

Synthesis and crystal structures of $n = 3$ Ruddlesden–Popper phase $\text{CaSr}_3\text{Mn}_{3-x}\text{Fe}_x\text{O}_{10}$ ($x = 1.5, 1.0$)

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Abstract

The triple layer Ruddlesden–Popper phases ($n = 3$ R–P phase) $\text{CaSr}_3\text{Mn}_{3-x}\text{Fe}_x\text{O}_{10}$ ($x = 1.5, 1.0$) were stabilized by solid state reaction in air atmosphere and their crystal structures were refined with neutron diffraction data obtained at room temperature and at 5 K by means of Rietveld method. Both phases adopt space group $I4/mmm$ and revealed no magnetic reflection at low temperature. Magnetic susceptibility data of $\text{CaSr}_3\text{Mn}_{1.5}\text{Fe}_{1.5}\text{O}_{10}$ and $\text{CaSr}_3\text{Mn}_2\text{FeO}_{10}$ compound showed spin glass transition at 25 and 12 K, respectively.

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1. Introduction

The rare earth manganese oxide compounds with doping divalent metals based on perovskite structure, $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ (Ln = rare earth ion, A = alkali or alkaline earth metal ion) have been studied extensively due to their interesting magnetotransport properties (CMR).^{1,2} Recently researches were extended to layered perovskite manganate since the observation of the CMR properties in R–P (Ruddlesden–Popper) phase $\text{La}_{1+x}\text{Sr}_{2-x}\text{Mn}_2\text{O}_7$.^{3–5}

The R–P phases with general formula of $(\text{AO})(\text{AMnO}_3)_n$ consists of $n(\text{AMnO}_3)$ perovskite blocks, separated by a rock salt-like layer of composition AO. The perovskite structure is the $n = \infty$ end member. The crystal structure of typical $n = 3$ R–P phase, Fig. 1, can be thought as triple layers of MO_6 octahedra along the c -axis separated by an insulating rock salt layer (AO).

It is well known that synthesis of manganate R–P phase $(\text{AO})(\text{AMnO}_3)_n$ is difficult, especially for $\text{A} = \text{Sr}$. In fact, attempts to stabilize any phase with nominal composition of $\text{Sr}_4\text{Mn}_3\text{O}_{10}$ lead to the formation of oxycarbonate, and partial substitution of Sr for Ba or partial substitution of Mn for Co lead to other different phases.^{6,7} Partial substitution of either Mn by Fe or Sr by Ca can stabilize $n = 3$ R–P and crystal structure and properties of several $n = 3$ R–P strontium manganate phases

were reported.^{8–10} But it takes long reaction time to prepare single phase of $n = 3$ compound in air atmosphere and sometimes wet chemical methods are needed.

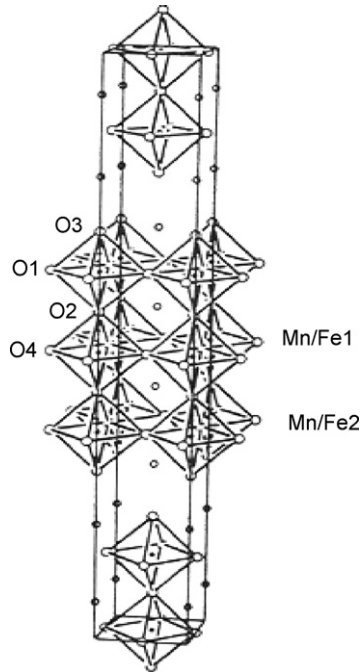
In this study, $n = 3$ Ruddlesden–Popper phase $\text{CaSr}_3\text{Mn}_{3-x}\text{Fe}_x\text{O}_{10}$ ($x = 1.5, 1.0$) were prepared relatively easily by double substitution of both Sr and Mn site with Ca and Fe with conventional solid state reaction. The crystal structure of this phase was refined by neutron diffraction data and magnetic properties were discussed.

2. Experimental procedure

In this experiment, a series of $n = 3$ Ruddlesden–Popper phases $\text{CaSr}_3\text{Mn}_{3-x}\text{Fe}_x\text{O}_{10}$ were prepared by conventional solid state reaction of SrCO_3 , CaCO_3 , MnO_2 , and Fe_2O_3 (99.9%, Aldrich). The powder mixture was pressed into a pellet and heated at 1000, 1200 °C and finally at 1400–1450 °C for 48 h in air atmosphere, with intermediate grindings. Phase analyses of the products were carried out by X-ray powder diffraction and neutron diffraction. Neutron diffraction data were recorded over the temperature range of 5–300 K on the high resolution powder diffractometer (HRPD) at KAERI (Korea Atomic Energy Research Institute), Korea.

Rietveld structural refinements were carried out with the Full-Prof Program Package.¹¹ Magnetic susceptibility curve of the sample was obtained using a Quantum Design SQUID magnetometer over the temperature range of 5–300 K in an applied field of 1000 G.

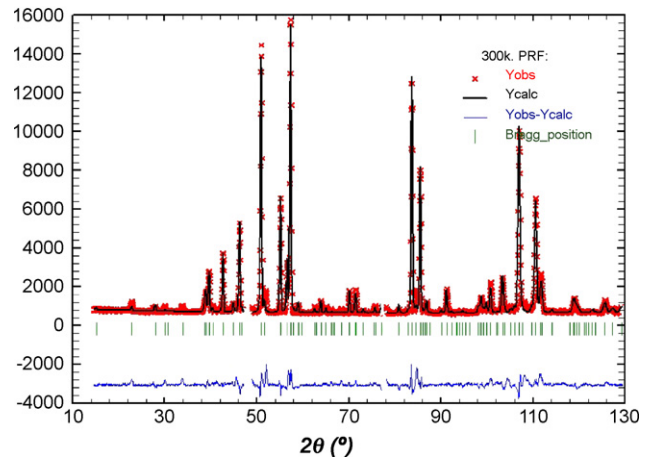
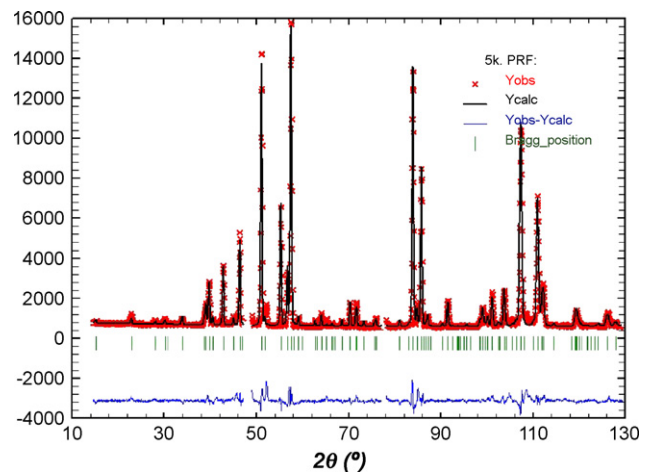
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Fig. 1. Crystal structure of $n = 3$ R–P phase.

3. Results and discussion

Single phases of triple layer R–P phase $\text{CaSr}_3\text{Mn}_{3-x}\text{Fe}_x\text{O}_{10}$ have been synthesized easily by conventional solid state reaction in air atmosphere when x was larger than 0.5. The optimum reaction temperatures were 1450°C for $x = 1.0$ and 1400°C for $x = 1.5$ sample, respectively.

The crystal structures were well refined by Rietveld method with room temperature and low temperature neutron diffraction on the basis of space group $I4/mmm$. Small amount of impurities were observed in the diffraction pattern and excluded for the Rietveld analysis. During the analysis oxygen occupancies were fixed to unity and isotropic thermal parameters were also fixed as $B_{\text{iso}} = 1.0$ to avoid the digresses of thermal parameters. The observed and calculated neutron diffraction pattern for $\text{CaSr}_3\text{Mn}_{1.5}\text{Fe}_{1.5}\text{O}_{10}$ at 300 and 5 K is given in Figs. 2 and 3.

Fig. 2. Observed, calculated and difference neutron diffraction profile for $x = 1.5$ sample at 300 K. Tick marks show diffraction peak positions for nuclear structure.Fig. 3. Observed, calculated and difference neutron diffraction profile for $x = 1.5$ sample at 5 K. Tick marks show diffraction peak positions for nuclear structure.

The resultant structural parameters are summarized in Table 1 and selected bond lengths are in Table 2.

Lattice parameters and cell volume of the $x = 1.5$ sample are larger than those of the $x = 1.0$ sample due to the substitution of

Table 1
Structural parameters of $\text{CaSr}_3\text{Mn}_{1.5}\text{Fe}_{1.5}\text{O}_{10}$ and $\text{CaSr}_3\text{Mn}_2\text{FeO}_{10}$ at 300 and 5 K (space group $I4/mmm$)

	Site	$x = 1.5$, 300 K	$x = 1.5$, 5 K	$x = 1.0$, 300 K	$x = 1.0$, 5 K
a (Å)		3.8255(1)	3.8169(1)	3.8207(3)	3.8117(3)
c (Å)		27.7437(10)	27.6931(10)	27.7016(2)	27.6463(02)
V (Å ³)		406.01	403.45	404.30	401.65
$z_{\text{Sr/Ca}}(1)$, B_{iso}	4e	0.5732(2), 1.8	0.5729 (2), 2.1	0.5705(3), 1.8	0.5707(3), 2, 1
$z_{\text{Sr/Ca}}(2)$, B_{iso}	4e	0.7019(1), 2.0	0.7016(2), 2.5	0.7007(3), 2.1	0.7009(3), 2.5
$z_{\text{Mn/Fe}}(1)$, B_{iso}	2a	0, 0.70	0, 0.96	0, 0.54	0, 0.97
$z_{\text{Mn/Fe}}(2)$, B_{iso}	4e	0.1386 (5), 1.1	0.1385(5), 1.3	0.13882(3), 1.2	0.13870(3), 1.4
$z_{\text{O}}(1)$, B_{iso}	8g	0.1375(2), 1.0	0.1378(2), 1.0	0.13868(3), 1.0	0.13872(3), 1.0
$z_{\text{O}}(2)$, B_{iso}	4e	0.0688(2), 1.0	0.0686(2), 1.0	0.0681(6), 1.0	0.0682(4), 1.0
$z_{\text{O}}(3)$, B_{iso}	4e	0.2108 (2), 1.0	0.2108(2), 1.0	0.2105(4), 1.0	0.2103(13), 1.0
$z_{\text{O}}(4)$, B_{iso}	4c	0.5, 1.0	0.5, 1.0	0.5, 1.0	0.5, 1.0
R_p		6.68	7.66	11.0	10.7
R_{wp}		9.75	10.9	16.1	14.7
χ^2		10.2	12.6	14.1	12.6

Table 2
Selected bond lengths (Å) in $\text{CaSr}_3\text{Mn}_{1.5}\text{Fe}_{1.5}\text{O}_{10}$ and $\text{CaSr}_3\text{Mn}_2\text{FeO}_{10}$ at 300 and 5 K

	$x = 1.5, 300 \text{ K}$	$x = 1.5, 5 \text{ K}$	$x = 1.0, 300 \text{ K}$	$x = 1.0, 5 \text{ K}$
Mn1/Fe1-O2 $\times 2$	1.9088	1.8995	1.8868	1.8849
Mn1/Fe1-O4 $\times 4$	1.9128	1.9085	1.9103	1.9058
Mn2/Fe2-O1 $\times 4$	1.9130	1.9086	1.9104	1.9060
Mn2/Fe2-O2 $\times 1$	1.9365	1.9360	1.9588	1.9795
Mn2/Fe2-O3 $\times 1$	2.0003	2.0023	1.9857	1.9436

larger Fe^{3+} for smaller Mn^{4+} . The octahedral distortion coordinate D , defined as $D = (\text{Mn-O}_{\text{apical}})/(\text{Mn-O}_{\text{equatorial}})$, of outer perovskite layer was 1.03 for $x = 1.5$ sample at room temperature which is larger than $D = 1.02$ reported in $\text{Sr}_4\text{Mn}_2\text{FeO}_{9.8}$ [8]. The unit cell volume of the samples contract isotropically on cooling and octahedral distortion coordinate does not change significantly. Neither of the neutron diffraction pattern recorded at 5 K revealed any antiferromagnetic ordering.

The temperature dependence of the molar magnetic susceptibility and inverse magnetic susceptibility of $\text{CaSr}_3\text{Mn}_{1.5}\text{Fe}_{1.5}\text{O}_{10}$ and $\text{CaSr}_3\text{Mn}_2\text{FeO}_{10}$ phase are shown in Figs. 4 and 5, respectively. Magnetic susceptibilities of these phases qualitatively showed very similar behaviors with the $\text{Sr}_4\text{Mn}_{3-x}\text{Fe}_x\text{O}_{10-\delta}$ ^{8–10} and the $n = 2$ R–P phase $\text{Sr}_3\text{Fe}_{2-x}\text{Co}_x\text{O}_{7-\delta}$.¹²

$\text{CaSr}_3\text{Mn}_2\text{FeO}_{10}$ phase shows a local maximum at 87 K which is typical of two dimensional antiferromagnetic ordering. But in $\text{CaSr}_3\text{Mn}_{1.5}\text{Fe}_{1.5}\text{O}_{10}$ phase, this local maximum is not observed. This implies that tendency for antiferromagnetic ordering decreases as the amount of Fe increase. The parameters derived by fitting the curve to a Curie–Weiss Law are $\theta = -24.2 \text{ K}$ and $C = 8.12$ for $x = 1.5$ and $\theta = -8.1 \text{ K}$ and $C = 7.56$ for $x = 1.0$. Both of the samples show divergence in ZFC and FC curves. ZFC susceptibility curve shows $T_g = 12 \text{ K}$ for $x = 1.0$ and $T_g = 25 \text{ K}$ for $x = 1.5$ sample. The divergence of ZFC and FC means that these triple R–P phases reveal spin glass transitions, which are also consistent with the absence of magnetic

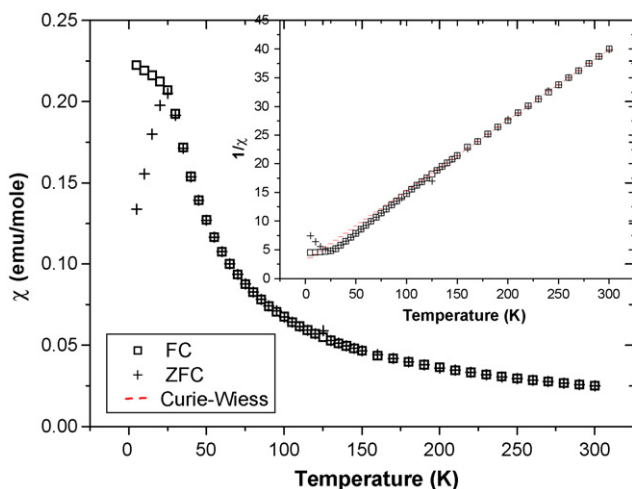


Fig. 4. The temperature dependence of the molar magnetic susceptibility and inverse magnetic susceptibility of $\text{CaSr}_3\text{Mn}_{1.5}\text{Fe}_{1.5}\text{O}_{10}$.

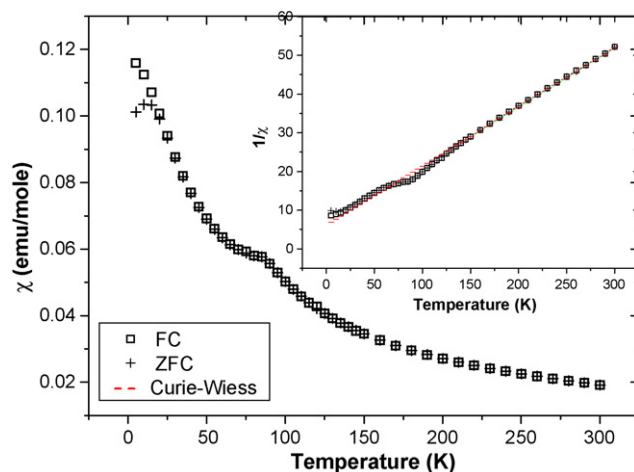


Fig. 5. The temperature dependence of the molar magnetic susceptibility and inverse magnetic susceptibility of $\text{CaSr}_3\text{Mn}_2\text{FeO}_{10}$.

super reflection from the neutron diffraction data collected at 5 K. This is typical of spin–glass type behavior seen in other R–P phase.^{8–10}

4. Conclusions

Triple layer Ruddlesden–Popper manganese phases $\text{CaSr}_3\text{Mn}_{3-x}\text{Fe}_x\text{O}_{10}$ ($x = 1.5, 1.0$) were synthesized by double substitution of both Sr and Mn site with Ca and Fe with conventional solid state reaction. The structural parameters of triple layer R–P phases $\text{CaSr}_3\text{Mn}_{1.5}\text{Fe}_{1.5}\text{O}_{10}$ and $\text{CaSr}_3\text{Mn}_2\text{FeO}_{10}$ have been refined by Rietveld method with room temperature and 5 K neutron diffraction data on the basis of space group $I4/mmm$.

Neutron diffraction patterns obtained at 5 K did not show any magnetic reflection. The temperature dependence of the ZFC and FC molar magnetic susceptibility curves show divergence at 12–25 K which implies that these triple layer R–P phase reveal spin–glass transitions.

Acknowledgements

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