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Chemical composition and magnetism of Ag doped $LaMnO_3$*

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By using a sol-gel clue, a set of polycrystalline perovskite samples $La_{1-x}Ag_xMnO_3$ with a nominal doping level x ranging from 0.05 to 0.45 has been synthesized. The chemical composition and the magnetism of the samples were investigated. A little Ag was found seeping from the samples in the sintering process when the doping level exceeded 0.05 and the sintering temperature was higher than 700°C resulting in the samples being in multiphase. The magnetic transition points of the samples have been found to decrease with increasing sintering temperature. A concentration-dependent T_c similar to that of bivalent metal ion doped perovskite, has been obtained. We believe that the Ag seeping in the sintering process is responsible for those magnetic characteristics.

Keywords: granular system, composite, magnetism
PACC: 7560J, 8160H, 7550D

1. Introduction

Granular manganese perovskites have been observed to show an interfacial-tunnelling-related giant magnetoresistance (ITMR),[1] which is quite different from the colossal magnetoresistance observed in crystals of the compound.[2] The former can exist in the whole range of temperature below the magnetic transition point T_c,[3] but the latter appears only in a temperature range of 20–30 K in the vicinity of T_c.[2,4] Thus, ITMR has shown advantages in potential applications, and has stimulated considerable interest in recent years.[5]

For the perovskite $R_{1-x}M_xMnO_3$ (R: rear earth ion, M: metal ion), most previous ITMR studies focused on the granular compounds doped with bivalent metal ions, such as Ca, Sr, or Ba.[1,6] However, research revealed that the bivalent-metal-ion doped granular perovskite showed a smaller ITMR. Their normalized room-temperature magnetoresistive ratio is generally less than 10%.[7] This value is not large enough for practical application.

In 2000, an ITMR with its room-temperature-magnetoresistance over 25.5 % was observed in granular $La_{1-x}Ag_xMnO_3$.[8] This observation has turned research interest to the granular materials doped with univalent metal-ions lately.[8–11] However, polycrystalline $La_{1-x}Ag_xMnO_3$ samples are known to be often in multiphase when the grain size is very small.[10] Several non-perovskite substances could exist in the compound. This suggests that the origin of the ITMR observed in granular $La_{1-x}Ag_xMnO_3$ could be different from those found in the granular perovskite doped with Ca, Sr, or Ba. For this reason, it is worthwhile to clarify the chemical composition of $La_{1-x}Ag_xMnO_3$ and the related magnetism firstly. In this paper, we will present a careful investigation in this aspect. We will show that the chemical composition and magnetism of granular $La_{1-x}Ag_xMnO_3$ are closely related to Ag content x and sintering temperature T_s.

2. Sample representation

The granular samples $La_{1-x}Ag_xMnO_3$ under investigation were synthesized by the sol–gel method as reported previously[12] with its nominal doping level x being changed from 0.05 to 0.45 in steps of 0.15. The powders of the starting materials were pre-sintered at

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450°C for 10 h in air, then pressed into small strips, and sintered at $T_s = 450$°C again for 10 h in air. After the samples being characterized, they were sintered at 500°C for the same time, and then characterized again. The above process was performed again with T_s being increased from 450 to 700°C in steps of 50°C.

The samples are characterized by x-ray diffraction (XRD) in a rotating anode diffractometer (D/max-rC Rigaku) using Cu Kα radiation. The patterns of XRD revealed that several other components existed in most of the fabricated samples besides perovskite phase. And the phase components or chemical compositions depend not only on T_s, but also on x of the sample.

3. Experimental results and discussion

The XRD patterns of 450 and 500°C sintered $La_{0.95}Ag_{0.05}MnO_3$ samples are shown in Fig.1. An orthorhombic perovskite structure, with the space group Pbnm, has formed and no secondary phase can be observed in $La_{0.95}Ag_{0.05}MnO_3$ sintered at 450°C as shown in the inset of Fig.1(a). While, when re-sintering the sample at 500°C, it transforms in rhombohedral structure, with a space group R3c, as shown in the inset of Fig.1(b).

The XRD patterns of the samples with concentration $x \geq 0.15$ are shown in Fig.2. It is found that all the 450°C sintered samples with $x \geq 0.15$ are nearly in amorphous state or in multiphase or admixtures of perovskite compound, Ag, MnO_2 and γ-Mn_2O_3 particles, as well as amorphous phase. In Fig.2, all the lines indexed by MnO_2 include MnO_2, β-MnO_2 and ε-MnO_2. To compare the experimental results shown in Fig.2 with those in the literature, several corresponding diffraction cards have been listed in Table 1. The data taken are in the range of $20° < 2\theta < 80°$.

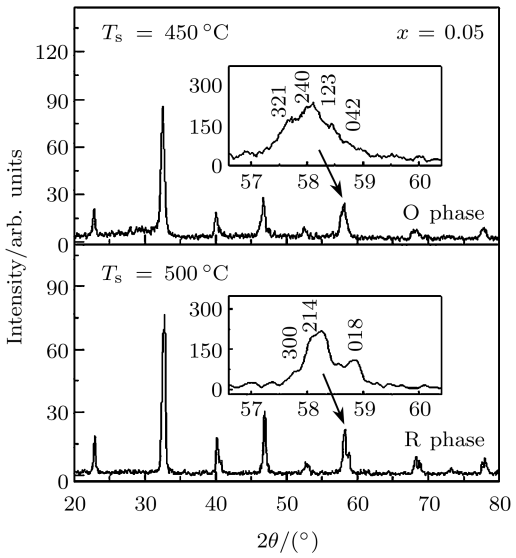


Fig.1. XRD spectra for $La_{0.95}Ag_{0.05}MnO_3$ sintered at 450°C (a) and 500°C (b); Insets: The fine structures of a part of the patterns.

Evidently, the practical doping level of the Ag-doped $LaMnO_3$ is generally not consistent with the nominal value in this case. But for convenience, we also use the nominal doping level to name these multiphase samples, including those sintered at higher temperatures.

It is found that, with increasing T_s, the amorphous phase gradually disappear and perovskite, in rhombohedral structure, forms and augments in succession. Meanwhile, Ag, MnO_2 and γ-Mn_2O_3 grains also exist, but their contents continuously decrease.

Table 1. Several corresponding diffraction cards from the literature.

substance	Ag			$\gamma-Mn_2O_3$			MnO_2			$\beta-MnO_2$			$\varepsilon-MnO_2$	
card No	4-0783			6-0540			7-222			24-735			12-141	
structure	cubic			tetragonal			orthorhombic			tetragonal				
	2θ	I/I_1	hkl	2θ	I/I_1	hkl	2θ	I/I_1	hkl	2θ	I/I_1	hkl	2θ	I/I_1
1	38.201	100	111	28.990	60	112	32.692	100	110	28.680	100	110	22.860	80
2	44.401	40	200	32.682	70	103	41.407	20	120	37.328	55	101	23.986	100
3	64.601	25	220	36.221	100	211	53.384	100	130	42.823	16	111	31.615	55
4	77.598	26	311	37.635	40	004	55.997	70	021	56.652	55	211	36.993	80
5				49.828	30	204	58.617	60	111	64.825	8	002	37.964	80
6				51.026	30	105	73.834	70	131	72.260	20	301	42.647	90
7				59.650	60	224							54.983	55

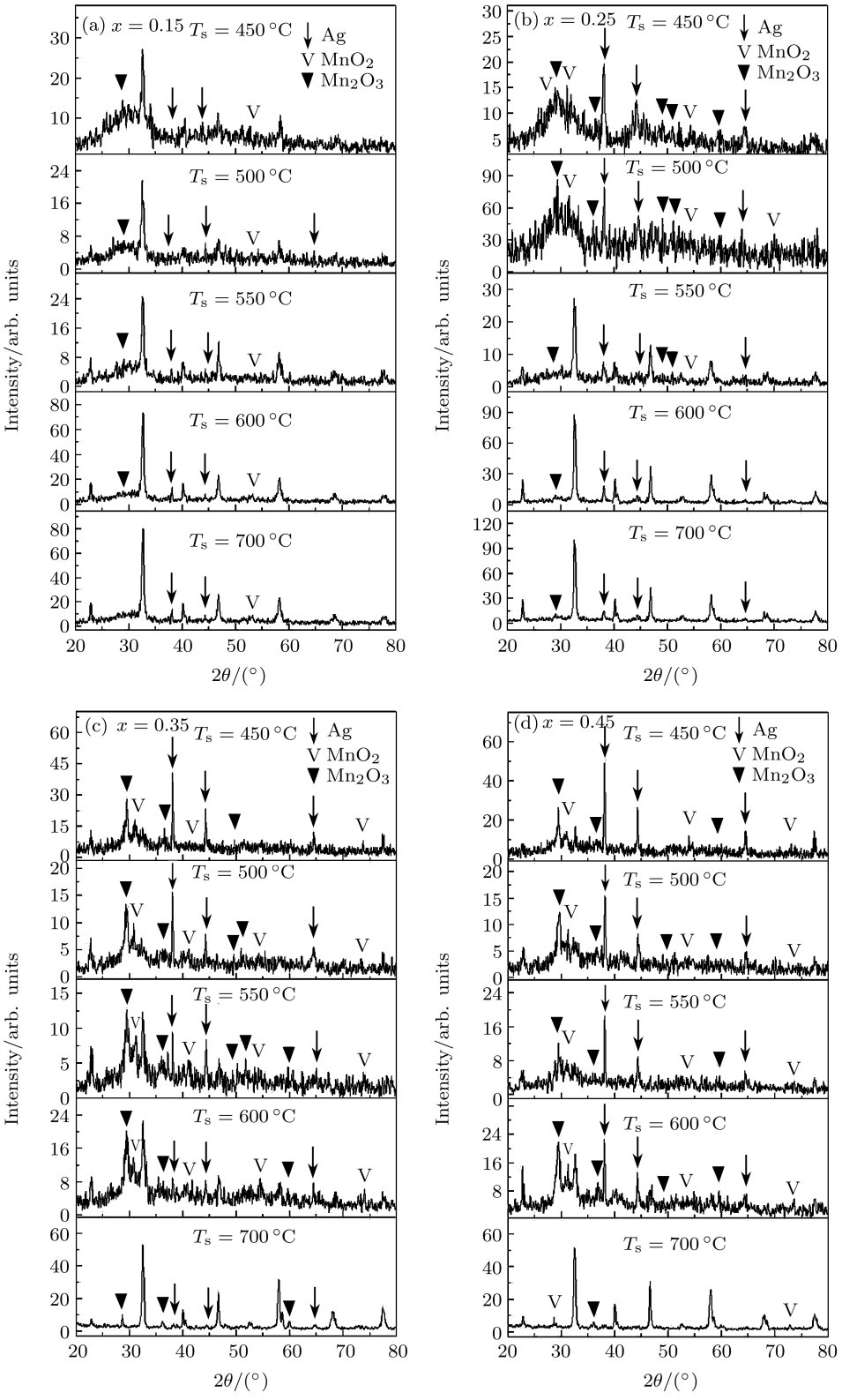


Fig.2. XRD spectra of different temperature sintered samples with nominal doping level $x = 0.15$ (a), 0.25 (b), 0.35 (c) and 0.45 (d).

Especially, it is interesting to find that the temperature of perovskite phase formation increases with increasing Ag content. Amorphous phase will basically disappear for nominal $La_{0.85}Ag_{0.15}MnO_3$ sintered at 550°C, but, not to disappear until T_s reaches 700°C for nominal $La_{0.65}Ag_{0.35}MnO_3$. This phenomenon has not been reported before.

When T_s reaches 700°C, no amorphous phase can be observed in all the samples with a nominal doping level $x \leq 0.45$. However, there are also a few Ag and manganese oxides in them besides the perovskite. By the way, our experimental results have also shown that the fabricated $La_{1-x}Ag_xMnO_3$ compound can not form perovskite structure when T_s is lower than 450°C.

It is well-known that Ag can be oxidized when temperature is higher than 200°C. In the present case, when T_s is higher than 200°C, Ag grains should also be oxidized and then decomposed gradually. Ag^{1+} could come into perovskite to substitute for La ions or combine with manganese oxides to form $AgMnO_3$, which can be a part of the perovskite. The higher the Ag content is, the higher T_s could be needed to make the Ag monomer fully oxidized and decomposed. Consequently, we see that the temperature of perovskite phase formation increases with increasing Ag content.

On the other hand, Ag could seep from the samples in sintering process. We have observed that a little Ag remains in the crucible employed for sintering the samples when T_s was higher than 700°C. Figure 3 shows the Ag content (in atom percent) as a function of T_s. The Ag content was measured by method of x-ray energy dispersive spectroscopy (XEDS—Thermo Noran Vantage-IV). As can be seen, Ag content diminishes monotonically and reaches about 1% as T_s increases. The result of XEDS substantiates again that only $La_{0.95}Ag_{0.05}MnO_3$ can stably exist in the samples. While the former suggests that a part of manganic oxides has left in the samples and can never participate to form the perovskite. This deduction has been supported from the XRD patterns of 1200°C sintered nominal $La_{0.65}Ag_{0.35}MnO_3$ and $La_{0.55}Ag_{0.45}MnO_3$, as shown in Fig.4. No characteristic lines of Ag can be observed in the patterns. But some magnetic oxides can still be found in the 1200°C sintered samples. In fact, the percentage Mn atoms have been found no evident variation in the XEDS test. Thus it can be conclude that Ag monomer can be fully oxidized to attach itself to the perovskite or seep from the samples as long as T_s is high enough.

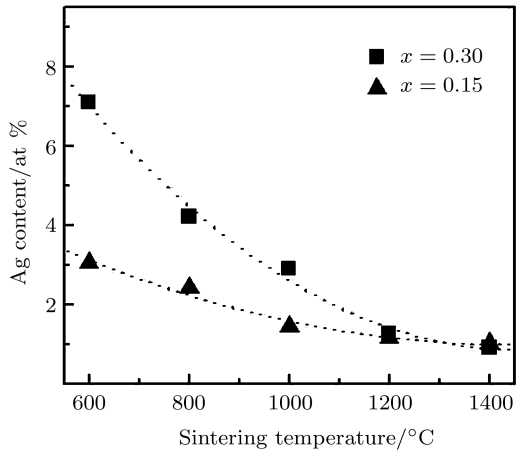


Fig.3. Percent Ag content as a function of sintering temperature for the compounds with nominal doping level $x = 0.15$ and 0.35. The points are measured data and the dot lines through the points are guides to the eye.

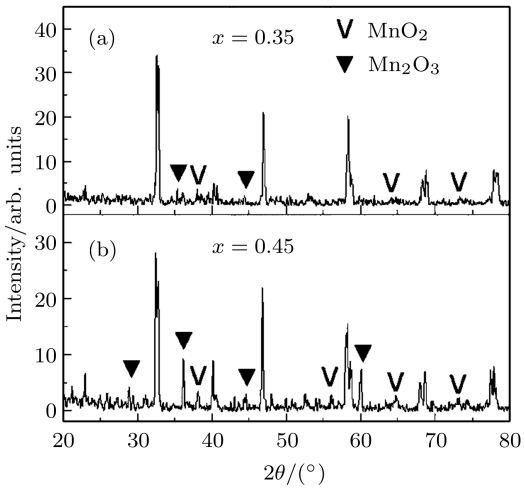


Fig.4. XRD spectra of the 1200°C sintered samples with nominal doping level $x = 0.35$ (a) and 0.45 (b).

For bivalent-metal-ion-doped perovskites (BIDP) and monovalent-metal-ion doped perovskites (MIDP), their structural formulae can be written as $R^{3+}_{1-x}M^{2+}_xMn^{3+}_{1-x}Mn^{4+}_xO^{2-}_3$ (M: Ca, Sr, Ba etc) and $R^{3+}_{1-x}M^{1+}_xMn^{3+}_{1-2x}Mn^{4+}_{2x}O^{2-}_3$(M: Ag, Na, K), respectively. All the Mn ions in a MIDP are in trivalent state (Mn^{3+}) when $x = 0$, and in tetravalent state (Mn^{4+}) when $x = 0.5$. MIDP with doping level $x > 0.5$ cannot exist. Thus, theoretically, the density of the charge carrier, namely Zener carrier,[13] in a MIDP with a doping level x should be as much as double of that in a BIDP with the same x, or equal to that in a BIDP with a doping level $2x$. However, since part of Ag presents as monomer or seeps in sintering process, the density of Zener carrier in a $La_{1-x}Ag_xMnO_3$

($x > 0.05$) compound is often less than the nominal value. The magnetism in the samples will be different from that expected.

Figure 5 shows the T_c versus nominal Ag content for the $La_{1-x}Ag_xMnO_3$ compounds under a 16 kA/m applied field. The T_c values in Fig.5 are obtained from the temperature-dependent magnetization, which is obtained by using a vibrating sample magnetometer, as shown in the insets of the figure. We find in Fig.5(a) that the x-dependent T_c for 1000°C sintered samples shows little difference from that of $La_{1-x}Sr_xMnO_3$ or $La_{1-x}Ca_xMnO_3$.[14,15] Namely, the T_c–x curve can be roughly fitted as a cubic function and the maximum of T_c is neighbouring $x = 0.4$.

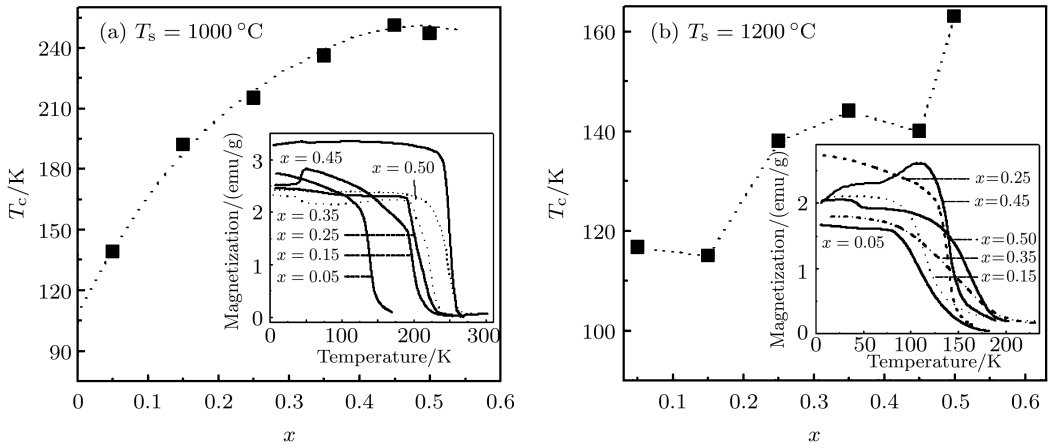


Fig.5. T_c as a function of nominal Ag concentration for 1000°C sintered $La_{1-x}Ag_xMnO_3$. The points are experimental values, and the dot line through the points is guide to the eye; Inset: Temperature-dependent magnetization for 1000°C sintered $La_{1-x}Ag_xMnO_3$ under a 16 kA/m magnetic field. (b) T_c as a function of nominal Ag concentration for 1200°C sintered $La_{1-x}Ag_xMnO_3$. The points are experimental values, and the dot line through the points is guide to the eye; Inset: Temperature-dependent magnetization for 1200°C sintered $La_{1-x}Ag_xMnO_3$ under a 16 kA/m magnetic field.

Many previous studies indicates that the magnetic properties of the perovskite are strongly dependent on its carrier density and structure.[14–18] Thus, x-dependent T_c of MIDP should display an obvious distinction from that of BIDP. However, the phenomenon expected cannot be observed from Fig.5(a). This point has ever bewildered us. But, considering that the concentration in $La_{1-x}Ag_xMnO_3$ is generally less than the nominal value, the inconsistency will be understandable.

For 1200°C sintered samples, the variable range of T_c versus x reduces greatly and shows no regularity, as shown in Fig.5(b). In both behaviours above the former might result from the decrease of perovskite phase, which dominates the magnetism of the samples. This point hints that the perovskite $La_{1-x}Ag_xMnO_3$ with $x > 0.05$ is unstable. But the later should be ascribed to the presence of much manganic oxides in the samples. MnO_2 and Mn_2O_3 are often in ferromagnetic or antiferromagnetic state. So magnetism of the samples containing both MnO_2 and Mn_2O_3 can be elusory.

4. Conclusions

Silver can exist as grains of single substance in the sol–gel method prepared resultant powder, which are used as a precursor of the perovskite $La_{1-x}Ag_xMnO_3$, when the nominal doping level x exceeds 0.05. This leads the samples sintered at a temperature lower than 700°C to be mixtures or multiphase materials of Ag, manganic oxides, the perovskite, and even amorphous state. With increasing T_s, Ag is oxidized and then decomposed. Silver oxide combined with manganic oxides to form perovskite, so that the non-perovskite phases decrease, and perovskite phase increases. Thus, the temperature of the perovskite phase formation increases with increasing Ag content. The practical Ag content is lower than the nominal value due to Ag seeping from the samples in the sintering process. Thus, the x-dependent T_c for nominal $La_{1-x}Ag_xMnO_3$ does not show an expected result, it should be different from that for $La_{1-x}Sr_xMnO_3$ or $La_{1-x}Ca_xMnO_3$.

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