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Various Valence States of Square-Coordinated Mn in A-Site-Ordered Perovskites

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Abstract: A-site-ordered perovskites $LaMn_3Cr_4O_{12}$ and $LaMn_3Ti_4O_{12}$ were synthesized under high-pressure and high-temperature conditions. The charge formula of $LaMn_3Cr_4O_{12}$ was found to be $LaMn^{3+}{}_3Cr^{3+}{}_4O_{12}$ with Mn^{3+} at the square-coordinated A site. The valence of the A-site Mn ions in $LaMn_3Ti_4O_{12}$ appeared to be less than +2, and the charge combination in this compound seemed to be $LaMn^{1.67+}{}_3Ti^{4+}{}_4O_{12}$. Although the square-coordinated A site in A-site-ordered perovskites has been widely known to be occupied by Jahn−Teller active Mn^{3+}, the present results show that the valence of Mn at the A site can vary from +3 to possible +1.67.

1. Introduction

In a simple ABO_3 perovskite, when 75% of the A-site cations are substituted by another element, an A-site-ordered double perovskite with a chemical formula of $A'A_3B_4O_{12}$ can be formed. Many of the A-site-ordered perovskites crystallize with a cubic $Im\bar{3}$ structure as shown in Figure 1. The BO_6 octahedra in this structure are fairly rigid but significantly tilted, leading to the formation of square-planar coordinated AO_4 units. Unlike the originally 12-fold-coordinated A site in a simple ABO_3 perovskite, this square-planar A site can be occupied by transition metal ions. As a result, these perovskites have interesting physical properties due to the presence of A−A and/or A−B interactions in addition to the usual B−B interaction seen in simple perovskite materials.[1,2]

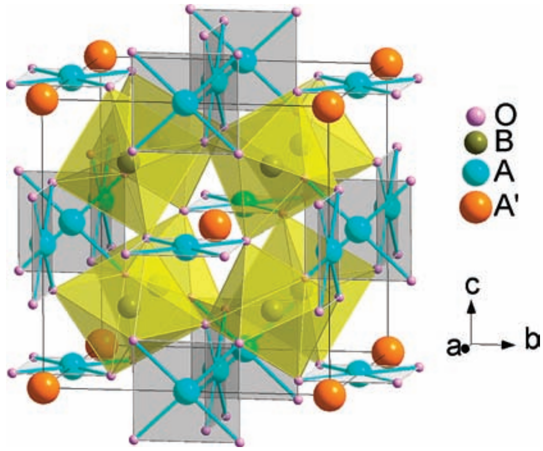

Figure 1. Crystal structure of A-site-ordered $A'A_3B_4O_{12}$ perovskite with $Im\bar{3}$ symmetry.

In $A'Cu_3Mn_4O_{12}$ (A′ = Ca, La, or Bi), for instance, high-temperature ferrimagnetic transitions due to the antiferromagnetic couplings between the spins at A-site Cu and B-site Mn were observed above room temperature (RT).[3−6] One interesting phenomenon concerning A−B interaction is the Cu−Fe intersite charge transfer found in $LaCu_3Fe_4O_{12}$.[7] The low-temperature $LaCu^{3+}{}_3Fe^{3+}{}_4O_{12}$ phase with a very rare Cu^{3+} state at the A site changes to the high-temperature $LaCu^{2+}{}_3Fe^{3.75+}{}_4O_{12}$ phase at 393 K, accompanying drastic changes in structural, magnetic, and transport properties. A similar intersite charge transfer was recently found in $BiCu_3Fe_4O_{12}$ but it occurs at a higher temperature, 428 K.[8] The energy levels of the high oxidation states of Cu^{3+} and $Fe^{3.75+}$ are comparable, and the delicate balance between the two states induce this unusual A−B intersite charge transfer when the temperature increases.

It has been widely known that Jahn−Teller active ions like Cu^{2+} and Mn^{3+} can be accommodated into the square-coordinated A site in the A-site-ordered perovskites,[3−6,9−13] and the results obtained with $La/BiCu_3Fe_4O_{12}$ have shown that the

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† Kyoto University.

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(1) Vasil'ev, A. N.; Volkova, O. S. *Low Temp. Phys.* **2007**, *33*, 895–914.

(2) Shimakawa, Y. *Inorg. Chem.* **2008**, *47*, 8562–8570.

(3) Zeng, Z.; Greenblatt, M.; Subramanian, M. A.; Croft, M. *Phys. Rev. Lett.* **1999**, *82*, 3164–3167.

(4) Weht1, R.; Pickett, W. E. *Phys. Rev. B* **2001**, *65*, 014415.

(5) Alonso, J. A.; Sánchez-Benítez, J.; De Andrés, A.; Martínez-Lope, M. J.; Casais, M. T.; Martínez, J. L. *Appl. Phys. Lett.* **2003**, *83*, 2623–2625.

(6) Takata, K.; Yamada, I.; Azuma, M.; Takano, M.; Shimakawa, Y. *Phys. Rev. B* **200776**; 024429.

(7) Long, Y. W.; Hayashi, N.; Saito, T.; Azuma, M.; Muranaka, S.; Shimakawa, Y. *Nature* **2009**, *458*, 60–63.

(8) Long, Y. W.; Saito, T.; Tohyama, T.; Oka, K.; Azuma, M.; Shimakawa, Y. *Inorg. Chem.* **2009**, *48*, 8489–8492.

(9) Shimakawa, Y.; Shiraki, H.; Saito, T. *J. Phys. Soc. Jpn.* **2008**, *77*, 113702.

(10) Bochu, B.; Chenavas, J.; Joubert, J. C.; Marezio, M. *J. Solid State Chem.* **1974**, *11*, 88–93.

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unusual Cu^{3+} state can also be stabilized at this special site. In the present study, we synthesized new A-site-ordered perovskites $LaMn_3Cr_4O_{12}$ (LMCO) and $LaMn_3Ti_4O_{12}$ (LMTO) and found that the valence state of Mn at the A site in LMCO is +3. The average valence state of Mn in LMTO, in contrast, seems to be less than +2, probably close to an unusual +1.67. In this paper we also discuss the magnetic behaviors related to A-site Mn spins.

2. Experimental Section

The A-site-ordered perovskites $LaMn_3Cr_4O_{12}$ and $LaMn_3Ti_4O_{12}$ were prepared by solid state reactions at high pressure and high temperature. A cubic anvil-type high-pressure apparatus was used for the reactions. The six anvils, which are made of a superhard sintered tungsten carbide alloy, synchronously compress the samples three-dimensionally through a pyrophyllite medium.[2,14] Finely mixed La_2O_3, Mn_2O_3, and either Cr_2O_3 or Ti_2O_3 in 1:3:4 molar proportions were treated at 8−10 GPa and 1273 K for 30 min.

For phase identification and structure analysis, synchrotron X-ray diffraction (SXRD) measurements with a 0.01° resolution were made at RT at beamline BL02B2 in SPring-8. Each sample was packed into a glass capillary with an inner diameter of 0.2 mm and was rotated during the measurement. The GSAS program was used to refine the structural parameters by the Rietveld method.[15]

The oxidization states of transition metal ions were investigated in X-ray absorption spectroscopy (XAS) measurements made at RT by a total electron yield method at BL27SU in SPring-8. The incident photon energy was calibrated by measuring the energies of the Ti-$L_{2,3}$ edges of TiO_2 and the Ni-$L_{2,3}$ edges of NiO. The energy resolution was ~0.1 eV.

A commercial superconducting quantum interference device magnetometer was used to measure magnetic susceptibility in zero-field-cooled and field-cooled modes between 2 and 300 K under an applied field of 0.1 T, and a physical property measurement system was used to collect specific heat data on cooling from 200 to 2 K at zero magnetic field. Resistivity was measured using a conventional method.

3. Results and Discussion

SXRD patterns for LMCO and LMTO are shown in Figure 2, and both compounds were found from the diffraction data to crystallize in the A-site-ordered perovskite structure with a cubic space group of $Im\bar{3}$. The refined structure parameters are listed in Table 1. Although it is difficult to detect mutual substitution between the A- and B-site transition metal ions from the SXRD data, no anomaly was observed in the occupation parameters at any sites and full occupancy was confirmed even for the oxygen site. Thus, these two ordered perovskites should have stoichiometric compositions.

Comparing the structural parameters between LMCO and LMTO, one sees that the lattice constant changes by only 2.5% but the shortest Mn−O bond lengths in MnO_4 units differ by 11.8%. This significant difference in the Mn−O distances strongly suggests that the valence states of the square-coordinated Mn cations differ between LMCO and LMTO. Bond valence sums (BVS)[16,17] calculated from the structural data clearly show the suggested discrepancy: in LMCO the calculated valences of Mn and Cr are both close to +3 (+2.74 and 2.89, respectively), whereas in LMTO the calculated

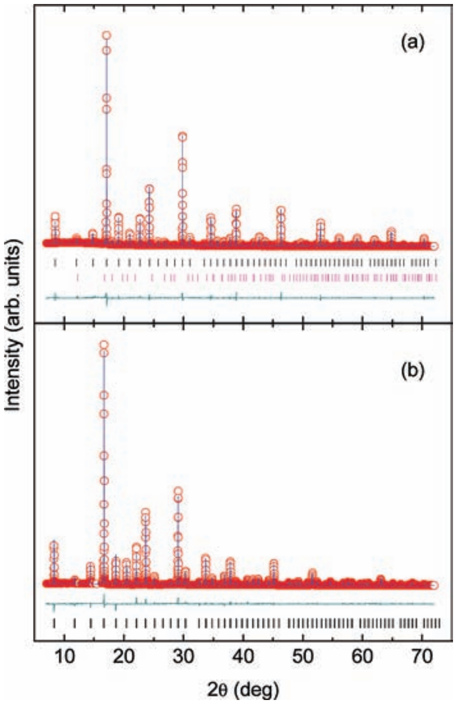

Figure 2. SXRD patterns and the structure refinement results for (a) LMCO and (b) LMTO. The observed (circles), calculated (line), and difference (bottom line) were shown. The ticks indicate the allowed Bragg reflections. For LMCO, a small amount of Cr_2O_3 impurity (4.2 wt %) was found. For LMTO, a few weak diffraction peaks from unknown impurities were excluded in the refinement.

Table 1. Refinement Structure Parameters of LMCO and LMTO and the BVS Values for Mn, Ti, and Cr[a,b]

	LMCO	LMTO
a (Å)	7.39832(3)	7.58175(6)
Z	2	2
V (Å^3)	404.948(5)	435.82(1)
O_x	0.3103(4)	0.2960(3)
O_y	0.1769(4)	0.1961(3)
U_{iso} (La) (100 × Å^2)	0.30(2)	0.40(2)
U_{iso} (Mn) (100 × Å^2)	0.36(2)	4.39(6)
U_{iso} (Cr/Ti) (100 × Å^2)	0.08(2)	0.51(3)
U_{iso} (O) (100 × Å^2)	0.22(7)	1.3 (1)
Mn−O (×4) (Å)	1.919(3)	2.145(2)
(×4) (Å)	2.772(5)	2.775(4)
(×4) (Å)	3.140(5)	3.216(4)
Cr/Ti−O (×6) (Å)	1.978(1)	1.9701(7)
BVS(Mn)	2.74	1.77
BVS(Cr/Ti)	2.89	3.95
R_{wp} (%)	6.72	7.90
R_p (%)	4.95	5.92

[a] The BVS values (V_i) were calculated using the formula $V_i = \Sigma_j S_{ij}$, and $S_{ij} = \exp[(r_0 - r_{ij})/0.37)]$. In LMCO, $r_0 = 1.708$ for Cr and 1.732 for Mn. In LMTO, $r_0 = 1.815$ for Ti and 1.765 for Mn. For the B-site Cr and Ti, 6-coordinated oxygen atoms were used. For the A-site Mn, 12-coordinated oxygen atoms were used. [b] Space group: $Im\bar{3}$; Atomic sites: La $2a(0, 0, 0)$, M_n $6b(0, 0.5, 0.5)$, Cr/Ti $8c(0.25, 0.25, 0.25)$, O $24g(x, y, 0)$.

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(11) Bochu, B.; Buevoz, J. L.; Chenavas, J.; Collomb, A.; Joubert, J. C.; Marezio, M. *Solid State Commun.* **1980**, *36*, 133–138.

(12) Prodi, A.; Gilioli, E.; Gauzzi, A.; Licci, F.; Marezio, M.; Bolzoni, F.; Huang, Q.; Santoro, A.; Lynn, J. W. *Nat. Mater.* **2004**, *3*, 48–52.

(13) Imamura, N.; Karppinen, M.; Motohashi, M.; Fu, D.; Itoh, M.; Yamauchi, H. *J. Am. Chem. Soc.* **2008**, *130*, 14948–14949.

(14) Takano, M.; Takeda, Y.; Ohtaka, O. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; John Wiley & Sons: Chichester, 1994; Vol. 3, p 1372.

(15) Larson, A. C.; von Dreele, R. B. General Structure Analysis System (GSAS). Report No. LAUR 86-748 (Los Alamos National Laboratory, 1994).

(16) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244–247.

(17) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192–197.

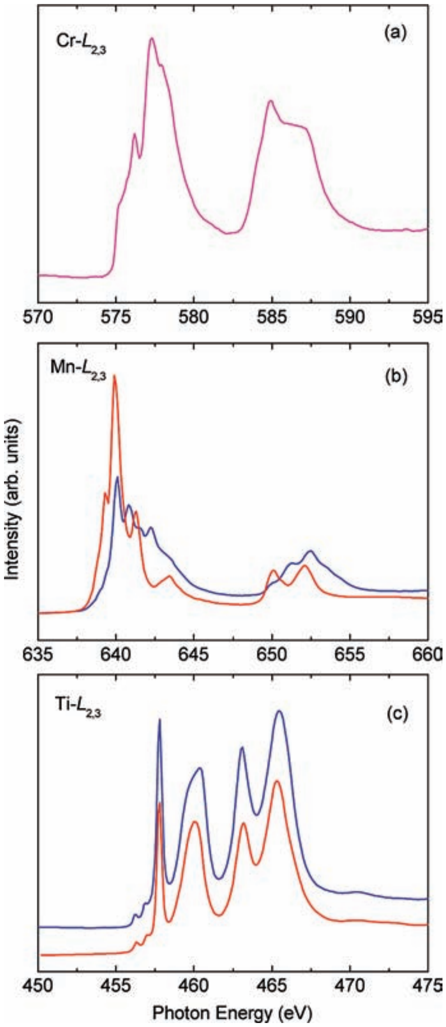

Figure 3. XAS spectra of (a) Cr-$L_{2,3}$ edges of LMCO, (b) Mn-$L_{2,3}$ edges of LMCO (blue) and LMTO (red), and (c) Ti-$L_{2,3}$ edges of LMTO (red) and $CaCu_3Ti_4O_{12}$ (blue).

valences of Mn and Ti are respectively +1.77 and +3.95 (Table 1). If we assume stoichiometric compositions, the BVS results indicate that the charge combination should be $La^{3+}Mn^{3+}{}_3Cr^{3+}{}_4O^{2-}{}_{12}$ for LMCO and $La^{3+}Mn^{1.67+}{}_3Ti^{4+}{}_4O^{2-}{}_{12}$ for LMTO.

The XAS spectra near the transition metal $L_{2,3}$ edges give useful information about the valence states of cations. As shown in Figure 3a, the observed spectrum of Cr-$L_{2,3}$ edges in LMCO is very similar to that observed in $CrFe_2O_4$ with octahedrally coordinated Cr^{3+},[18] suggesting that the valence of the B-site Cr in LMCO is +3. Although there is no reported XAS result for Mn in a square-planar coordination by oxygen atoms, the Mn-*L* absorption edge energy of LMCO (Figure 3b) seems to be similar to that observed in $NdMnO_3$ with Mn^{3+}.[19] These results are consistent with the structural analysis suggesting that the charge formula is $LaMn^{3+}{}_3Cr^{3+}{}_4O_{12}$. On the other hand, as shown in Figure 3c, the spectrum near the Ti-$L_{2,3}$ edges of LMTO is quite similar to that of the isostructural $CaCu_3Ti_4O_{12}$ with Ti^{4+} at the B site, which indicates that the valence of Ti in LMTO is +4. Interestingly, the observed Mn-$L_{2,3}$ XAS spectrum of LMTO is essentially different from that of LMCO, and the absorption edge energy in LMTO apparently shifts toward lower energy (Figure 3b). These results imply that the valence of the A-site Mn in LMTO is less than +3. Indeed, the observed Mn-$L_{2,3}$ spectrum of LMTO looks similar to the reported spectrum of MnO with Mn^{2+} even though the coordination environments of Mn are different in these two compounds.[20,21] Therefore, the valence of Mn in LMTO appears to be close to +2. This is also in agreement with the $LaMn^{1.67+}{}_3Ti^{4+}{}_4O_{12}$ charge combination obtained from the BVS calculations.

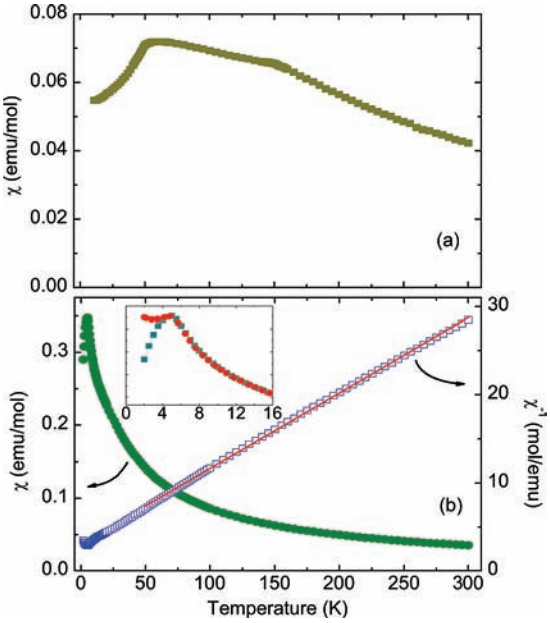

Figure 4. Temperature dependence of susceptibility χ of (a) LMCO and (b) LMTO. In (b), temperature dependence of χ^{-1} and the result of Curie–Weiss fitting (line) are also shown. The inset of (b) shows zero-field-cooled (squares) and field-cooled (circles) susceptibility curves at low temperature.

All the results of structural analysis and XAS measurements strongly suggest that the valence of Mn at the A site can vary from +3 in LMCO to most probably +1.67 in LMTO. Although the square-planar coordinated A site has been thought to be occupied by Jahn–Teller active Mn^{3+}, the present results clearly show that it can also be occupied by Mn ions with a lower oxidation state. It is interesting to note that in LMTO the charge combination $LaMn^{3+}{}_3Ti^{3+}{}_4O_{12}$ expected from the starting materials (Mn_2O_3 and Ti_2O_3) cannot be produced. Another possible charge combination, $LaMn^{2+}{}_3Ti^{3.75+}{}_4O_{12}$, also seems to be ruled out. Although many of the transition metal perovskite oxides with mixed valence ions at the B site exhibit conducting properties,[22] the present LMTO shows an insulating behavior with high electrical resistivity (>10^7 Ω·cm below RT), revealing the single tetravalent state of the B-site Ti ions. LMCO with Mn^{3+} and Cr^{3+} is also an insulator.

The magnetic behaviors of LMCO and LMTO are of special interest because these compounds contain magnetic Mn ions at the A site. As shown in Figure 4a, two magnetic transitions are

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(18) Mizumaki, M.; Agui, A.; Saitoh, Y.; Nakazawa, M.; Matsushita, T. *Surf. Rev. Lett.* **2002**, *9*, 849–853.

(19) Liu, R. S.; Wu, J. B.; Chang, C. Y.; Lin, J. G.; Huang, C. Y.; Chen, J. M.; Liu, R. G. *J. Solid State Chem.* **1996**, *125*, 112–115.

(20) Ghiringhelli, G.; Matsubara, M.; Dallera, C.; Fracassi, F.; Tagliaferri, A.; Brookes, N. B.; Kotani, A.; Braicovich, L. *Phys. Rev. B* **2006**, *73*, 035111.

(21) Mitra, C.; Hu, Z.; Raychaudhuri, P.; Wirth, S.; Csiszar, S. I.; Hsieh, H. H.; Lin, H.-J.; Chen, C. T.; Tjeng, L. H. *Phys. Rev. B* **2003**, *67*, 092404.

(22) Imada, M.; Fujimori, A.; Tokura, Y. *Rev. Mod. Phys.* **1998**, *70*, 1039–1263.

found in LMCO at approximately 150 and 50 K, respectively. Two magnetic transitions were also observed in the A-site-ordered perovskites $LaMn_3Mn_4O_{12}$ and $BiMn_3Mn_4O_{12}$.[13,23,24] In $LaMn_3Mn_4O_{12}$, the antiferromagnetic transition due to the ordering of the B-site Mn^{3+} spins occurs at 76 K and the antiferromagnetic transition due to the ordering of the A-site Mn^{3+} spins occurs at 20 K. In $BiMn_3Mn_4O_{12}$, the ferromagnetic ordering of B-site Mn^{3+} spins occurs at 59 K and the antiferromagnetic ordering of A-site Mn^{3+} spins occurs at 28 K. By analogy from these results, the two transitions in LMCO should correspond to independent magnetic orderings of the A-site spins and the B-site spins. This is in sharp contrast to the ferrimagnetic ordering of $LaCu_3Mn_4O_{12}$, in which the A-site Cu spins and the B-site Mn spins couple simultaneously.[5] We note here that the simple perovskite $YCrO_3$ shows antiferromagnetic ordering at 146 K through the B-site $Cr^{3+}-O-Cr^{3+}$ antiferromagnetic superexchange interactions.[25] Considering that the Cr−O−Cr bond angle in LMCO (139°) is comparable to the average Cr−O−Cr bond angle in $YCrO_3$ (146°),[26] the magnetic transition at ~150 K in LMCO should be attributed to the antiferromagnetic ordering of the B-site Cr^{3+} spins. The slightly higher transition temperature in LMCO with regard to that in $YCrO_3$ may be related to the shorter Cr−O bond lengths in LMCO. Consequently, the transition at a lower temperature (~50 K) in LMCO should be due to the antiferromagnetic ordering of the A-site Mn^{3+} spins.[27] Two sharp λ-type anomalies at approximately 150 and 50 K in the specific heat measurement shown in Figure 5a confirm the long-range orderings of the spins, agreeing with the results of magnetic measurements.

In LMTO, on the other hand, there is only one magnetic transition at ~5 K (Figure 4b). Below the transition temperature, the zero-field-cooled and field-cooled susceptibility curves differ considerably and the field-cooled data are almost constant (inset of Figure 4b). And in the specific heat measurement a broad peak instead of a λ-type anomaly appears near the magnetic transition temperature (Figure 5b). All these features are typical characteristics of spin-glass-like behavior.[28] Because the B-site Ti^{4+} is nonmagnetic, this transition should be ascribed to the A-site Mn spins. The inverse magnetic susceptibility of LMTO above the transition temperature (Figure 4b) obeys the Curie−Weiss law, and the fitted Weiss constant is negative (−35.3 K). The effective moment (5.58 μ_B/Mn) obtained from the fit is close to but a little lower than the theoretical value for a Mn^{2+} spin (5.92 μ_B/Mn) with a high spin configuration. Given that the mixed $Mn^{1.67+}$ in LMTO is composed of Mn^{2+} and Mn^{+} ($3Mn^{1.67+} = 2Mn^{2+} + Mn^{+}$), the spin-glass-like magnetic behavior of LMTO can be understood by a random distribution of the aliovalent Mn ions with different spins giving rise to a random distribution of ferromagnetic and antiferromagnetic interactions between them. Therefore, the observed magnetic behavior also suggests the presence of the anomalous mixed valence of Mn which is less than +2 at the square-planar coordinated A site. In other words, the observed single magnetic transition also supports the $LaMn^{1.67+}{}_3Ti^{4+}{}_4O_{12}$ charge formula with the single tetravalent Ti at the B site.

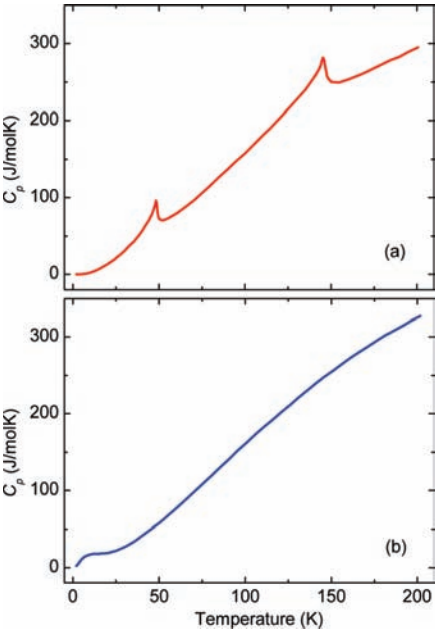

Figure 5. Temperature dependence of specific heat C_p of (a) LMCO and (b) LMTO.

In conclusion, two new A-site-ordered perovskite structure oxides, $LaMn_3Cr_4O_{12}$ and $LaMn_3Ti_4O_{12}$, were prepared by using high-pressure synthesis. The BVS calculations from the structural analysis and the XAS results revealed that LMCO has Jahn−Teller active Mn^{3+} ions at the square-coordinated A site and Cr^{3+} ions at the B site. This means that its charge formula is $LaMn^{3+}{}_3Cr^{3+}{}_4O_{12}$. Two independent antiferromagnetic transitions were observed: one at 150 K due to the B-site Cr^{3+} spin ordering and the other at 50 K due to the A-site Mn^{3+} spin ordering. The BVS and XAS results for LMTO, on the other hand, strongly suggest that the valence state of Mn at the A site is close to or less than +2 and that the valence state of Ti at the B site is close to +4. The highly resistive insulating property and the spin-glass-like magnetic behavior with a single transition are consistent with the expected properties of the A-site mixed valence state of $Mn^{1.67+}$ and the B-site single tetravalent state of Ti^{4+}. Thus, the most probable charge composition of LMTO is $LaMn^{1.67+}{}_3Ti^{4+}{}_4O_{12}$ with the unusual Mn ions at the square-planar A site.

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(23) Prodi, A.; Allodi, G.; Gilioli, E.; Licci, F.; Marezio, M.; Bolzoni, F.; Gauzzi, A.; De Renzi, R. *Physica B* **2006**, *55*, 374–375.

(24) Mezzadri, F.; Calestani, G.; Calicchio, M.; Gilioli, E.; Bolzoni, F.; Cabassi, R.; Marezio, M.; Migliori, A. *Phys. Rev. B* **2009**, *79*, 100106.

(25) Serrao, C. R.; Kundu, A. K.; Krupanidhi, S. B.; Waghmare, U. V.; Rao, C. N. R. *Phys. Rev. B* **2005**, *72*, 220101.

(26) Ramesha, K.; Llobet, A.; Proffen, Th.; Serrao, C. R.; Rao, C. N. R. *J. Phys.: Condens. Matter* **2007**, *19*, 102202.

(27) Similar magnetic results in LMCO were presented by I. Yamada at the meeting of the Phys. Soc. Jpn. (Tokyo, March 2009). Two transitions, the B-site Cr^{3+} magnetic transition at 150 K and the A-site Mn^{3+} magnetic transition at 50 K, were confirmed by Mössbauer spectroscopy measurements. The results are consistent with our model.

(28) Binder, K.; Young, A. P. *Rev. Mod. Phys.* **1986**, *58*, 801–976.