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Impact of the Bi substitution on the structural and charge density distribution of $\text{Ca}_{0.7}\text{La}_{0.3-x}\text{Bi}_x\text{MnO}_3$ ($x = 0, 0.1$)

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Abstract. The Bi substitution effect on the structure of $\text{La}_{0.3-x}\text{Bi}_x\text{Ca}_{0.7}\text{MnO}_3$ ($x = 0, 0.1$) is observed through the X-ray powder diffraction pattern. The effect of Bi substitution does not significantly change the unit cell size itself. This is due to the size of the Bi^{3+} ionic radius which is relatively almost the same as the ionic radius of La^{3+} . Through Rietveld refinement, it is confirmed that the samples have the orthorhombic structure with $Pnma$ space group. Changes of the charge density distribution between the atoms of bonds with the Bi substitution are investigated using maximum entropy method (MEM). MEM which is based on the refined structure factors extracted from the Rietveld method provide the information of charge ordering with respect to stronger regularity pattern of charge density distribution.

1. Introduction

Perovskite manganite $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (LCMO) with a variation of the concentration of Ca atoms has a very diverse magnetic phase structure. At the value of atomic concentration around 5/8, LCMO has a nature of long-range charge ordering (CO) [1]. The physical properties of perovskite are determined by the crystal structure expressed by the Goldschmidt tolerance factor. The perovskite structure is stable at $t = 1$ (unity) with a cubic structure, and for small deviations $t < 1$, the structure of the cubic crystal changes to rhombohedral or orthorhombic symmetry. Because of Bi^{3+} and La^{3+} ionic radii (1.3 Å and 1.302 Å respectively) are not significantly different, therefore it has almost no effect on the crystal structure with or without Bi substitution [2]. Nevertheless, from various studies it is found that Bi doping on LCMO results in the enhancement of CO temperature (T_{CO}) [3].

In this work, an observation was made to see the Bi substitution effect on LCMO, particularly, its effect on CO conditions. From some research, it is concluded that the change of CO is caused more by the 6s2 lone pair of Bi^{3+} which is highly polarized in certain Bi-O bond direction [2][3]. To see the relation with CO change, the maximum entropy method (MEM) is used to investigate qualitatively the impact of charge density distribution (CDD) due to the substitution of Bi atoms at the La site. Particularly to observe CDD between the atoms Mn-O and La/Bi-O. In this method the information for the electron charge is obtained from the entropy determined by the equation [4]:

$$S(\rho) = - \sum_k^{N_{pix}} \rho_k \log \rho_k \quad (1)$$



Where N_{pix} is the number of pixels and ρ_k is the charge density. Charge distribution ρ_k is obtained from MEM by maximizing entropy under conditions where the structural factor calculated from MEM charge density $F_{MEM}(h_j)$ coincides with the observed structure factor $F_{obs}(h_j)$ in a certain standard deviation σ_j . This condition is explained by the following expression [4]:

$$C(\rho) = \frac{1}{M_{ref}} \sum_{j=1}^{M_{ref}} \frac{1}{\sigma_j^2} |F_{obs}(h_j) - F_{MEM}(h_j)|^2 < 1 \quad (2)$$

Where M_{ref} is the number of structure factors used in the analysis.

2. Experimental

Samples were prepared by standard sol-gel method and after calcined at 550 °C for 6 hours then sintered with temperatures at 800 and 1000 °C for 8 hours for $\text{La}_{0.3}\text{Ca}_{0.7}\text{MnO}_3$ (LCMO) and $\text{La}_{0.2}\text{Bi}_{0.1}\text{Ca}_{0.7}\text{MnO}_3$ (LCBMO), respectively. In order to obtain the details of structure, X-ray diffraction (XRD) is done using Panalytical X-pert Pro diffractometer with Cu K α radiation ($k = 1.56406 \text{ \AA}$). The data is collected in the range of angles from 10° to 90° with step size of 0.02° and a counting time of 15 second per step. CDD is obtained from Rietveld refinement output file using Fourier analysis done with Fullprof program.

3. Results and discussion

The fitted powder XRD profile is shown in figure 1 (a) and (b) for LCMO and LCBMO respectively. Based on the results of the Rietveld refinement, it is confirmed that both LCMO and LCBMO samples have orthorhombic crystal structures with the $Pnma$ space group. The value of R_f and χ^2 obtained for two samples shows a refinement with good quality for both samples. The structural parameters of the two samples are shown in table 1. It seems that both samples have lattice parameters that really are not much different. Therefore, size of the cell volume of the both can be said to be the same. Likewise, the distance between Mn1-O1 atoms of the two is slightly different, and the angle of Mn1-O1-Mn1 which has only 0.21 degrees difference indicates that Bi substitution on LCMO hardly changes the crystal structure. Figure 2 shows that the LCMO and LCBMO crystal structures does not imply significant differences.

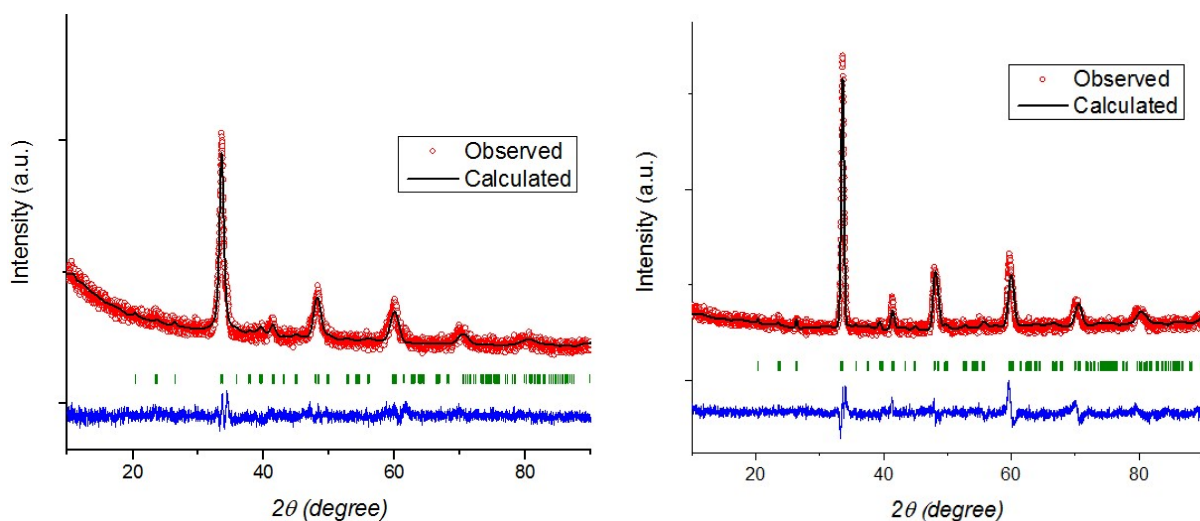
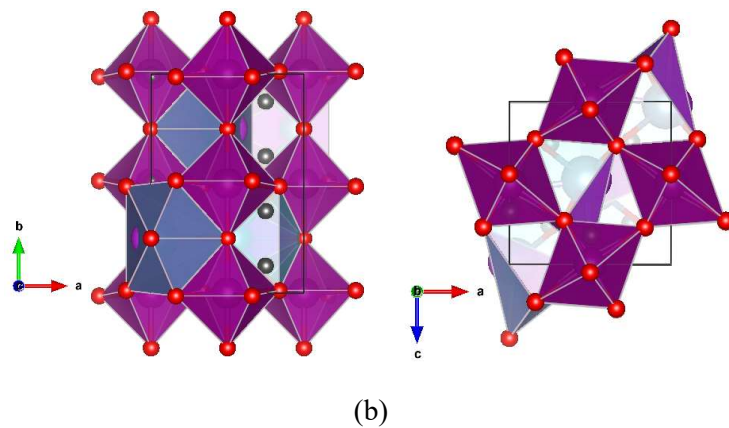
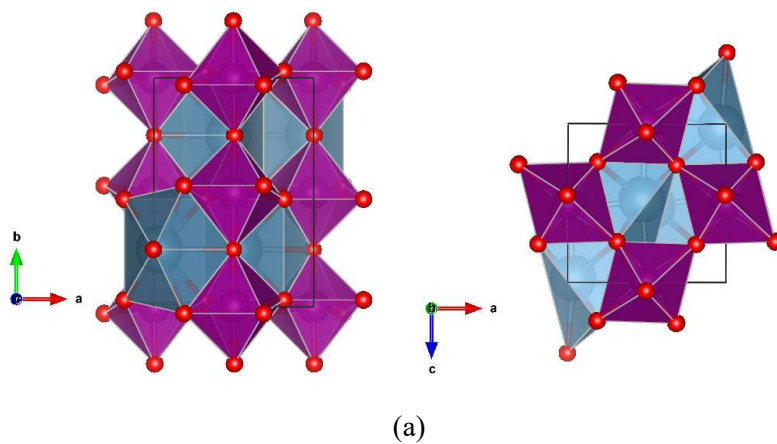


Figure 1. Fitted powder XRD profile of (a) $\text{La}_{0.3}\text{Ca}_{0.7}\text{MnO}_3$ and (b) $\text{La}_{0.2}\text{Bi}_{0.1}\text{Ca}_{0.7}\text{MnO}_3$

Table 1. Structural parameter of $\text{La}_{0.3}\text{Ca}_{0.7}\text{MnO}_3$ and $\text{La}_{0.2}\text{Bi}_{0.1}\text{Ca}_{0.7}\text{MnO}_3$.

	$\text{La}_{0.3}\text{Ca}_{0.7}\text{MnO}_3$	$\text{La}_{0.2}\text{Bi}_{0.1}\text{Ca}_{0.7}\text{MnO}_3$
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Pnma</i>	<i>Pnma</i>
<i>a</i> (Å)	5.3087	5.3040
<i>b</i> (Å)	7.5962	7.5979
<i>c</i> (Å)	5.3409	5.3427
$\alpha=\beta=\gamma$ (°)	90	90
Volume (Å ³)	215.38	215.30
Mn1-O1 (Å)	1.9208	1.9194
La1/Bi-O1 (Å)	2.5280	2.5154
Mn1-O1-Mn1 (°)	162.75	163.54
<i>R</i> _f	4.35	4.98
χ^2	1.66	2.62

**Figure 2.** Crystal structure of (a) $\text{La}_{0.3}\text{Ca}_{0.7}\text{MnO}_3$ and (b) $\text{La}_{0.2}\text{Bi}_{0.1}\text{Ca}_{0.7}\text{MnO}_3$

To investigate the further influence of Bi substitution on LCMO, several studies have seen that the role of $6s^2$ lone pair from Bi^{3+} ions is far more dominant than due to changes in crystal structure [2][3]. $\text{La}_{0.3}\text{Ca}_{0.7}\text{MnO}_3$ is a charge ordering nature type of perovskite manganite. In order to see the effect of the Bi substitution, the maximum entropy method (MEM) is used. MEM performs subsequent calculation of electron-density distributions based on extraction from structure-factors on Rietveld refinement program [5]. Figure 3 (a) and (d) show that on (001) planes, the maximum CDD of Mn ion in LCMO and LCBMO are about $27.114 \text{ e}\text{\AA}^{-3}$ and $31.734 \text{ e}\text{\AA}^{-3}$ respectively. Mn-O2 forms partial covalent bond in both LCMO and LCBMO and have minimum of about $0.011 \text{ e}\text{\AA}^{-3}$ in LCMO which is much lower than Mn-O2 covalent bond in CLBMO with a value of $0.281 \text{ e}\text{\AA}^{-3}$. Bi doping effect on LCBMO may increase Mn-O2 partial covalent bonds and provide higher regular pattern than in CLMO. This may elucidate the occurrence of CO strengthening due to the role of Bi $6s^2$ lone pair. In accordance with research in [2], it implies that the role of $6s^2$ lone pair in Bi-doping is not only couple with the $\text{O:}2p_\sigma$ orbitals in the A-site, but also compete directly for the $\text{O:}2p_\pi$ electrons with the Mn:t_{2g} orbitals.

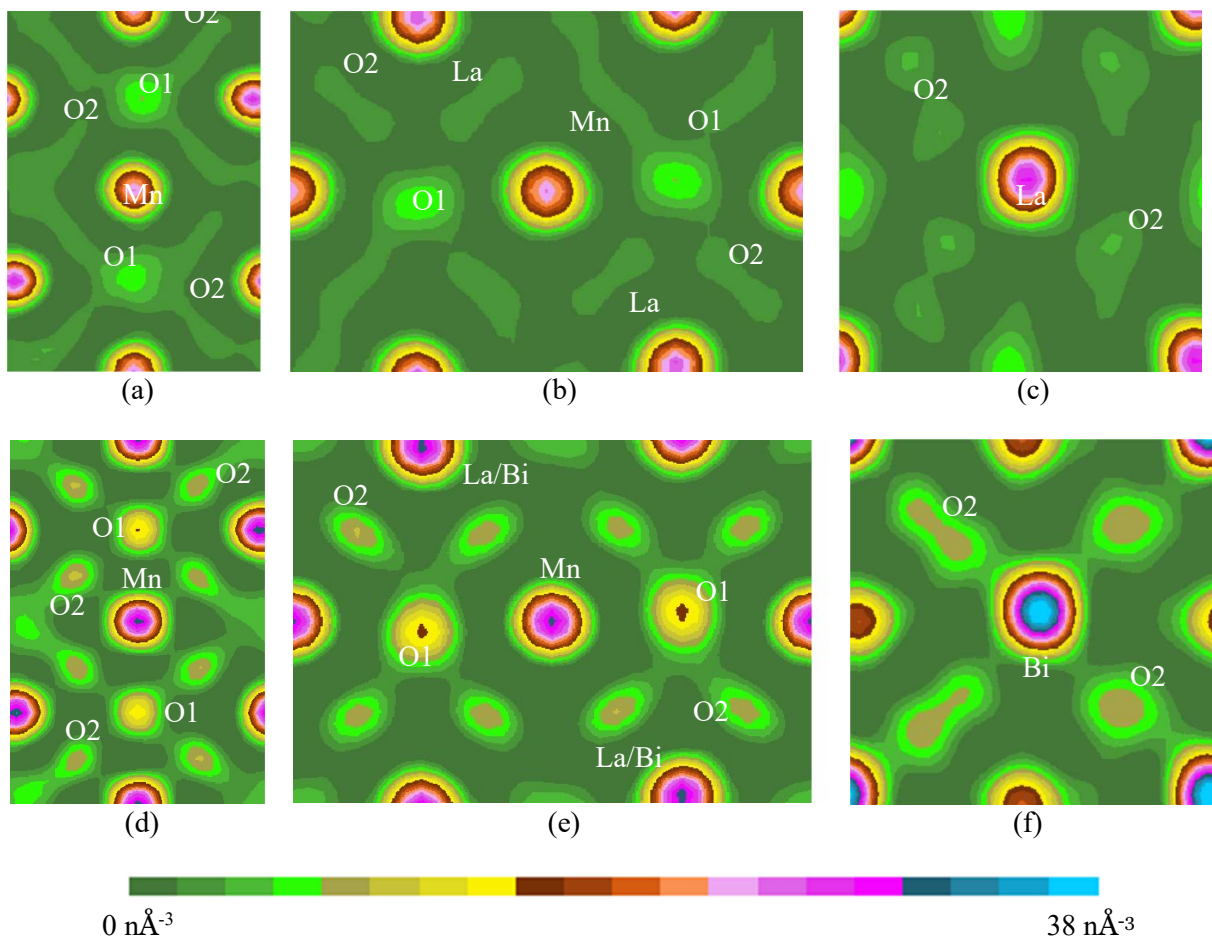


Figure 3. Charge density distribution along the atomic bond distance shown on (a) – (c) for $\text{La}_{0.3}\text{Ca}_{0.7}\text{MnO}_3$ and (d) – (f) for $\text{La}_{0.2}\text{Bi}_{0.1}\text{Ca}_{0.7}\text{MnO}_3$ viewed on the planes as follows: (a) and (d) for (001) plane, (b) and (e) for (100) plane, (c) and (f) for (010) plane.

On the (100) plane as shown in figure 3 (b) and (e) both La-O2 in LCMO and Bi-O2 in LCBMO naturally maintain ionic bonds with some partial covalent bonds which is in agreement with research conducted by Thenmozhi and Saravanan [6]. And again, LCBMO demonstrate stronger regular pattern of CDD than LCMO. The maximum CDD of La ion in LCMO and Bi ion in LCBMO are $27.114 \text{ e}\text{\AA}^{-3}$ and $31.734 \text{ e}\text{\AA}^{-3}$ respectively but with more centralized density of charge than Mn have either in LCMO

or LCBMO. Figure 3 (c) shows ionic bond on (010) with partial covalent bonds characteristic of $0.011 \text{ e}\text{\AA}^{-3}$ for La-O2 and maximum CDD of $27.114 \text{ e}\text{\AA}^{-3}$ for La ion in CLMO. In the other hand, figure 3 (f) confirms that Bi-O2 in LCBMO represent more covalent bond characteristic with stronger regularity on (010) planes. Bi-O2 has covalent bond of $0.281 \text{ e}\text{\AA}^{-3}$ and Bi ion with maximum CDD of $31.734 \text{ e}\text{\AA}^{-3}$.

4. Conclusion

Bi substitution in LCMO does not significantly change the crystal structure. The changes in charge ordering structure and other physical properties (electricity, magnetism, thermoelectric) are more influenced predominantly by the presence of the $6s^2$ lone pair of Bi^{3+} . Maximum entropy method (MEM) can provide information qualitatively about the role of the $6s^2$ lone pair of Bi^{3+} where Mn-O2 in LCBMO have strongly partial covalent bonds compare with LCMO. And more importantly it forms charge density distribution with stronger regularity of pattern that may be used as an indication of the formation of charge ordering structure.

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