SYNTHESIS AND PHYSICAL PROPERTIES OF RUDDLESDEN–POPPER PHASE $Sr_3Mn_{2-x}Fe_xO_{7-\delta}$ (x = 0.15 ~ 1.0)

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Double layer R–P manganate phases $Sr_3Mn_2O_{7-\delta}$ were stabilized by partial substitution of Mn with Fe in air atmosphere. The minimum amount of Fe needed to stabilize single phase of R-P in air atmosphere was about x = 0.15. As the Fe content x increased, the optimum reaction temperatures were lowered from 1530°C for x = 0.15 sample to 1400°C for x = 1.0 sample. The structural parameters were refined on the basis of space group I4/mmm by Rietveld method with powder X-ray diffraction data. Magnetic susceptibility data indicate that these samples have very complicate magnetic properties. It also shows spin-glass like transitions at low temperatures when x was larger than 0.5.

INTRODUCTION

The manganese-based Ruddlesden–Popper (R–P) phase $(AO)(AMnO_3)_n$ with n = 2 has received considerable attention recently since the observation of the colos-sal magnetoresistance (CMR) in $La_{1+x}Sr_{2-x}Mn_2O_7$ [1-6]. R–P phases have the general formula $(AO)(AMO_3)_n$ and they consist of n consecutive perovskite blocks $(AMO_3)_n$, which are separated by rock salt layers (AO) where the perovskite structure is the n = ∞ end member. The n = 2 R–P phase, figure 1, can be thought as of double layers of MO_6 octahedra along the *c*-axis separated by an insulating rock-salt layer (AO).

It is well known that the titanium-based R–P phases $A_{n+1}Ti_nO_{3n+1}$ are relatively easily obtained for A = Ca or Sr, but the homologous manganate $A_{n+1}Mn_nO_{3n+1}$ can only be synthesized in the case of calcium in conventional oxide method [7]. In case of strontium, it is much more difficult to synthesize R–P phase and the substitution of lanthanide for strontium is necessary [8,9]. Mono layer R–P phase (K_2NiF_4 type) β-Sr_2MnO_4 is transformed into low temperature type α phase at 1600°C, which is in fact a mixed phase of SrO and $Sr_7Mn_4O_{15}$ [10]. High temperature β-Sr_2MnO_4 can be obtained by only quenching from above 1600°C to room temperature [11]. Triple layer manganate R–P phase $Sr_4Mn_{3-x}Fe_xO_{10-\delta}$ could be stabilized by partial substitution of Mn with Fe, and their properties were investigated by Fawcett et al.[12]. Synthesis of triple layer R–P phase $Sr_4Mn_{3-x}Fe_xO_{10-\delta}$ requires long heating times.

The smaller the value of x, the longer the heating time needed to obtain a single R–P phase. The minimum amount of Fe needed to obtain pure R–P phase was x = 0.4. These phases showed semiconducting, and strong antiferromagnetic interactions and spin-glass type behavior at low temperature [12-14]. Synthesis of double layer R–P phase $Sr_3Mn_2O_{7-\delta}$ which is the parent compound of the n = 2 CMR manganate $La_{1+x}Sr_{2-x}Mn_2O_7$ was first reported by Mizutani et al.[15] and its properties were investigated by Mitchell et al. [16]. It is metastable below 1660°C and must be quenched into dry ice to prevent its decomposition to α-Sr_2MnO_4 and $Sr_4Mn_3O_{10}$, neither of which is a layered R–P phase. The oxygen vacancies were in the MnO_2 plane and could be reversibly filled at 400°C to yield stoichiometric $Sr_3Mn_2O_7$ which was antiferromagnetic insulator with T_N = 160K. A series of Mn substituted R–P strontium ferrate were prepared and their structure and magnetic properties were reported by Veith et al. [17].

Recently the oxygen deficient double layer perovskite $Sr_3Mn_2O_6$ phases were synthesized in N_2 atmosphere and its structure and properties are reported [18]. TEM experiment showed that this phase crystallized in a superstructure of the simple R–P subcell. Magnetic susceptibility studies suggested a canted antiferromagnetic transition and showed no divergence between ZFC and FC curves [18].

In this study, double layer R–P manganate phase was stabilized in air atmosphere without quenching by partial substitution of Mn with Fe. The synthesis and magnetic properties are discussed in detail.
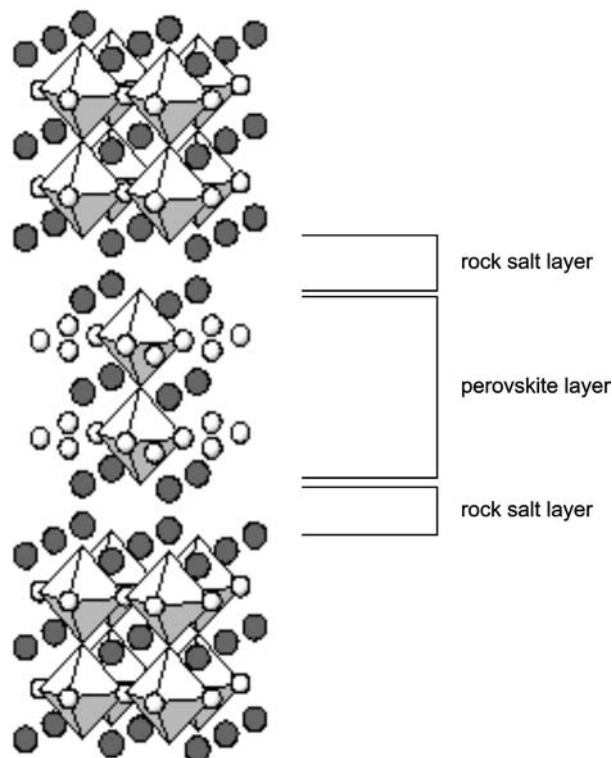

Figure 1. The n = 2 Ruddlesden–Popper Structure.

EXPERIMENTAL

Polycrystalline phases of $Sr_3Mn_{2-x}Fe_xO_{7-\delta}$ were prepared by conventional solid state reaction of $SrCO_3$, MnO_2, and Fe_2O_3 (99.9 %, Aldrich). Mixtures of these starting materials in desired ratios were heat treated at 800°C, 1000°C, and 1400°C for 24hrs, respectively, with intermittent grinding. Finally pelletized samples were reacted for 48hrs at optimum reaction temperature between 1450°C and 1530°C. The samples then furnace cooled in air atmosphere. The progress of the reactions was monitored by x-ray powder diffraction in every step. Powder x-ray diffraction data were collected with a Rigaku diffractometer with momochromatized Cu Kα radiation in the range of 5°-120°, with a step size of 0.02°. X-ray data were analyzed with the Rietveld program FullProf [19].

The oxygen stoichiometries of the samples were determined by iodometric titration method [20]. About 25 mg of samples were weighed directly in the titration cell. Excess oxygen free KI solution (10 wt.%, 10 ml) and diluted HCl solution were added in sequence. The formed I_2 was back titrated by the standardized $Na_2S_2O_3$ solution. The entire iodometric titrations were carried out under a nitrogen atmosphere to avoid the formation of I_2 by oxidation in air. The magnetic susceptibility curves of the samples were obtained using a Quantum Design SQUID magnetometer over the temperature range of 5-300 K. Data were collected after cooling in the absence (ZFC) and with an applied magnetic field (FC) of 1000 gauss, respectively. Electrical resistivity of the sample was measured using a standard four-probe method over a temperature range of 200-300 K.

RESULTS AND DISCUSSION

X-ray powder diffraction data showed that single phase of $Sr_3Mn_{2-x}Fe_xO_{7-\delta}$ compounds were stabilized successfully when x was larger than 0.15 by solid state reaction in air atmosphere. When x was less than 0.15, $Sr_7Mn_4O_{15}$ phase formed at about 1200°C did not transform into R–P phase completely, even when the reaction temperature was higher than 1600°C. This was most likely due to the effects of size and the stable $Sr_7Mn_4O_{15}$ phase formed during the reaction in air atmosphere. As the amount of Fe increased, the optimum reaction temperature was lowered and the reaction time needed to prepare a single phase was shortened. In fact, when x was 0.15, the range of the optimum reaction temperature for the pure R–P phase was around 1530°C ± 10°C. When x was around 1.0, however, the reaction temperature could be lowered to around 1400°C and the range of the reaction temperature was about 1400°C ± 50°C. When the reaction temperature was higher than optimum temperature, the R–P phase began to decompose to perovskite and unknown phases.

The crystal structures of $Sr_3Mn_{2-x}Fe_xO_{7-\delta}$ phases were refined by Rietveld method based on the space group I4/mmm with the parameters from Mizutani et al. [15]. The background was modeled by Chebyschev polynomials of the first kind and the peak shape was described by a Pseudo-Voigt function. The oxygen occupancies were assumed to 1.0 during the refinement. The observed and calculated diffraction pattern of $Sr_3Mn_{1.5}Fe_{x0.5}O_{7-\delta}$ is given in figure. 2. The structural parameters are listed in table 1.

As expected the lattice parameters and unit cell volumes increase with the increasing Fe content due to the substitution of large Fe^{3+} for smaller Mn^{4+} and oxygen vacancies. But c/a ratio of the lattice parameters decrease with increasing Fe content, which is different from the results reported by Fawcett et al.[12] for the n=3 phase. Oxygen vacancies determined by iodometric titration were listed in table 1. The oxygen vacancies increased as the amount of Fe increased due to the dif-

ficulty of synthesizing Fe^{4+} containing compounds in air. Assuming that Fe is only presents in the +3 state the mean oxidation states of Mn is 3.67 and 3.88 for the sample with x = 0.2 and x = 1.0, respectively.

Some of the R–P phases showed phase instability in ambient air at room temperature because they react with CO_2 gas or moisture present in ambient air [21]. X-ray diffraction patterns for the $Sr_3Mn_{2-x}Fe_xO_{7-\delta}$ samples exposed to ambient air atmosphere for 1 month did not show any sign of decomposition, which means these phases are fairly stable at air atmosphere.

The temperature dependence of the molar magnetic susceptibility and inverse magnetic susceptibility of the $Sr_3Mn_{2-x}Fe_xO_{7-\delta}$ phases are shown in figure 3. The parameters derived by fitting the high temperature region (150-300 K) to a Curie-Weiss law are listed in table 2. Magnetic susceptibilities of the n=2 R–P phases qualitatively showed very similar behaviors with the n=3 R–P phase $Sr_4Mn_{3-x}Fe_xO_{10-\delta}$ [12,13] and the n=2 R–P phase $Sr_3Fe_{2-x}M_xO_{7-\delta}$ (M = Co, Mn) [18,21]. As the Fe content increased the Weiss constant increased from -95.2 K for the x=0.2 compound to -3.13K for the x=1.0 compound. The large negative value of the Weiss constant indicates that the antiferromagnetic interaction dominates in these compounds. It also shows a local maximum at 120 K and 80 K for the x=0.2 and x=0.5 samples, respectively. This is in good agreement with the previous report in n=3 R–P phases [12,17]. When x was small, the ZFC and FC curves showed no divergence, but when x was larger than 0.5 these curves showed divergence with a maximum in the ZFC curve at 10 K for the x=0.5, and 20 K for the x=1.0. The tendency for magnetic frustration increases as the amount of Fe increases. This is typical of spin-glass type behavior seen in other R–P [12,17]. In fact, these triple layer manganate R–P phase $Sr_4Mn_{3-x}Fe_xO_{10-\delta}$ revealed spin glass transitions at about 10 K when x was 1.0 .
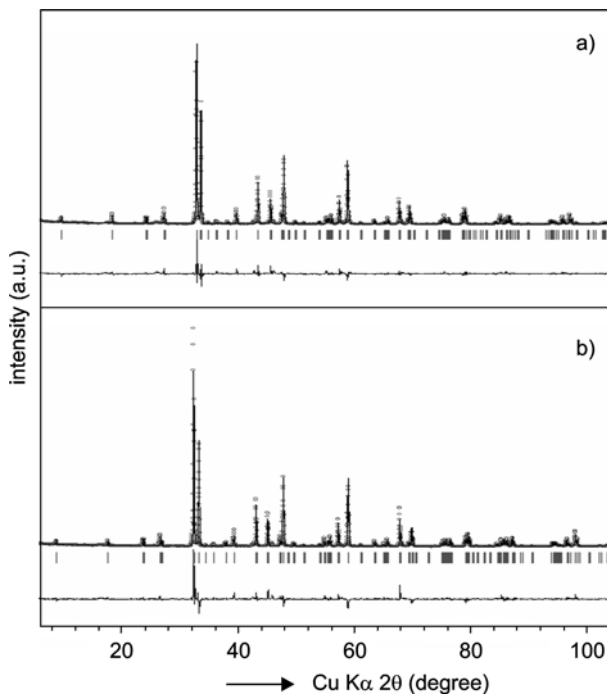

Figure 2. X-ray Rietveld Refinement Profile contains room temperature XRD patterns, calculated profiles, peak positions, and the difference between the observed and calculated profiles for (a) $Sr_3Mn_{1.8}Fe_{0.2}O_{7-\delta}$, and (b) $Sr_3Mn_{1.0}Fe_{1.0}O_{7-\delta}$.

Table 2. Magnetic properties of $Sr_3Mn_{2-x}Fe_xO_{7-\delta}$.

	T_N (K)	T_G (K)	θ (K)	C	μ_{eff}
$Sr_3Mn_{1.85}Fe_{0.15}O_{7-\delta}$	115	–	-148.7	3.53	5.32
$Sr_3Mn_{1.8}Fe_{0.2}O_{7-\delta}$	120	–	-95.23	3.85	5.55
$Sr_3Mn_{1.7}Fe_{0.3}O_{7-\delta}$	110	–	-45.76	4.53	6.02
$SrMn_{1.5}Fe_{0.5}O_{7-\delta}$	80	10	-24.33	5.13	6.41
$Sr_3Mn_{1.3}Fe_{0.7}O_{7-\delta}$	–	15	-6.43	6.18	7.04
$Sr_3Mn_{1.0}Fe_{1.0}O_{7-\delta}$	–	20	-3.13	7.5	7.75

Table 1. Structural parameters of $Sr_3Mn_{2-x}Fe_xO_{7-\delta}$.

| Parameters	x = 0.15	x = 0.20	x = 0.30	x = 0.50	x = 0.70	x = 1.0
Space group[a]	I4/mmm	I4/mmm	I4/mmm	I4/mmm	I4/mmm	I4/mmm
a (Å)	3.8088(1)	3.8120(1)	3.8183(1)	3.8262(1)	3.8335(1)	3.8422(1)
c (Å)	20.1030(5)	20.1035(5)	20.1059(4)	20.112(1)	20.1215(4)	20.1319(4)
V (Å³)	291.633	292.131	293.132	294.436	295.698	297.197
^{z}Sr(2)	0.1832(1)	0.18325(5)	0.1831(1)	0.1828(1)	0.1830(1)	0.1828(1)
^{z}Mn/Fe	0.0974(2)	0.0976(6)	0.0979(2)	0.0984(2)	0.0987(2)	0.0995(2)
^{z}O(2)	0.1931(5)	0.1943(9)	0.1947(6)	0.1945(5)	0.1937(5)	0.1920(6)
^{z}O(3)	0.0974(4)	0.0970(5)	0.0974(4)	0.0976(1)	0.0971(3)	0.0964(4)
R_p	0.1	0.115	0.107	0.103	0.0959	0.0961
R_{wp}	0.132	0.147	0.138	0.133	0.125	0.124
χ^2	6.43	6.41	4.48	4.75	4.17	5.44
δ	0.18	0.40	0.47	0.50	0.52	0.54

The temperature dependent resistivity plots in figure 4 show that all of these samples are insulating and the resistivity of the samples decreased with the addition of Fe. The thermal activation energy of the samples with x=0.7 and x=1.0 are 0.126eV and 0.119eV, respectively.

Figure 4. The temperature dependence of the resistivities of $Sr_3Mn_{2-x}Fe_xO_{7-\delta}$.
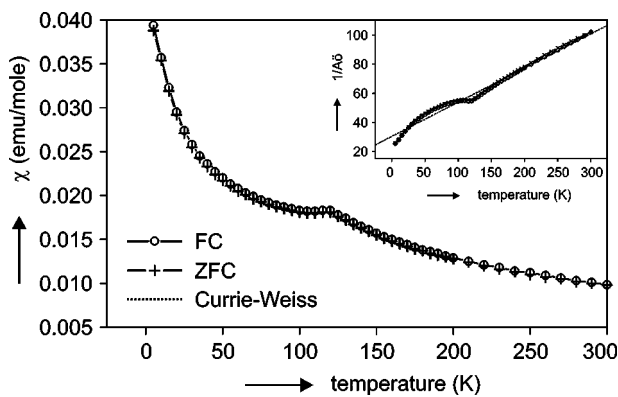
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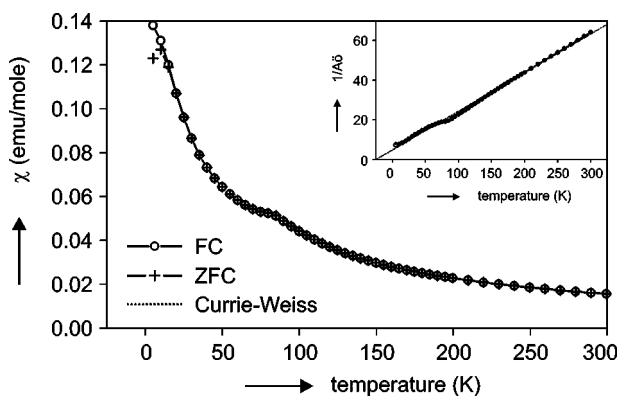
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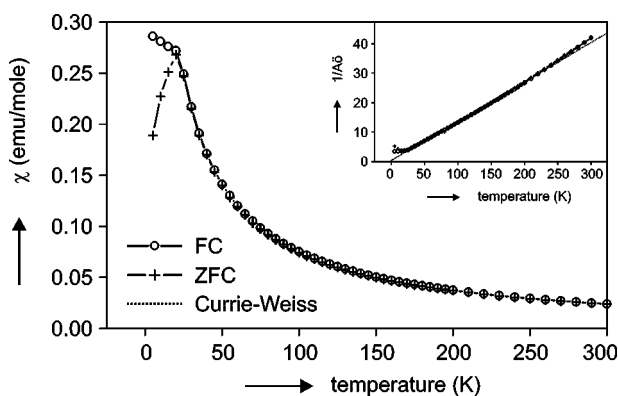
c)

Figure 3. The temperature dependence of the molar magnetic susceptibility and inverse magnetic susceptibility(inset) for a) $Sr_3Mn_{1.8}Fe_{0.2}O_{7-\delta}$, b) $Sr_3Mn_{1.5}Fe_{0.5}O_{7-\delta}$, and c) $Sr_3Mn_{1.0}Fe_{1.0}O_{7-\delta}$.
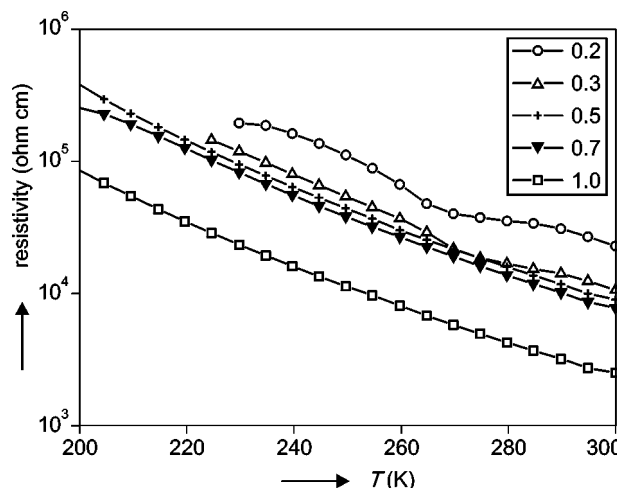
CONCLUSIONS

In this study, double layer R–P phases $Sr_3Mn_{2-x}Fe_xO_{7-\delta}$ have been successfully synthesized by the conventional oxide method in air atmosphere and their structural parameters were refined by Rietveld method with powder X-ray diffraction data on the basis of space group I4/mmm. The minimum amount of Fe needed to stabilize R–P phase was about 0.15 and as the Fe content x increased, the optimum reaction temperature was lowered. These phases showed very complicated magnetic properties and revealed spin-glass like transitions at low temperatures when x was larger than 0.5.

References

1. Laffez P., Tendeloo G., Seshadri R., Hervieu M., Martin C., Maignan A., Raveau B.: J.Appl.Phys. *80*, 5850 (1996).
2. Battle P. D., Green M. A., Lago J., Millburn J. E., Rosseinsky M. J., Vente J. F.: Chem.Mater. *10*, 658 (1998).
3. Louca D., Kwei G. H.: Phys.Rev.Lett. *80*, 3811 (1998).
4. Asano H., Hayakawa J., Matsui M.: Phys.Rev. B *57*, 1052 (1998).
5. Yuan C. L., Yu T., Song W. H., Ye S. L., Wang S. G., Dai J. M., Sun Y. P.: Phys. Stat. Sol. A *178*, 771 (2000).

6. N. Shah N., Green M. A., Neumann D. A.: J.Phys. Chem.Solids *63*, 1779 (2002).
7. Fawcett I. D., Sunstrom IV J. E, Greenblatt M.: Chem. Mater. *10*, 3643 (1998).
8. Floros N., Hervieu M., Tendeloo G., Michel C., Maignan A., Raveau B.: Solid State Sci. *2*, 1 (2000).
9. Sloan J., Battle P. D., Green M. A., Rosseinsky M. J., Vente J.: J. Solid State Chem. *138*, 135 (1998).
10. Feltz A., Kriegel R., Polzl W.: J. Mater.Sci.Lett. *18*, 1693 (1999).
11. Bouloux J. C., Soubeyroux J. L., Glem G. L., Hagenmuller P.: J. Solid State Chem. *38*, 34 (1981).
12. Fawcett I. D., Veith G. M., Croft M., Nowik and I.: J. Solid State Chem. *155*, 96 (2000).
13. Battle P. D., Branford W. R., Mihur A., Rosseinsky M. J., Singleton J., Sloan J., Spring L. E., Vente J. F.: Chem.Mater. *11*, 674 (1999).
14. Chen R., Greenblatt M.: Chem.Mater. *13*, 4094 (2001).
15. Mizutani N., Kitazawa A., Nobuyuki O., Kato M.: J. Chem. Soc.(Jpn.) Ind.Ed. *73*, 1097 (1970).
16. Mitchell J. F., Millburn J. E., Medarde M., Short S., Jorgensen J. D.: J. Solid State Chem. *141*, 599 (1998).
17. Veith G.M., Fawcett I.D., Greenblatt M., Croft M., Nowik I.: Int.J.Inorg.Mater. *2*, 2513 (2000)
18. Gillie L. J., Wright A. J., Hadermann J., Tendeloo G., Greaves C.: J. Solid State Chem. *175*, 188 (2003).
19. Carvajal R.: J. *Collected Abstract of Satellite Meeting on Powder Diffraction of 2ᵗʰ Congress of the International Union of Crystallographie*, International Union of Crystallographie, Toulouse, France 1990.
20. Er-Rakho, Michel L., Raveau C. B.: J. Solid State Chem. *73*, 514 (1988).
21. Prado F., Manthiram A.: J. Solid State Chem. *158*, 307 (2001).

SYNTÉZA A FYZIKÁLNÍ VLASTNOSTI
RUDDLESDEN–POPPEROVÝCH FÁZÍ
Sr₃Mn₂₋ₓFeₓO₇₋δ (x = 0.15 ~ 1.0)

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Podvojné vrstevnaté Ruddlesden–Popperovy (R–P) manganičitany Sr₃Mn₂O₇₋δ byly stabilizovány částečnou substitucí manganu železem na vzduchu. Minimální množství Fe stabilizující jednofázové R–P fáze na vzduchu bylo kolem x = 0.15. S rostoucím obsahem Fe se snižuje optimální syntetická teplota z 1530°C při x = 0.15 na 1400°C při x = 1.0. Strukturní parametry byly upřesněny na základě prostorové grupy symetrie I4/mmm Rietveldovou metodou z dat rentgenové práškové difrakce. Podle magnetické susceptibility mají vzorky velmi složité magnetické vlastnosti. Rovněž je z nich patrný přechod do stavu podobného spinovému sklu při nízkých teplotách při x > 0,5.