1100 °C for 24 h in air. The resulting powders were reground, and then pelletized at a pressure of 10 MPa and sintered at 1350 °C for 24 h. The *X*-ray Diffraction (XRD) pattern indicate that the synthesized samples are of single phase and no obvious impurities. The magnetization (*M*) was measured with Superconducting Quantum Interference Device (SQUID-VSM, Quantum Design), the electron spin resonance (ESR) and pulse high magnetic field magnetization measurements were performed in Wuhan National High Magnetic Field Center. For each measurement, the samples were warmed above to room temperature (~ 380 K) to remove any magnetic history as possible.

3. Results and discussion

Taking into account the possible change of the crystalline structures due to Sr dopant, the XRD patterns were measured in room temperature with crushed samples, and Rietveld refinements were performed to test these possibilities with the orthorhombic *Pnma* structure. The XRD patterns and Rietveld refinements of $La_{1-x}Sr_xFeO_3$ are shown in Fig. 1. All the XRD curves indicate that the synthesized samples are a single phase without detectable impurity phases. Using the Rietveld powder diffraction profile fitting technique, the fitted structural parameters, show the crystallizing in orthorhombic symmetry with *Pnma* space group, and the detail fitting parameters and fit reliability factors are given in Table 1. In order to compared with data given by other authors, some of neutron data were added in the table. As shown in Fig. 1(a), all the doped samples show a similar XRD patterns, indicating the widen Sr doping levels have not distorted the perovskite structure obviously, the structure schematic of the FeO_6 octahedron is shown in Fig. 2(a), in which the La^{3+} ions are removed for clarity. Due to the Sr dopant, the net of the FeO_6 octahedrons shows some of distortion both along c-axis and in ab-plane. For a FeO_6 octahedron, a doping level dependent distortion was also observed from the fitting lattice parameters as given in Table 1. In Fig. 1(a), two different O^{2-} sites are labeled with O1 and O2 in a FeO_6 octahedron. Analyzing the crystal lattices (a, b, and c) and cell volume, all the lattice parameters decrease due to the Sr dopant, but shows a nonlinearly dependent on the Sr doping levels. Especially, as shown in Fig. 1(a), the main peaks shift to higher angle, showing the lattice decrease, the slight decrease of lattice parameters cannot simply be explained due to the different ionic size between the Sr^{2+} and La^{3+} ions. In fact, the ionic size of the doped Sr^{2+} ion (1.12 Å) larger than that of La^{3+} ion (1.06 Å), usually, the larger ionic radii of Sr^{2+} would be expected to result in an increase in

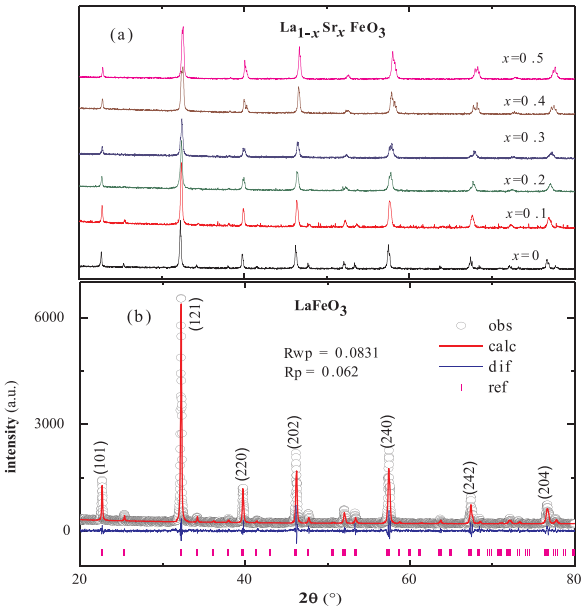

Fig. 1. (a) The XRD patterns of $La_{1-x}Sr_xFeO_3$ with $x = 0$, 0.1, 0.2, 0.3, 0.4 and 0.5 measured at room temperature, and (b) the experimental observed (obs) and calculated (calc) XRD profile from the Rietveld refinements of $LaFeO_3$. The Rietveld refinements of other samples did not shown for clarity.

lattice parameters. However, the introduction of divalent Sr cations caused a decrease in the lattice parameters of $La_{1-x}Sr_xFeO_3$ as given in Table 1. Thus, the decreasing in lattice constants suggests that other influence from the Sr dopant should be considered. This results can be partially explained if charge compensation is dominated by the conversion of Fe^{3+} into Fe^{4+}; The formation of Fe^{4+} would cause a reduction in lattice parameters due to the smaller ionic radius of Fe^{4+} (0.585 Å) as compared to Fe^{3+} (0.645 Å). Accompany with the charge disproportionation, the distortion of the net of FeO_6 octahedron may be exist in the Sr doped samples. In order to confirm the distortion related charge disproportionation of Fe ions, we fitted the distances and angles of Fe–O bonds from XRD patterns, and the possible schematics with bond shrink and expansion of both Fe1-O1 and Fe1-O2 are shown in Fig. 2(b)–(d). According to the fitted lattice parameters of bond angles of $< \theta_{Fe1\text{-}O1\text{-}Fe1} >$ and $< \theta_{Fe1\text{-}O2\text{-}Fe1} >$, a zigzag nets of FeO_6 octahedron is assumed as shown in Fig. 2(a), in which both the angles of the Fe1-O1-Fe1 along *c*-axis and Fe1-O2-Fe1 in ab-plane deviates a 180°. The fitting parameters show that the magnitude of the angles are related to the Sr doping levels, the different bond angles may result in different magnetic coupling strength and different magnetic behavior.

The temperature dependence of magnetization (*M-T*) of $La_{1-x}Sr_xFeO_3$ with $x = 0$, 0.1, 0.2, 0.3, 0.4 and 0.5 measured in various magnetic fields are shown in Fig. 3(a)–(f) respectively. For the end member $LaFeO_3$ ($x = 0$), which has a high AFM ordering temperature $T_N \sim 740$ K, [20] with decreasing temperature, the magnetization increases slowly as shown in Fig. 3(a), indicating a weak ferromagnetic (FM) behavior due to canted AFM. At $T_1 \sim 50$ K it undergoes a CO-AFM transition, below T_1, magnetization drops slowly resulting from the formation of $Fe^{3+} - Fe^{3+}$ CO phase (AFM). With increasing of the applied magnetic field, the magnetic moment increases due to the increase of the weak FM (canted AFM) phases, however, the temperature dependence of the magnetization has no obvious change, which indicates that the AFM CO phase of $LaFeO_3$ is robust in the lower magnetic field regime.

For the Sr doped samples, it seems that substitution strongly affects the magnetization behavior, especially the magnetic hysteresis loop in low temperature regions and phase transitions in higher temperature ones. For the samples with the lower Sr doping levels of $x = 0.1$ and 0.2, obviously magnetic hysteresis behaviors were observed below $T_2 \sim$

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