



Temperature and Magnetic Field Dependence of the Coexistent Phases in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_{3+\delta}$ ($x = 0.47, 0.49$)

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X-ray diffraction measurements under high and low temperature, and magnetic field have been performed for the doped $\text{La}_{1-x}\text{Ca}_x\text{MnO}_{3+\delta}$ polycrystals to clarify the coexistent phases and their structures around the composition of $x \sim 0.5$. By measurements at high temperature, the transition from a $Pnma$ to an $Imma$ space group symmetry phase has been firstly observed in this system at the temperature between 500°C and 600°C. At low temperature, the importance of the measurement of (131) reflection is noticed and the phase fraction of two similar $Pnma$ phases with ferromagnetic and anti-ferromagnetic states is determined. It is found that the application of the magnetic field by 5 T and the slight change of the composition x by 0.02 remarkably affect this phase fraction.

KEYWORDS: X-ray diffraction, manganites, perovskites, CMR, $Pnma$, $Imma$

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1. Introduction

Since the discovery of a very large negative magnetoresistance (CMR) in various perovskite manganites with the chemical formula $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ (R = trivalent rare earth element and A = alkaline earth element),^{1–3} strong interest in these manganites has been attracted owing to their potential for the technological applications. The physical properties are very complicated; they are related with the charge ordering of Mn^{+3} and Mn^{+4} ions,⁴ orbital and spin ordering of 3d electrons,⁵ and the strong electron-ion interaction manifested by Jahn–Teller lattice distortion.⁶ Among these manganites, the investigation for the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (LCMO) system has a long history, started from Jonker and van Santen⁷ more than 50 years ago. Figure 1 shows a phase diagram of the LCMO system presented by Fujishiro *et al.*⁸ The LCMO system exhibits a transition from a paramagnetic insulator (PM-I) to a ferromagnetic metal (FM-M) state upon cooling for the Ca concentration of $0.2 < x < 0.48$. For the higher doping range of $x > 0.5$, the ground state is an anti-ferromagnetic insulator (AFM-I) with the charge/orbital (CO) ordering. The composition discussed here is just the border of FM-M and AFM-I phases, showing the high sensitivity of phase stability to the external perturbation such as the magnetic field.⁹ The difficulty for study has further increased, because no one has succeeded in growing the single crystal around this composition of $x \sim 0.5$.

By the synchrotron X-ray and the neutron powder diffraction techniques, Radaelli *et al.*^{10,11} reported that the crystal structure at $x = 0.5$ could be described as a $Pnma$ symmetry above 190 K. At the temperature range between 190 K and 160 K, the unusual (202)–(040) doublet peak broadening was observed and suggested the models of a continuous distribution of lattice parameters with several maxima or a constitution of several phases more than two by applying Rietveld analysis. Huang *et al.*¹² have investigated

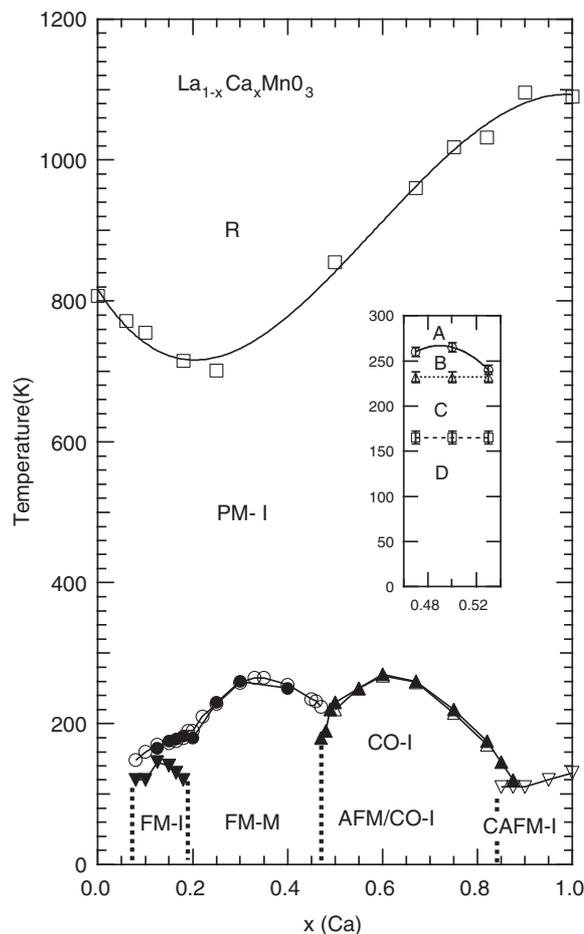


Fig. 1. The phase diagram of the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ system compiled by one of the authors.⁸ R means a high-temperature phase and the structure is identified to be an $Imma$ symmetry in this study, PM-I the paramagnetic insulator, FM-I the ferromagnetic insulator, FM-M the ferromagnetic metal, CO-I the charge ordered insulator, AFM/CO-I the anti-ferromagnetic/charge ordered insulator and CAFM-I the canted anti-ferromagnetic insulator, respectively. The inset showed the more detail diagram around $x \sim 0.5$ given by Huang *et al.*¹² Symbol A stands for PM-I (F-I), B for FM-M (F-I/FM), C for two-phase of FM-M and CO-I (A-II), D for two-phase of FM-M and AFM/CO-I (A-II/AFM), respectively where the symbols in the parenthesis are named by Huang *et al.*

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a similar problem in detail and proposed the phase diagram as shown the inset in Fig. 1. According to their Rietveld analysis, single-phase state with a $Pnma$ symmetry was realized around room temperature. On cooling, a second $Pnma$ symmetry phase appeared at 230 K, that coexisted with the $Pnma$ phase at room temperature and constituted a two-phase state below this temperature. Their start point for identification of two-phase state was based on the peak separation of (031) reflection from overlapping (211) and (112) ones. This analysis leaves some ambiguity because of the handling three peaks simultaneously. By our inspection in this LCMO system, we find a single peak in this complex diffraction pattern; this peak is found to be useful for the two-phase problem.

It is known that the $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ system takes an $Imma$ symmetry¹³⁾ as the high temperature phase. The $Imma$ structure has a higher symmetry than the $Pnma$ one and all the reflections of the $Imma$ phase should overlap to those of the $Pnma$ one if lattice parameters of both phases are identical. In reality, there may be a slight difference in lattice parameter, then the overlapped reflections will appear as broad peaks if both phases coexist. About the phase diagram above room temperature, one of the authors⁸⁾ described the phase boundary by the thermal diffusivity and the specific heat, although the structure designated as 'R' in Fig. 1 has not been determined.

In this paper, we will first examine the presence of the $Imma$ phase by utilizing high temperature X-ray diffraction. Secondly, we will treat the two-phase problem at low temperature and determine the phase fraction of ferromagnetic and anti-ferromagnetic $Pnma$ phases related to the magnetization. For this, we utilize the analysis other than the Rietveld method, and see the effect of slight change of composition x and the applied magnetic field for $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ around $x \sim 0.5$.

2. Materials and Methods

The $\text{La}_{1-x}\text{Ca}_x\text{MnO}_{3+\delta}$ ($x = 0.47, 0.49$) was prepared from stoichiometric mixtures of La_2O_3 , CaCO_3 and Mn_3O_4 powders.¹⁴⁾ The mixtures were calcined at 1000°C for 24 h in air, pressed into pellets and then sintered at 1500°C for 8 h in air. The densities of each sample were determined by measuring the volume and the weight; those were confirmed to be more than 85% of the ideal value. The deviation of oxygen content from the stoichiometry was measured by iodometric titration, suggesting that the estimated deviation is $\delta \sim 0.03$ for the present samples.

The X-ray diffraction data was collected using a combined system under low-temperature down to 8 K and magnetic field up to 5 T.¹⁵⁾ The X-ray source was a conventional $\text{CuK}\alpha$ radiation (40 kV \times 20 mA) using a curved graphite monochromator for detection of diffraction beam. For weak reflection like the (131) as described later for its significance, the sampling time was 700 s for each 0.04° step scan. For high-temperature X-ray diffraction, we measured only for composition $x = 0.49$, utilizing Philips X'pert-Pro diffractometer. The powdered sample was mixed with alcohol and pasted on Pt substrate. The sample temperature was increased up to 700°C by 100°C steps in air. The magnetization was measured by utilizing a superconducting quantum interference device (SQUID) magnetometer.

3. Results and Discussion

First, we treat of the structure of the high-temperature phase. The X-ray diffraction for the sample of composition $x = 0.49$ in air was tried. Figure 2(a) shows the comparison of diffraction patterns at 20°C and 700°C for a wide range scattering angle, and Fig. 2(b) shows the selected (131) reflection at various temperatures. The difference between the $Pnma$ and the $Imma$ symmetry is characterized by the extinction rule; if the parity of $h + k + l$ is odd, the reflection disappears for the $Imma$ symmetry, where h, k , and l are all non zero integer values. The (131) reflection peak remained at 500°C and then vanished at 600°C. In this way, the sample showed transformation from a $Pnma$ to an $Imma$ symmetry between 500°C and 600°C. The structural phase transformation recovered again after cooling to room temperature, as shown in Fig. 2(b). This transition corresponded to the observation at high temperature, as shown in Fig. 1. The Rietveld analysis was applied utilizing Rietan2000¹⁶⁾ for confirmation, as shown in Fig. 3. In this way, the existence of the $Imma$ phase of LCMO ($x = 0.49$) system has been

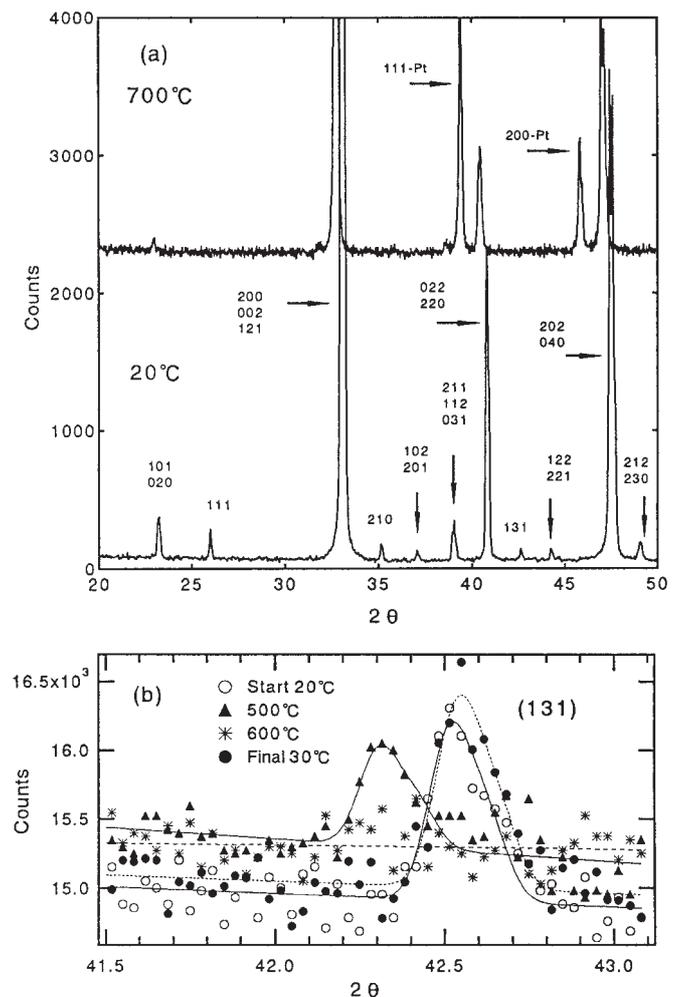


Fig. 2. X-ray diffraction results for the sample of composition $x = 0.49$. (a) The profiles at 20°C and 700°C. The Pt-substrate was used for the measurement at 700°C. (b) The (131) reflection profiles at various temperatures. The lines are least-squares fitting using the Gaussian function taking into consideration of $K\alpha_1$ and $K\alpha_2$ contributions. The disappearance of the diffraction peak can be seen at the temperature between 500°C and 600°C.

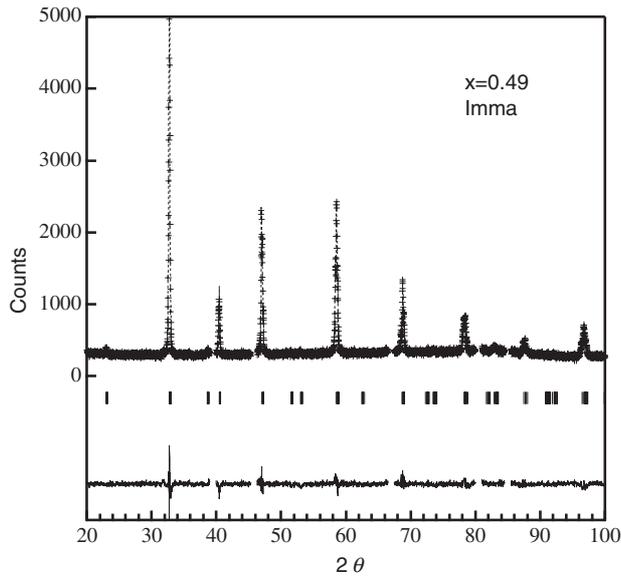


Fig. 3. The Rietveld analysis for the *Imma* phase at 700°C for the sample of composition $x = 0.49$. The diffraction due to the Pt substrate (five peaks) are excluded. The *R* weighted pattern (*Rwp*) and the goodness of fit (*S*) are 6.57% and 1.26 respectively. The obtained orthorhombic lattice parameter is $a = 5.4468 \pm 0.0002 \text{ \AA}$, $b = 7.6897 \pm 0.0003 \text{ \AA}$, and $c = 5.4665 \pm 0.0002 \text{ \AA}$. The errors obtained from the analysis may be under estimated values.

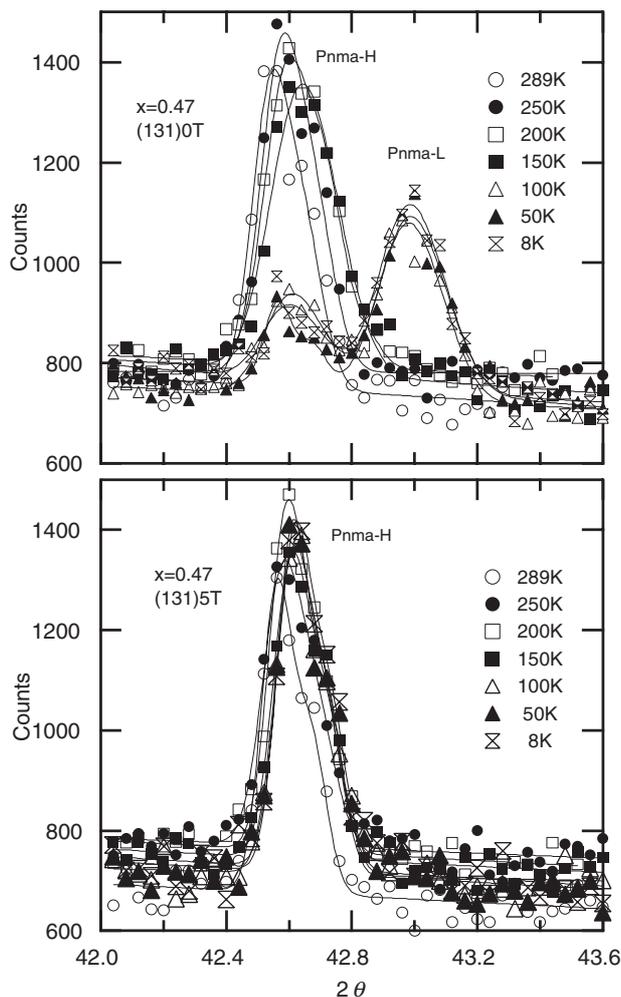


Fig. 4. Temperature dependence of (131) profiles under 0 T (top) and 5 T (bottom) fields for the sample of composition $x = 0.47$. The lines have the same meaning as those in Fig. 2(b).

settled for the first time.

Next, we treated the problem of the coexistent phases below room temperature. Although most of reflections were overlapped by some others by looking at the overall diffraction spectrum, we observed three exceptions, i.e., (111), (210) and (131) reflections, as seen from Fig. 2(a). Because of poor resolution for (111) and (210) due to lower angle positioning, we concentrated the attention only the (131) reflection and measured the profile change with temperature under the magnetic field. Figures 4 and 5 shows the (131) diffraction profiles with decreasing temperature for samples of $x = 0.47$ and $x = 0.49$ under the magnetic fields of 0 T and 5 T. Under zero field, it was observed that the *Pnma* single-phase state was realized around room temperature (named as *Pnma*-H). With decreasing temperature, the peak of the *Pnma*-H phase showed abrupt decrease between 150 K and 100 K. At a temperature below 100 K, the low-temperature *Pnma* single phase (named as *Pnma*-L) state realized for $x = 0.49$ as shown in Fig. 5. Under 5 T field, the *Pnma*-H single-phase state is well stabilized from room temperature down to 8 K for $x = 0.47$ as shown in Fig. 4. Figure 6 shows the phase fraction (*PH*/*PT*) of the *Pnma*-H to the total which was obtained from the $K\alpha_1$ peak integrated intensity of the (131) reflection assuming Gaussian profile,

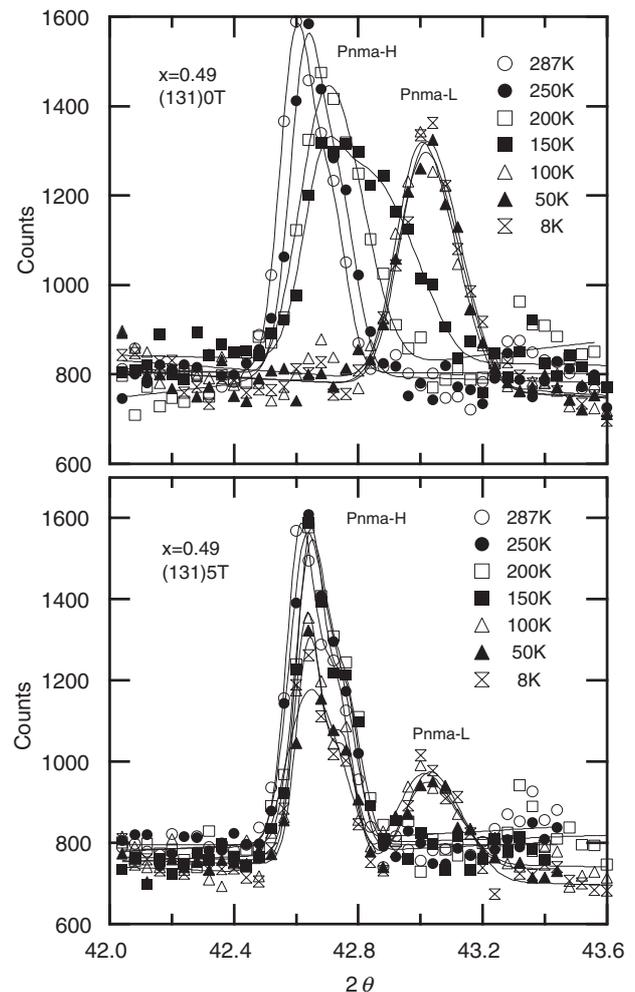


Fig. 5. Temperature dependence of (131) profiles under 0 T (top) and 5 T (bottom) for the sample of composition $x = 0.49$. The solid lines have the same meaning as Fig. 2(b).

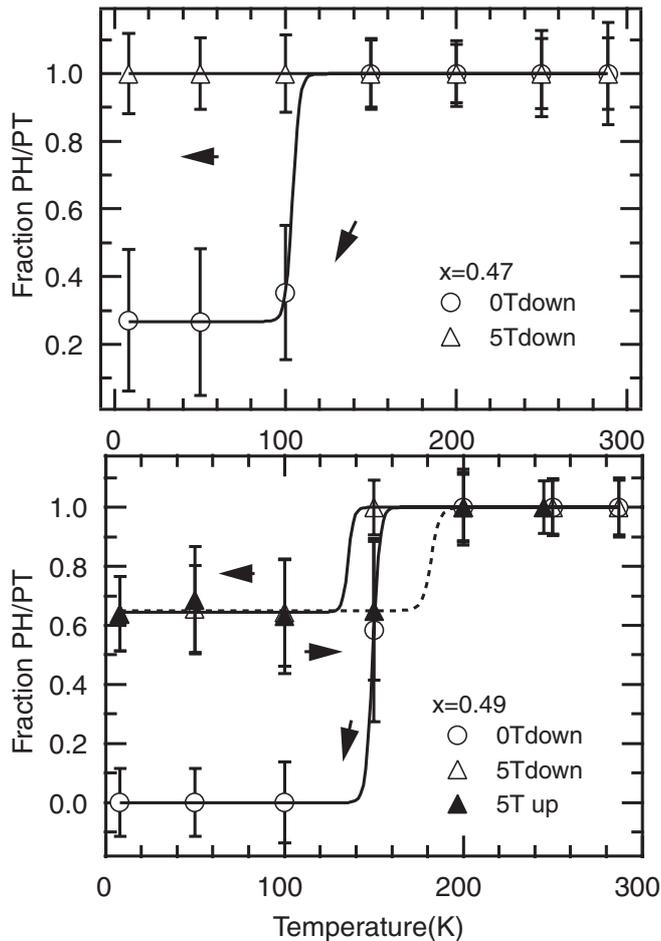


Fig. 6. The phase fraction (PH/PT) of the $Pnma$ -H (PH) phase to the total of the $Pnma$ one ($PT = Pnma\text{-H} + Pnma\text{-L}$) for compositions $x = 0.47$ and 0.49 . Open circles show the data without field and open triangles under the field of 5 T. The fraction obtained by warming under the field of 5 T is also shown by closed triangles for $x = 0.49$. For curve fitting of the data, the Sigmoid function is applied.

where PH stands for the fraction of $Pnma$ -H, PL does for $Pnma$ -L and PT does for the sum ($PT = PH + PL$). The above results are in contrast to those of Huang *et al.*;¹² they concluded that the two-phase state of the $Pnma$ -H and the $Pnma$ -L were realized below 230 K under zero field for compositions from $x = 0.47$ to 0.53 , as shown in the inset of Fig. 1.

For composition of $x = 0.49$, the measurement was repeated by temperature increase under 5 T, showing the hysteresis behavior. Similar hysteresis in the magnetic field was also observed for $x = 0.47$, where the single $Pnma$ -H state was realized at 8 K under magnetic field of 5 T. Then, removal of the field at 8 K did not recover the $Pnma$ -L phase at all.

Figure 7 shows the values of full width at half maximum (FWHM) for (131) reflection that are evaluated from the variance of the Gaussian profiles of $K\alpha_1$ component. From this figure, two points are generally acknowledged: the FWHM of the $Pnma$ -L phase was broader than that of $Pnma$ -H, and the FWHM of the $Pnma$ -H phase was more sharp under the field of 5 T than that under zero field. Since the FWHM reflects the domain size contributing to the reflection, the above two points are acceptable as follows: the domain size of the $Pnma$ -L phase was smaller than that of

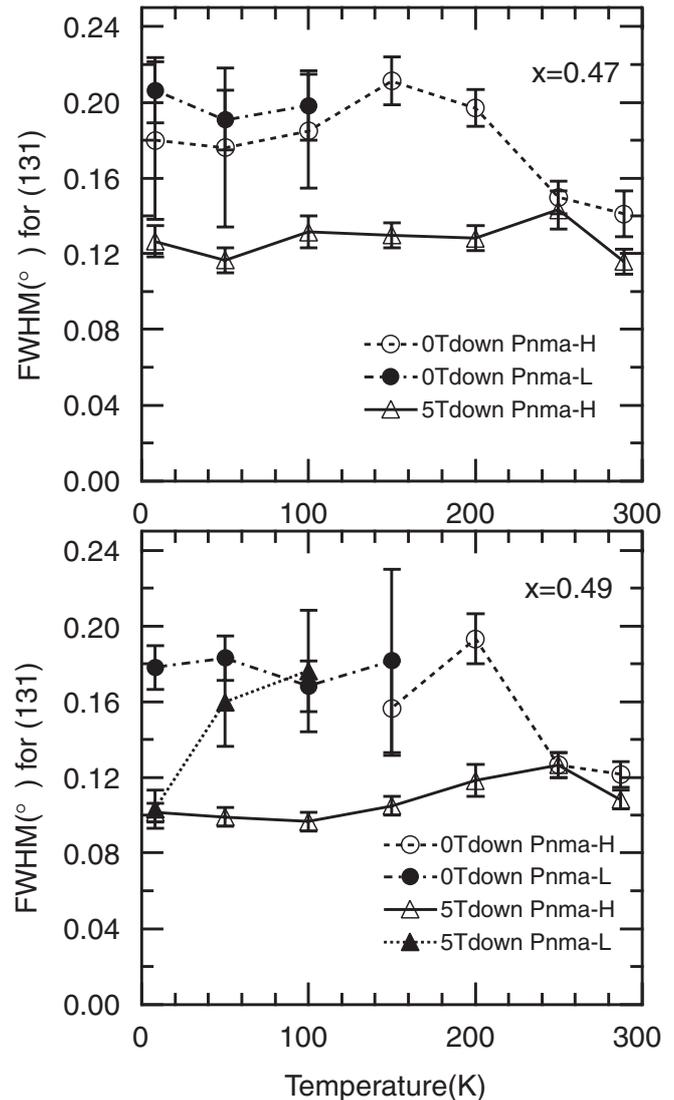


Fig. 7. The FWHM (Full width at half maximum) of the (131) reflection with decreasing the temperature under zero and 5 T fields for compositions $x = 0.47$ and $x = 0.49$. The two-phase region of the $Pnma$ -H and the $Pnma$ -L is recognized by an open and full symbol of the same shapes together at their respective temperatures.

the $Pnma$ -H, and the similar size of the $Pnma$ -H was larger under the magnetic field of 5 T than under zero field. Huang *et al.* reported the temperature dependence of FWHM values by utilizing (031) reflection of $Pnma$ -L phase (A-II by their designation). They showed the sharp decrease in the values of FWHM for $Pnma$ -L phase (or A-II) from 0.55° at 200 K to 0.32° at 160 K under zero field, suggesting a large increase of the domain size by this temperature decrease. In our case, the $Pnma$ -L (or A-II) phase was observed below 150 K and we could not find such a change in FWHM for composition of $x = 0.49$.

The temperature dependence of the magnetization for $x = 0.47$ and 0.49 samples under the field of 5 T are shown as Fig. 8. The general trend is in agreement with Fig. 6. For composition of $x = 0.47$, the magnetization showed the steady increase with decreasing temperature which agrees well with the fraction of PH/PT value under the field of 5 T. As for the composition of $x = 0.49$, the magnetization showed maximum at about 130 K, then decreased, which corresponded to the PH/PT in the cooling process. How-

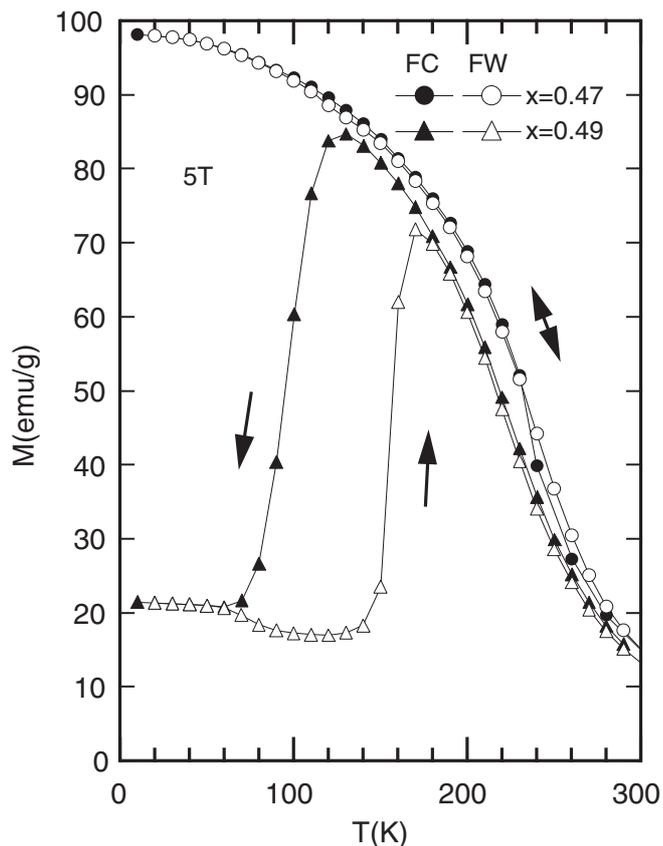


Fig. 8. Temperature dependence of the magnetization curve for compositions $x = 0.47$ and 0.49 under the field of 5 T. Solid symbols correspond to cooling (FC) and open ones correspond to warming (FW), respectively.

ever, there is a clear difference between the temperature of the minimum in magnetization and that of PH/PT for cooling process, i.e., the former is about 80 K while the latter is more than 100 K. This difference must be caused by a reason other than the phase fraction. Since the phase fraction PH/PT still keeps a high value at temperature below 100 K as shown in Fig. 6, it is supposed that the difference will be derived from the change of the magnetic ordering in this remnant $Pnma$ -H phase with decreasing temperature. In connection to this, we are now preparing the investigation using a single crystal for a similar perovskite manganite.

4. Summary

By application of the high temperature X-ray diffraction, the transformation of a $Pnma$ to an $Imma$ symmetry phase

was found in $La_{1-x}Ca_xMnO_3$ ($x = 0.49$) system at temperature between 500°C and 600°C. From the low temperature measurements under the magnetic fields of zero and 5 T, we determined the phase fraction of the ferromagnetic phase ($Pnma$ -H) to the total one with temperature change by utilizing the (131) reflection, and showed the usefulness of this method for the determination of the phase fraction.

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