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Synthesis and Magnetic Properties of Double B Mixed Perovskite Series $La_{0.75}K_{0.25}Mn_{1-x}Fe_xO_3$

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A series of double B mixed perovskite oxides $La_{0.75}K_{0.25}Mn_{1-x}Fe_xO_3$ ($x = 0.2$–0.5) were synthesized under mild hydrothermal conditions and characterized by powder X-ray diffraction, SEM, ICP, XPS, iodometric titration, and SQUID. All the compounds corresponded to orthorhombic structure of space group *Pnma* and presented a cuboid morphology. The oxidation state of Fe is +3 whereas Mn is a mixed valence of Mn^{3+}/Mn^{4+}. The curves *M* vs. *T* for all the compositions indicated the coexistence of ferro- and antiferromagnetic contribution.

The mixed-valent manganites $La_{1-x}A_xMnO_3$ ($A^{2+} = Ca^{2+}$, Sr^{2+}, Ba^{2+}, and Pb^{2+}) have attracted worldwide attention due to their unique electrical and magnetic properties.[1] The conventional routes to modify the physical properties of such oxides are partial substitutions of A-site and B-site cations by other metal cations.[2] Among the double B mixed perovskites, the case of Fe is particularly interesting because it does not cause considerable lattice distortion[3] due to the close ionic radii of Fe^{3+} and Mn^{3+},[4] which is a special model to study the particular properties of manganites. Up to now, most attention has been concentrated on Fe-doped manganites with divalent alkaline earth in A sites. However, reports on Fe-doped manganites with monovalent alkaline metal in A site are very scarce. Only one example of such compounds, as far as we know, is $La_{5/6}Na_{1/6}Mn_{1-y}Fe_yO_3$ reported by Liu and co-workers.[5] Actually, alkali-metal-doped manganites have attracted much interest lately because of important modifications in the physical properties.[6] On the other hand, $LaMn_{1-x}Fe_xO_3$ has revealed many interesting phenomena.[7] The different features of glassy states in $LaMn_{1-x}Fe_xO_3$ depend on the degrees of Fe substitution.[7a] The unusual glassy states with two different kinds of dynamic freezing processes were observed in $LaMn_{0.5}Fe_{0.5}O_3$.[7b] Therefore, it is worthwhile to study the effects of doping an alkaline cation in A sites of $LaMn_{1-x}Fe_xO_3$. Herein, we explored the feasibility of the synthesis of a K-doped $LaMn_{1-x}Fe_xO_3$ system via appropriate methods. As a facile, mild, and easily controlled method, hydrothermal synthesis has been adopted to prepare numerous perovskite oxides.[8] In fact, we have successfully synthesized Fe-doped manganites by a hydrothermal method.[9] Thus, it is also applicable to synthesis of such K-doped double B mixed perovskites. In the present work, a series of the perovskite oxides of the formula $La_{0.75}K_{0.25}Mn_{1-x}Fe_xO_3$ ($x = 0.2$–0.5) were synthesized under mild hydrothermal conditions. We also investigated their primarily magnetic properties.

Experimental details are given in Supporting Information. In the hydrothermal process, it has been found that the appropriate ratio of initial reagents, alkalinity, and the reaction temperature and time are critical influencing factors for the crystal growth of our samples (Figure S1).[12] The doping level (x) in $La_{0.75}K_{0.25}Mn_{1-x}Fe_xO_3$ can be adjusted by changing the appropriate ratio of Mn/Fe. However, the K content is not adjustable no matter the ratio of La/K. This can be associated with the matching of ionic radii and the synthesis conditions. In addition to the ratio of initial reagents, it has been found that the compounds cannot be obtained when the reaction temperature is lower than 240 °C, as well as when the reaction time is less than 12 h, due to the formation of $La(OH)_3$ and $Fe(OH)_3$. Moreover, the high alkalinity of the reaction system is required, because it considerably influences the crystallization of the compounds. KOH not only maintains the alkalinity but also acts as mineralizing agent. If the alkalinity is less than 8 M, we cannot obtain the samples but a powder mixture of $La(OH)_3$, $K_xMnO_2 \cdot 0.5$–$0.7H_2O$, and $Fe(OH)_3$. With increasing the alkalinity, the crystallization degree is better. The content of La, K, Mn, and Fe was confirmed by ICP analysis. The oxygen contents in our samples obtained from iodometric titration approached 3.

The room-temperature powder X-ray diffraction patterns for $La_{0.75}K_{0.25}Mn_{1-x}Fe_xO_3$ are shown in Figure 1 and refined by the Pawley method (Figure S2).[12] It is found that all the powders are perovskite phases with orthorhombic structure (space group *Pnma*) and show a high degree of crystallization. The lattice parameters for $La_{0.75}K_{0.25}Mn_{1-x}Fe_xO_3$ are listed in Table 1. There are slight increases in the unit cell volumes with increasing Fe content. According to the rule given in the alkaline-metal-doped manganites,[6] the formula of our compounds can be written as $La_{0.75}K_{0.25}Mn^{4+}{}_{0.5}Mn^{3+}{}_{0.5-x}Fe^{3+}{}_xO_3$. Hence, the substitution of Fe^{3+} should not introduce noticeable lattice distortion due to the close ionic radii of Fe^{3+} and Mn^{3+} (0.645 Å for Fe^{3+} and 0.64 Å for Mn^{3+}), which is consistent with the results reported in the La–A–Mn–Fe–O systems (A for alkaline-earth ions).[10] Considering Mn and Fe can hardly form an ordered structure due to the similar ionic radii, the large lattice parameters can be properly explained by the ordered arrangement of K and La along *c* axis. With increasing the Fe content, the ordered arrangement was weakened gradually because the disordered Fe and Mn induced the randomness of the structure. This can be confirmed by the disappearance of some Bragg peaks with specific Miller indices, such as (002), (011), etc., as shown in Figure 1B. The good crystallization of the products obtained by hydrothermal synthesis was observed by SEM image shown in Figure S3.[12] SEM photographs of the samples show clearly the materials to be made up from cuboid small crystallites, around 10 µm in a narrow particle-size distribution. EDX results showed the presence of all four metals in area analyzed with a constant ratio (Figure S4).[12]

In order to detect the valence states of manganese and iron, we first measured their average valences by iodometry. The average valence state of B site obtained from iodometry is close to the theoretical value of 3.5 calculated from the neutrality for

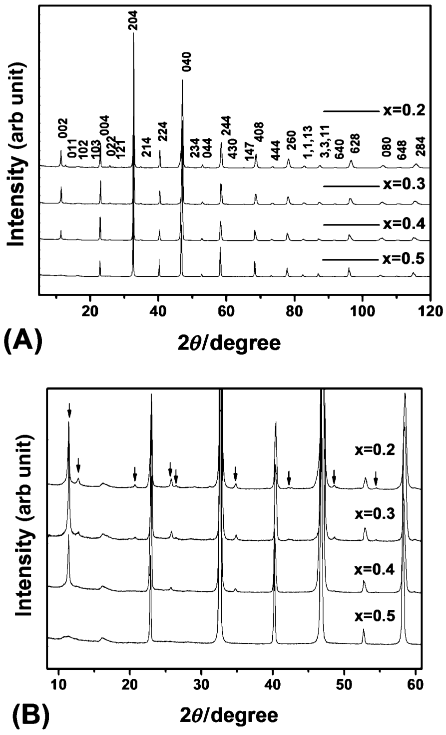

Figure 1. (A) Powder XRD pattern of $La_{0.75}K_{0.25}Mn_{1-x}Fe_xO_3$. (B) Changes of some Bragg peaks marked by arrows.

Table 1. Lattice parameters of $La_{0.75}K_{0.25}Mn_{1-x}Fe_xO_3$ powders

Composition	a/Å	b/Å	c/Å	V/Å^3
$x = 0.2$	7.7046(5)	7.7185(5)	15.4857(7)	920.9(2)
$x = 0.3$	7.7557(3)	7.7139(1)	15.4816(1)	926.2(2)
$x = 0.4$	7.7528(8)	7.7647(3)	15.4564(4)	930.4(6)
$x = 0.5$	7.7491(7)	7.7567(9)	15.5180(2)	932.7(7)

the title compounds. X-ray photoelectron spectroscopy (XPS) was applied to determine oxidation state of solid-state materials too (Figure S5).[12] In all our cases, the binding energy of Fe (711.0 eV) is characteristic of Fe^{3+}, and the binding energy of Mn ranged from 641.9 to 642.5 eV which indicated that the Mn^{3+} content decreased gradually. Therefore, the oxidation state of Fe in our samples is +3 whereas Mn is a mixed valence of Mn^{3+}/Mn^{4+}.

The magnetic measurements were performed using both field cooled (FC) and zero-field cooled (ZFC) at 100 Oe applied field procedures as shown in Figure 2. Observed from the ZFC curves ($x = 0.2$, 0.3, 0.4, and 0.5), the M value initially increases gradually with the decrease of temperature and then remarkably drops at $T_f \approx 170$, 160, 150, and 160 K, respectively (T_f is defined as spin frozen temperature). All the ZFC curves do not coincide with FC curves just below T_f indicating a large inhomogeneity of the magnetic distribution for all the compounds. From the derivative of the curves M vs. T for the compositions with $x = 0.2$–0.4 (as shown in the inserts of Figure 2), two peaks can be observed and reveal the existence of ferro- and antiferromagnetic contribution at lower temperature. With decreasing x, a typical double-exchange interaction occurs due to the existence of mixed-valence Mn^{3+}/Mn^{4+} in this system, which induces the appearance of FM phase in AFM background. And this is consistent with the previously reported in the La–A–Mn–Fe–O systems.[10] The introduction of Fe in those samples causes an important decrease in the intensity and temperature of ferromagnetic ordering, which can be also observed in our system. For $x = 0.5$, the saturation in FC curve suggested a weak ferromagnetic behavior occurred in this composition due to the partially superexchange of Mn^{4+}–O–Fe^{3+} according to the Kanamori–Goodenough theory.[11] Contrasted to the $LaMn_{0.5}Fe_{0.5}O_3$,[7] the introduction of K inhibited the glassy states and gave rise to a large difference in the magnetic arrangement.

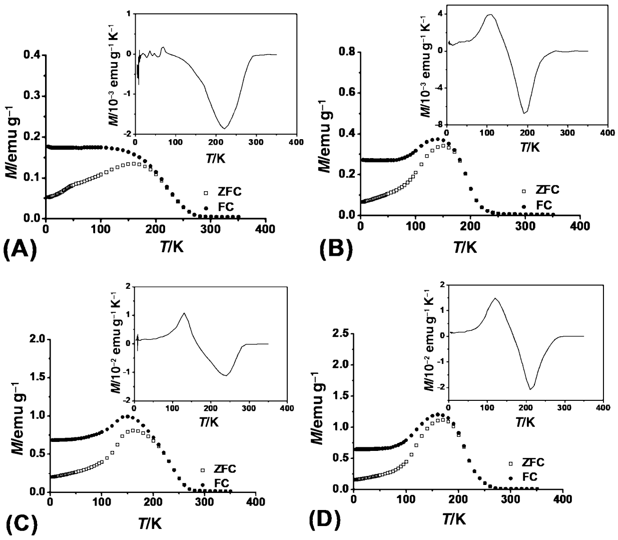

Figure 2. ZFC and FC magnetization curves of $La_{0.75}K_{0.25}Mn_{1-x}Fe_xO_3$ in an applied field of 100 Oe (A: $x = 0.5$; B: $x = 0.4$; C: $x = 0.3$; D: $x = 0.2$). The insets show the derivative of the curves M vs. T.

A series of the perovskite oxides $La_{0.75}K_{0.25}Mn_{1-x}Fe_xO_3$ ($x = 0.2$–0.5) have been synthesized hydrothermally. Our study indicated that the hydrothermal method is another route to the synthesis for more complicated perovskites.

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12 Supporting Information is available electronically on the CSJ-journal Web site; http://www.csj.jp/journals/chem-lett/index.html.