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# Evidence of the $\text{Bi}^{3+}$ lone-pair effect on the charge-ordering state: resistivity and thermoelectric power of $\text{Bi}_{0.5-y}\text{La}_y\text{Sr}_{0.5}\text{MnO}_3$ ( $0.0 \leq y \leq 0.4$ )

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## Abstract

Polycrystalline samples of  $\text{Bi}_{0.5-y}\text{La}_y\text{Sr}_{0.5}\text{MnO}_3$  ( $0.0 \leq y \leq 0.4$ ) (BLSMO) have been synthesized to investigate the  $\text{Bi}^{3+}$  lone-pair effect on the long-range charge-ordering (CO) state. Since the ionic size of  $\text{La}^{3+}$  is similar to that of  $\text{Bi}^{3+}$  and the Mn valence state does not change with La doping, we obtained the Bi lone-pair effect on the CO state without disturbance by other effects. The resistivity  $\rho(T)$  and thermoelectric power  $S(T)$  of BLSMO have been measured. A hysteretic behaviour was observed in both  $\rho(T)$  and  $S(T)$  for  $y = 0.1$  and  $0.2$ . From the onset of the hysteretic behaviour, we defined a charge-ordering temperature ( $T_{\text{CO}}$ ) and compared it to that of  $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$  (BSMO). Finally, we found that the  $\text{Bi}^{3+}$  lone pairs play an important role in the anomalously high  $T_{\text{CO}}$  in BSMO.

## 1. Introduction

Charge-ordering (CO) phenomena occur through the interaction between charge carriers and phonons accompanied by orbital ordering and lattice distortion [1]. CO is considered as a spatially ordered distribution of  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ions in the lattice in a purely ionic picture [2]. In the CO state, carriers are localized, causing a long-range ordering throughout the crystal. CO behaviour is found in various compounds: in  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  [3, 4],  $\text{Pr}_{0.5}(\text{Sr}, \text{Ca})_{0.5}\text{MnO}_3$ ,  $\text{Nd}_{0.5}(\text{Sr}, \text{Ca})_{0.5}\text{MnO}_3$ ,  $\text{Sm}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  [5]. The charge-ordered state of these materials appears only below 300 K. The highest charge-ordering temperature ( $T_{\text{CO}}$ ) of around 500 K in  $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  has been reported [6–9]. It has been proposed that the anomalously high  $T_{\text{CO}}$  is related to the  $6s^2$  characteristic of  $\text{Bi}^{3+}$  which is highly polarized in a certain Bi–O

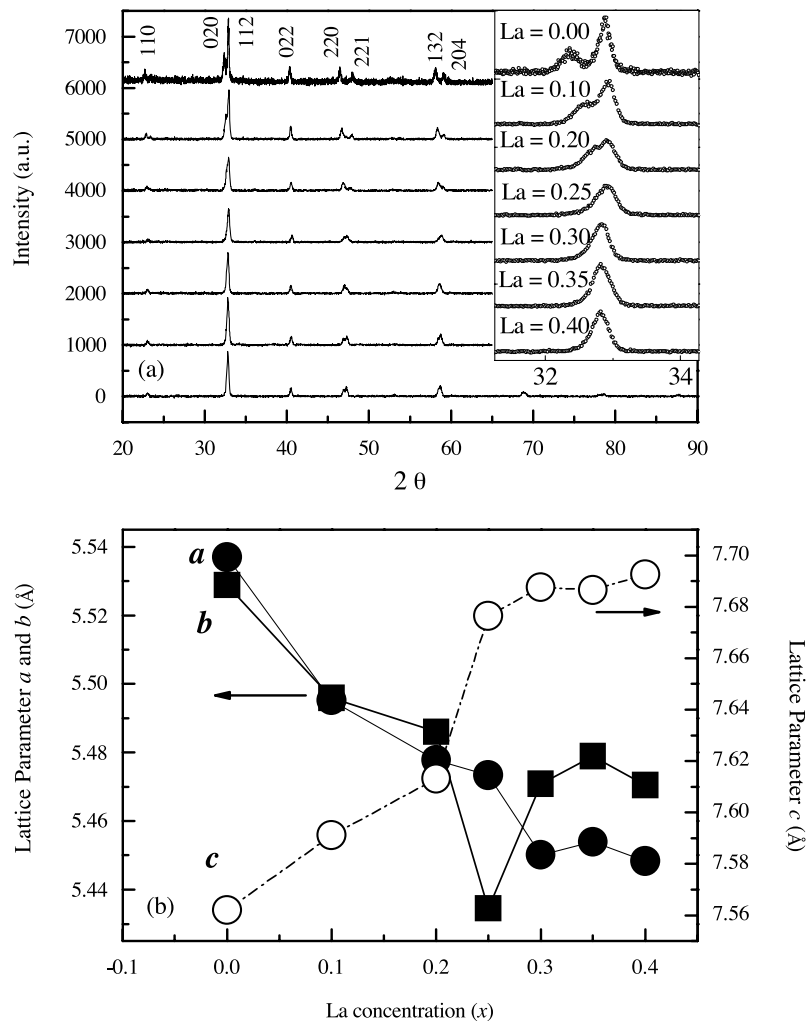
bond direction [6–8, 10]. Such an effect of the Bi lone pair manifests itself in the structure of  $\text{BiMnO}_3$ . The structure of  $\text{BiMnO}_3$  is distorted because of the shift of the bismuth cations from the centre of the hexagon of the oxide anions due to the lone pair of electrons on the bismuth cation [11]. Thus the additional lattice distortion due to the  $\text{Bi}^{3+}$  lone pairs is regarded as the origin of the extraordinarily high  $T_{\text{CO}}$  of divalent (Sr or Ca: A-site cation) doped  $\text{BiMnO}_3$ . The CO transition is a first-order phase transition whose general characteristic is a thermal hysteretic behaviour in the temperature dependence of transport measurement. In  $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$  (BSMO) the temperature range where the hysteresis occurs is more than 200 K. This thermal hysteresis range of BSMO is much larger than that of other charge-ordering materials (50–150 K) [12–15]. As the Sr concentration increases, the  $T_{\text{CO}}$  of BSMO shifts to lower temperature but the CO phase is maintained up to  $x = 0.8$  [8]. The change of the  $T_{\text{CO}}$  with doping may indicate that the  $\text{Bi}^{3+}$  lone pairs play an important role in the formation of the CO state. However, there is no direct evidence of the  $\text{Bi}^{3+}$  lone-pair effect on the CO state of BSMO because the change of the Mn valence state and the ionic size of the A-site cation affect the ground state of the manganite systems [1]; when the ionic size of the A-site cation is relatively small compared to the Mn–O bond length, the mobility of the itinerant  $e_g$  electrons is significantly suppressed due to the lattice distortion. In order to determine the  $\text{Bi}^{3+}$  lone-pair effect on the CO state of BSMO without other effects, it is necessary to substitute the  $\text{Bi}^{3+}$  ions with other trivalent cations of the same size as the  $\text{Bi}^{3+}$  ion. Since the  $\text{La}^{3+}$  ion has almost same ionic size as the  $\text{Bi}^{3+}$  ion and it does not affect the Mn valence state,  $\text{Bi}_{0.5-y}\text{La}_y\text{Sr}_{0.5}\text{MnO}_3$  ( $0.0 \leq y \leq 0.4$ ) (BLSMO) was synthesized and its resistivity and thermoelectric power (TEP) were measured in order to investigate the  $\text{Bi}^{3+}$  lone-pair effect on the charge-ordered state.

## 2. Experimental details

Polycrystalline samples of BLSMO were prepared by a conventional solid-state reaction method. The stoichiometric composition of high-purity ( $\geq 99.99\%$ )  $\text{Bi}_2\text{O}_3$ , SrO,  $\text{La}_2\text{O}_3$ , and  $\text{Mn}_2\text{O}_3$  powders were mixed, pelletized and calcined at  $850^\circ\text{C}$  in air for 10 h. These mixtures were thoroughly ground again, pelletized, and reheated at  $1050^\circ\text{C}$  in air for 12 h. Then the final sintering of the samples was done at  $1350^\circ\text{C}$  for 24 h followed by slow cooling. The annealing process was performed at  $1000^\circ\text{C}$  for 3 days in oxygen atmosphere. Each sample was characterized by x-ray diffraction (Bruker D5005, Germany) ( $\text{Cu K}\alpha$  radiation). Temperature-dependent resistivity was measured using the conventional four-probe method. For TEP measurements, a low-frequency AC steady-state method was used [16, 17]. X-ray absorption near edge structure (XANES) spectroscopy was performed at the 7C1 beam line in the Pohang Accelerator Laboratory.

## 3. Results and discussion

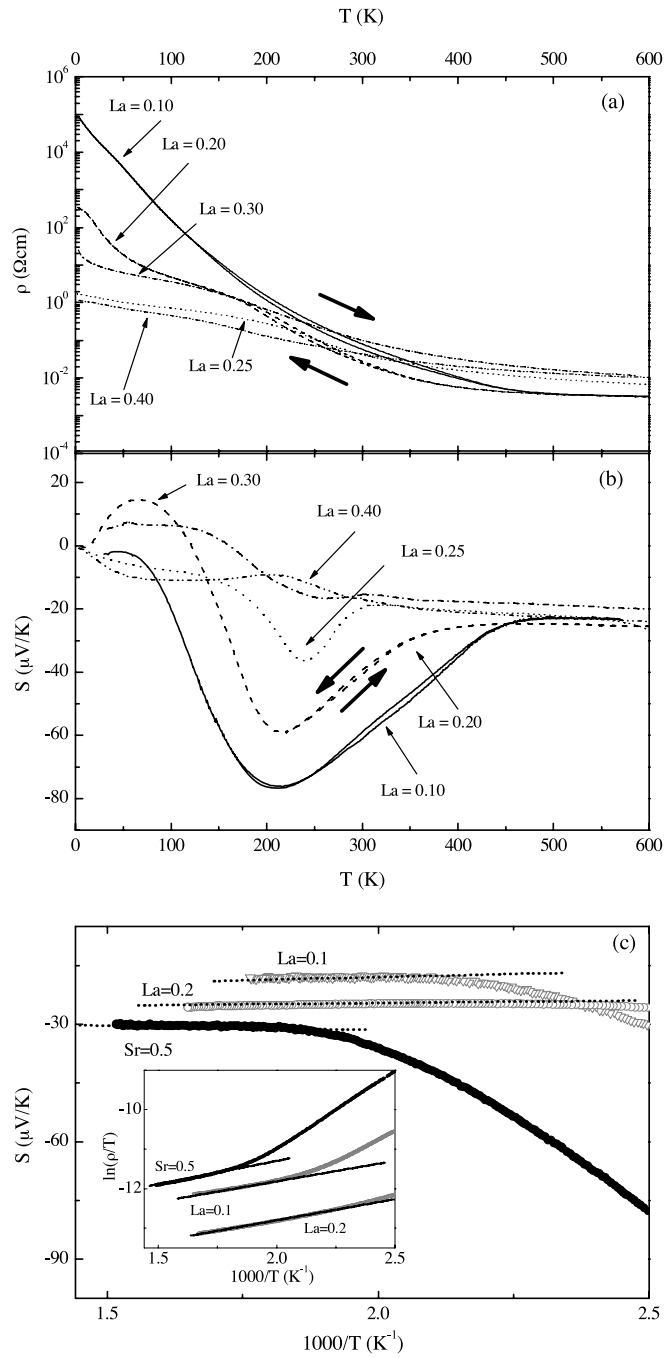
Figure 1(a) shows the typical x-ray diffraction (XRD) patterns for BLSMO at room temperature. The XRD data show that the samples have a single phase with a orthorhombic lattice structure ( $Pbnm$ ,  $a \simeq b > c$ ) which is different from the tetragonal lattice structure of BSMO because we used  $P4mm$  symmetry to analyse for BSMO [8]. As the La concentration increases, the x-ray diffraction peaks shift a little to higher angle (see the inset of figure 1(a)). Figure 2(b) shows the lattice parameters obtained by least-square fitting. The lattice parameters  $a$  (filled circles) and  $b$  (filled squares) become smaller with La doping but the parameter  $c$  becomes larger. This is different from the change of the lattice parameter  $c$  of BSMO. It means that the Bi lone pairs not only are polarized along the diagonal direction of the  $a$ – $b$  plane [8] but also affect the  $c$ -axis. Note that there is an abrupt change of the parameters  $b$  and  $c$  at



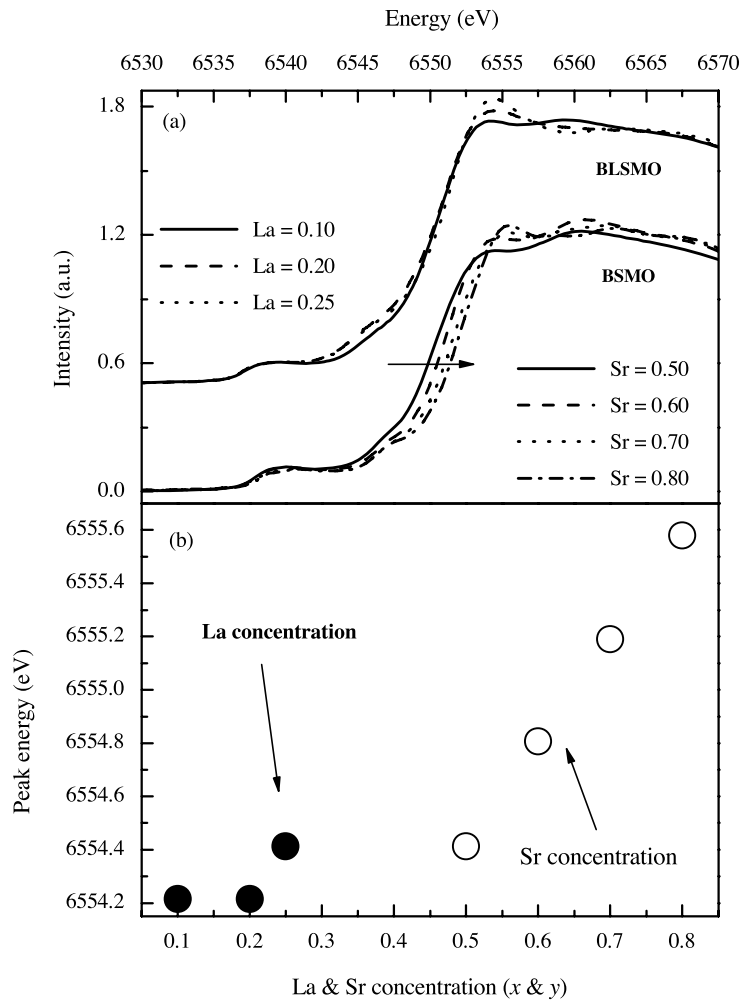
**Figure 1.** (a) Typical powder x-ray diffraction patterns for polycrystalline samples  $\text{Bi}_{0.5-y}\text{La}_y\text{Sr}_{0.5}\text{MnO}_3$  ( $0.0 \leq y \leq 0.4$ ). The inset shows an enlarged view of the (002) and (112) peaks. (b) Lattice parameters  $a$  (filled circle),  $b$  (filled square), and  $c$  (open circle) as a function of La concentration.

La concentration  $y = 0.25$  where the CO transition disappears (the CO transition of BLSMO will be discussed later). This indicates that the structural change affects the CO state.

The temperature dependence of resistivity  $\rho(T)$  for BLSMO is shown in figure 2(a). The temperature coefficients of the resistivities of BLSMO are negative in the whole range of temperature, i.e. they show an insulating behaviour. The variation of  $\rho(T)$  becomes smaller by six orders of magnitude with La doping; the difference between  $\rho(2\text{ K})$  and  $\rho(600\text{ K})$  for  $\text{La} = 0.1$  is about  $10^8\ \Omega\text{ cm}$  and that for  $\text{La} = 0.4$  is about  $10^2\ \Omega\text{ cm}$ . This indicates that the carrier density increases with the increase of La doping. There is a slope change near the  $T_{\text{CO}}$  for  $\text{La} = 0.1$  and  $0.2$ , which is attributed to the suppression of carrier hopping due to the CO. Figure 2(b) shows the temperature dependence of TEP,  $S(T)$ . At high temperatures,  $S(T)$  is weakly dependent on temperature. As the temperature decreases, the slope of  $S(T)$

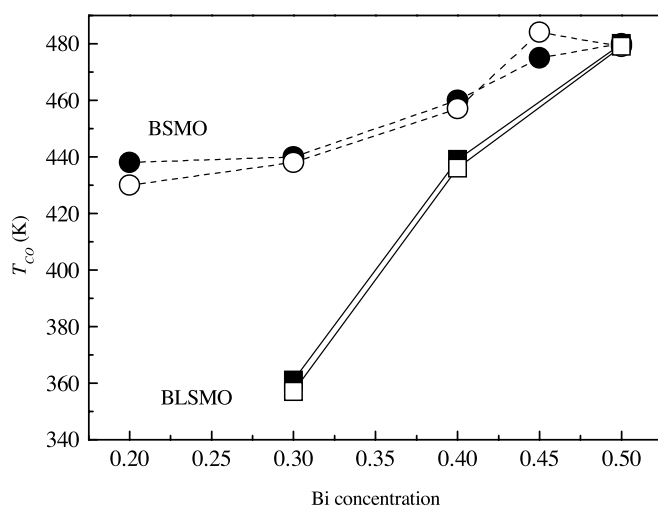


**Figure 2.** Temperature dependence of (a) resistivity and (b) TEP for BLsMO. The thermal hysteretic behaviour is shown in both TEP and resistivity for  $\text{La} = 0.1$  and  $0.2$ , which weakens with the increase of La concentration. (c) TEP and resistivity (see the inset) as a function of inverse temperature for  $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  and BLsMO ( $\text{La} = 0.1$  and  $0.2$ ). The dotted lines in the high-temperature regime show the best-fitting curves using the small-polaron hopping model [18]. The thick arrows represent the cooling and heating process.



**Figure 3.** (a) The normalized Mn K-edge XANES spectra at room temperature for BSMO ( $0.5 \leq x \leq 0.8$ ) and BLSMO ( $0.1 \leq x \leq 0.25$ ). (To compare the change of Mn valence state with the increase of divalent cations, we present XANES data for BSMO.) (b) The main peak near 6555 eV of La = 0.1 and 0.2 samples does not change but that of BSMO shifts to higher energy with Sr doping.

changes rapidly for La = 0.1 and 0.2, which suggests that the  $e_g$  electrons are trapped for a longer time and, as a result, the effective number of carriers participating in transport is significantly decreased upon the CO transition. In both  $\rho(T)$  and  $S(T)$ , a thermal hysteretic behaviour occurs for La = 0.1 and 0.2 samples but not for La  $\geq 0.25$ . (In this paper, since we focused on the CO behaviour of BLSMO, other characteristics in the transport property will be discussed elsewhere.) In the high-temperature regime, the transport properties of perovskite manganites have been extensively discussed in terms of a polaronic transport mechanism [18]. In figure 2(c) the small-polaronic behaviour of TEP and  $\rho(T)$  (inset of figure 2(c)) for BLSMO (La = 0.0, 0.1 and 0.2) is shown. It was reported that a strong increase of polaron binding energy  $E_b$  for the lattice polaron occurs as the  $Mn^{3+}$  concentration increases:  $\Delta E_b / \Delta Mn^{3+} \sim 100 \text{ meV} / 0.1$  [19]. However, the polaron binding energy  $E_b$  for the La = 0.1



**Figure 4.** The Bi concentration-dependent  $T_{CO}$  for BLSMO (squares) and BSMO (circles) from TEP (filled symbols) and resistivity (opened symbols). The slope of  $T_{CO}$  to Bi concentration in BLSMO is larger than that in BSMO.

and 0.2 samples is 167.8 meV and 175.3 meV, respectively. The difference in  $E_b$  between  $\text{Bi}_{0.4}\text{La}_{0.1}\text{Sr}_{0.5}\text{MnO}_3$  and  $\text{Bi}_{0.3}\text{La}_{0.2}\text{Sr}_{0.5}\text{MnO}_3$  is very small. Hence it is suggested that the change of the Mn valence state is ignorable. Therefore, the lattice polaron concentration has to be unchanged with La doping. With the equation of transport coefficients for small-polaronic behaviour [18], we obtained the polaron concentration for La = 0.0, 0.1 and 0.2 samples, which is almost independent of La concentration (0.3576 for La = 0.0, 0.3541 for La = 0.1, and 0.3562 for La = 0.2).

In order to clarify the valence state of the Mn ion, Mn K-edge XANES spectra of BLSMO and BSMO were obtained at Pohang Accelerator Laboratory (PAL). Several pre-edges ( $\sim 6538$  and  $6545$  eV) and main edge ( $\sim 6555$  eV) are shown in figure 3(a). In general, the pre-edge feature corresponds to the transitions into empty  $e_g$  and  $t_{2g}$  states in manganites. The main edge of BLSMO is less split than that of BSMO. This indicates that the local distortion weakens in the case of La doping in BSMO. It was reported that the main edge shifts to higher energy as the  $\text{Mn}^{4+}$  concentration increases [20]. Therefore we focus on the shift of the main edge peak. In the case of BSMO, as the  $\text{Mn}^{4+}$  concentration increases the peak shifts from 6554.4 eV (for Sr = 0.5) to 6555.6 eV (for Sr = 0.8) as shown in figure 3(b). However, there is no change of the main edge in BLSMO (La = 0.1 and 0.2). This indicates that the Mn valence state of La = 0.1 and 0.2 samples does not vary with La doping.

As mentioned above, the A-site cation size and Mn valence state affect the ground state of the manganese compounds. Since the ionic size of  $\text{La}^{3+}$  is similar to that of  $\text{Bi}^{3+}$  and there is no change of the Mn valence state in BLSMO, we can investigate the Bi lone-pair effect on the CO state without perturbation by other effects. Figure 4 shows the Bi concentration-dependent  $T_{CO}$  of BLSMO and BSMO. Below the CO transition temperature the phase is separated and then the thermal hysteresis in the transport data is developed. Therefore the  $T_{CO}$  is determined by the onset of the hysteretic behaviour as reported in [8]. In the case of BSMO, the  $T_{CO}$  decreases with the decrease of Bi concentration but it is still above room temperature up to  $x = 0.8$ . This robustness of charge ordering with doping is in strong contrast to that of the other CO manganites which show the CO phase in a rather narrow doping region. The

$T_{CO}$  of BLSMO also decreases as the Bi concentration decreases, but it is strongly suppressed compared with that of BSMO. The CO state is maintained only up to  $La = 0.2$ . The slope of  $T_{CO}$  against the Bi concentration in BLSMO ( $\Delta T_{CO}/\Delta Bi$ ) is larger than that in BSMO ( $\Delta T_{CO}/\Delta Bi$ ):  $\Delta T_{CO}/\Delta Bi \geq 40$  K/0.1 for BLSMO and  $\Delta T_{CO}/\Delta Bi \sim 20$  K/0.1 for BSMO. The Bi lone-pair effect on the CO state is clearly seen in BLSMO. This indicates that the CO state strongly depends on the number of  $Bi^{3+}$  cations. Namely, the highest  $T_{CO}$  in doped  $BiMnO_3$  is mainly due to the polarized Bi lone pairs.

In summary,  $La^{3+}$  ions were substituted for the  $Bi^{3+}$  ions in order to investigate the  $Bi^{3+}$  lone-pair effect on the CO state in BSMO without perturbation by the ionic-size effect of the A-site cation and the change of the Mn valence state. XRD data show that lattice parameters  $b$  and  $c$  change abruptly at the La concentration 0.25. From the polaronic transport mechanism and the XANES study of the Mn K-edge, it is confirmed that there is no change of the Mn valence state. The  $T_{CO}$  of BLSMO decreases with the increase of La concentration more strongly than that of BSMO with Sr doping. This shows that the highest  $T_{CO}$  in BSMO results from the structural distortion due to the polarized  $Bi^{3+}$  lone pairs.

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