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High pressure effects on the Jahn–Teller distortion in perovskite $La_{0.5-x}Bi_xCa_{0.5}MnO_3$

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Abstract

X-Ray diffraction studies were carried out on the distorted perovskite $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ (x=0, 0.05, 0.1, 0.15, 0.2, 0.25) under high pressure at room temperature by the energy-dispersive technique. The unusual expansion of the 202−040 *d*-spacing under pressure was observed and accompanied by a remarkable decrease of the Jahn–Teller distortion in MnO_6 octahedra. The change of the Mn–O bond angle brings about the disappearance of the basal-plane distortion mode Q_2. The substitution of Bi^{3+} for La^{3+} in the system introduces more distortions, which is ascribed to the unique lone pair characteristics of bismuth.

Keywords: High pressure; Perovskite manganite; X-Ray diffraction; Synchrotron radiation

1. Introduction

The recent rediscovery of 'colossal magnetoresistance' (CMR) in perovskite $La_{1-x}A_xMnO_3$ (A=Ca, Sr, Ba) has generated considerable interest in these materials [1]. As a function of temperature, doping, applied pressure, and A-site ionic radius, these systems display various magnetic and crystallographic transitions. For x~0.5, the solid solution $La_{0.5}Ca_{0.5}MnO_3$ is known to undergo transitions from a paramagnetic to ferromagnetic state at T_C~240 K on cooling and then to an antiferromagnetic charge-ordered state at T_N~135 K (185 K on warming) [2]. This intriguing behavior has been attributed to the competition between ferromagnetic double exchange and antiferromagnetic superexchange coupling. On the other hand, a strong coupling among the electronic, magnetic, and structural degrees of freedom could be an important factor. And structural anomalies between T_C and T_N, which are associated with the development of a strong Jahn–Teller type distortion of the MnO_6 octahedra with decreasing temperature, have been reported [3]. The present experiment aims to study the structural stability of Bi-doped $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ under high pressure. Pressure as a fundamental thermodynamic variable can facilitate a controlled volume change of the physical systems and the study of their behavior under high pressure would be of value for a better understanding in these correlated electron systems. In this paper, we carried out in-situ high pressure X-ray diffraction studies on $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ with synchrotron radiation. The internal pressure generated by the substitution of Bi for La has contrary effects other than an external pressure by application of hydrostatic pressure. The former induces more lattice distortions to the crystal structure but the latter favors a reduction of the Jahn–Teller distortion that is accompanied by the disappearance of the vibrational mode Q_2 component in the MnO_6 octahedra.

2. Experimental

Polycrystalline samples of $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ (x=0, 0.05, 0.1, 0.15, 0.2, 0.25) were synthesized by solid-state reaction. The mixture of stoichiometric La_2O_3, Bi_2O_3, $CaCO_3$ and MnO_2 powders were calcined at 700°C for 24 h in air. The resulting powder was then reground and reacted at 1050°C for 24 h. This step was repeated once before pressing into pellets, and sintering at 1100°C in air for 48 h. Powder X-ray diffraction data for the specimens were collected using a REGAKU diffractometer with monochromatic Cu Kα radiation, and all were found to be single phase. The unit cell dimensions were determined

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from observed *d*-spacings by the least squares method. The physical characterization involved ambient-pressure resistivity, magnetization measurements, which are similar to those of the earlier reports for $La_{0.5}Ca_{0.5}MnO_3$, and infrared absorption spectra will be reported in detail later [3,4].

All the high-pressure X-ray diffraction patterns employed an energy-dispersive method and were recorded on the wiggler beamline (3W1A) of the Beijing Synchrotron Radiation Laboratory (BSRL). A diamond anvil cell (DAC) with type-I diamonds was driven by an accurately adjustable gear-worm-level system. The powder samples were loaded into the sample chamber of a stainless steel gasket with very fine platinum or with aurum powder, which serves as the inner pressure calibrant. A mixture of methanol/ethanol 4:1 was used as the pressure medium. Pressure was determined from (111), and (220) peaks of Au or Pt along with its respective equation of state. We can obtain the *d*-values of the prepared specimens according to the energy dispersion equation:

$$E \cdot d = \frac{0.619927}{\sin \theta} \ (\mathrm{keV \cdot nm})$$

The polychromatic X-ray beam was collimated to a 60×60 μm sized spot with the storage ring operating at 2.8 GeV. The diffracted beam was collected between 5 and 40 keV and the diffraction 2θ angle between the direct beam and the detector was set at ~16°.

3. Results and discussion

In the ABO_3 perovskite structure, the mismatch between the A–O and B–O bond lengths is given by a tolerance factor. This Goldschmidt tolerance factor t that measures the stability of ABO_3 perovskite structures, is given by

$$t = \frac{(r_A + r_O)}{\sqrt{2}(r_B + r_O)}$$

where r_A, r_B and r_O are the radii of 'A' cation, 'B' cation and oxygen, respectively, and can be calculated from the data of empirical ionic radii [5]. If $t=1$, ABO_3 compounds would be in a perfect cubic structure. So it is a useful parameter to measure the distortion in the perovskite structure. The X-ray diffraction results of $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ ($x=0$, 0.05, 0.1, 0.15, 0.2, 0.25) are shown in Fig. 1. From powder X-ray diffraction patterns at room temperature and at ambient pressure, the orthorhombic unit cell was adopted for all the samples investigated because of only a small shift of the diffraction peaks. The lattice properties of $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ are given in Table 1. A small expansion of the molar volume and tolerance factor with bismuth substitution is due to the fact that the ionic radius of Bi^{3+} is slightly larger than that of La^{3+} (Bi^{3+}~1.24 Å, La^{3+}~1.22 Å, in nine-coordination).

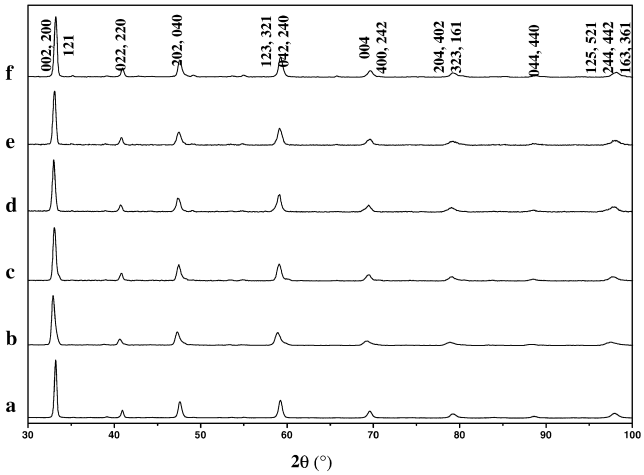

Fig. 1. The ambient-pressure X-ray diffraction patterns of $La_{0.5-x}Bi_xCa_{0.5}MnO_3$. The value of concentration x for spectra from (a) to (f) is 0, 0.05, 0.1, 0.15, 0.2 and 0.25, respectively.

Six separate runs for $x=0$, 0.05, 0.1, 0.15, 0.2 and 0.25 were carried out up to 45.9, 24.1, 19.9, 14.8, 45.8 and 43.9 GPa, respectively. In the energy-dispersive runs, not all diffraction peaks could be included but only four main peaks are chosen to examine, because of the narrow energy range (between 5 and 40 keV). The energy-dispersive X-ray diffraction patterns for $x=0$ composition at selected pressures are shown in Fig. 2. As can be seen, at the beginning of the spectrum, there are fluorescence peaks coming from La, and Au. During the process of compression, there are no major changes occurring in the spectra. However, higher pressure leads to a decrease in the intensities of peaks and a general degradation of the peak-to-background ratio in the diffraction pattern. This is related to the strength of the materials. The broadening of the peaks may be caused by the deviatoric stress in the sample chamber under high pressure.

For the system $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ ($x=0$, 0.05, 0.1, 0.15, 0.2, 0.25), most *d*-spacings behave normally as they all decrease smoothly with increasing pressure. However, it is unusual for 202–040 *d*-spacing as shown in Fig. 3, which expands under compression from the beginning, and then contracts when further pressurized above a certain pressure. This phenomenon is quite reproducible and pressure reversible with a small hysteresis associated with the process. The abnormal change of 202–040 *d*-spacing

Table 1
The lattice properties of $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ ($x=0$, 0.05, 0.1, 0.15, 0.2, 0.25) compositions

x	a (Å)	b (Å)	c (Å)	V (cm^3/mol)	Tolerance factor
0	5.393	7.616	5.394	221.56	0.9245
0.05	5.394	7.619	5.397	221.77	0.9249
0.1	5.394	7.637	5.404	222.59	0.9253
0.15	5.394	7.639	5.407	222.79	0.9257
0.2	5.407	7.651	5.418	224.14	0.9262
0.25	5.408	7.643	5.426	224.27	0.9266

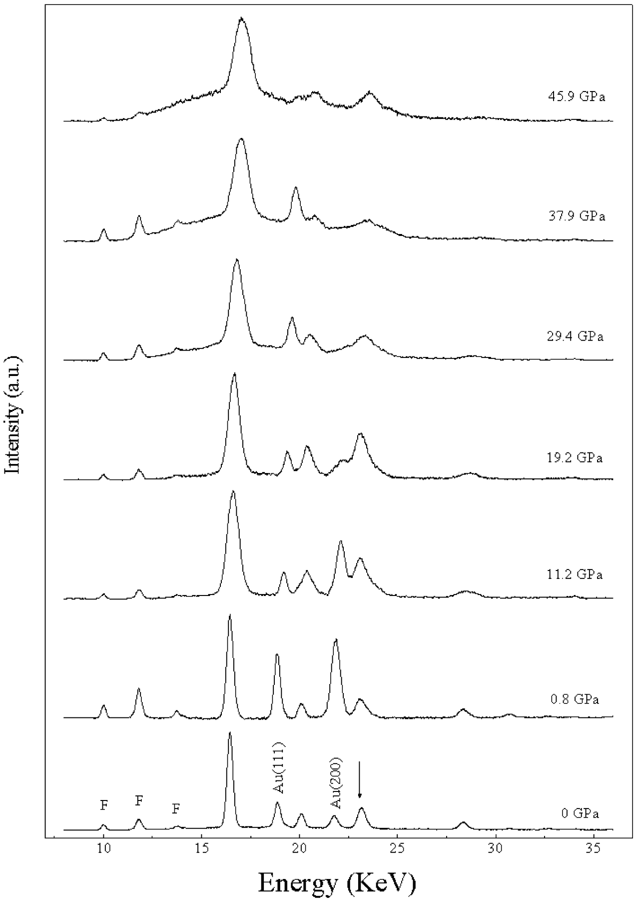

Fig. 2. Energy-dispersive X-ray diffraction patterns of $La_{0.5}Ca_{0.5}MnO_3$ as a function of pressure. F is the X-ray emission line of Au. The 2θ angle between the direct beam and the detector was set at ~16°. The arrow indicates the special change of the 202–040 peak upon compression.

should be intimately related to the structural characteristics of ABO_3 compounds, especially for manganites. Generally, Mn^{3+} as a Jahn–Teller ion in the MnO_6 octahedra can bring about severe deformation to the crystal lattice, and the Jahn–Teller distortions can be described by the combination of the octahedral stretching modes Q_2 and Q_3. The deformed oxygen octahedra have been clearly seen in the end member $LaMnO_3$ [6]. In the present work, we have not been able to determine positional parameters and we have no direct evidence of the cation distribution. However, some qualitative estimates can be derived from our diffraction data. The appearance of change in Fig. 3 would be associated with the displacement of the cations and coordination oxygen atoms under high pressure. In a simple view, the 202–040 reflections can reflect the variations of $a-c$ plane and b axis in the deformed MnO_6 octahedra directly. The pressure dependence of two distorted modes Q_2 and Q_3 is quite different. At ambient pressure, one can assume that the stretch modes Q_2 and Q_3 in MnO_6 due to Jahn–Teller distortion coexist. Applying pressure favors the displacement of the basal plane oxygen atoms contracting and apical oxygen atoms extending from their ideal positions in a Q_3 type way. During the course of compression, the distorted mode Q_3 becomes more dominant than the mode Q_2 in this process. With pressure up to a certain point, the basal-plane distortion Q_2 progressively vanishes and the results are reflected in the special change of 202–040 d-spacing.

Fig. 4 is the plot of this turning pressure dependence of concentration x. With doping of larger Bi^{3+} ions, it needs a higher turning pressure. Although the value of the tolerance factor t of the specimens should increase with doping x increasing, one can assume that there would be less distortions in the structure. On the contrary, from our experimental results, the substitution of Bi^{3+} for La^{3+} produces more distortions in the entire lattice structure, and these distortions may come from the contributions of the lone pair characteristics of bismuth. When the bismuth cation shifts from the center of the hexagon of the oxide anion, it has a tendency to result in a lowering of the symmetry of the whole structure, which behaves more prominently in $BiMnO_3$ [7]. With doping of Bi^{3+} ions increasing, it needs higher pressure to overcome the extra elastic-energy cost of the deformations and therefore raises the turning pressure. Previous research on perovskite-type manganites has revealed that a structural transition may occur depending on temperature and the change in composition in the series of solid solutions [8]. However, our high pressure experiments show that the structure remains stable up to the highest pressure (45.9 GPa) reached.

In conclusion, we have carried out an in-situ X-ray diffraction study of the behavior of Jahn–Teller distortion in $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ ($x=0$, 0.05, 0.1, 0.15, 0.2, 0.25) using synchrotron radiation. Application of pressure brings about the competition between two types of the Jahn–Teller distortion modes Q_2 and Q_3 in the MnO_6. An abnormal change of 202–040 d-spacing was observed and suggested the disappearance of the distortion mode Q_2 within the a–b basal plane. This is consistent with the fact that applying external pressure can progressively reduce the Jahn–Teller split of the e_g band that is related to the distortion mode Q_2. From the consideration of the Goldschmidt tolerance factor t that describes the stable of ABO_3 perovskite structure, an increase in the tolerance factor would result in a reduction of lattice distortions. However, the substitution of lanthanum with a larger bismuth cation produces more distortions in the structure, and this is ascribed to the unique characteristics of its polarized lone pair.

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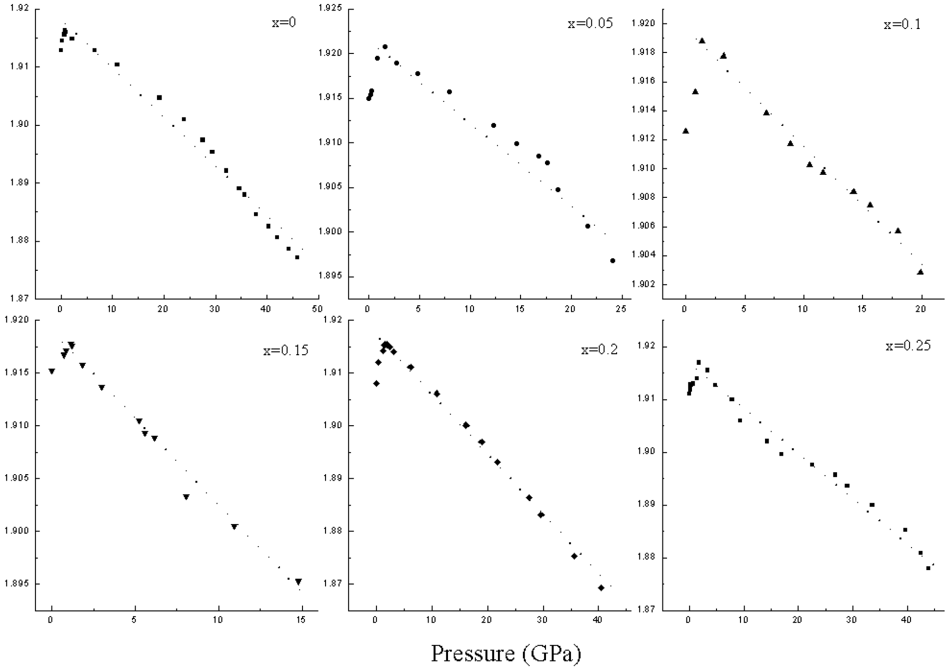

Fig. 3. The effect of pressure on the 202–040 *d*-spacings of $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ ($x=0$, 0.05, 0.1, 0.15, 0.2, 0.25). Lines are guides for the eye.

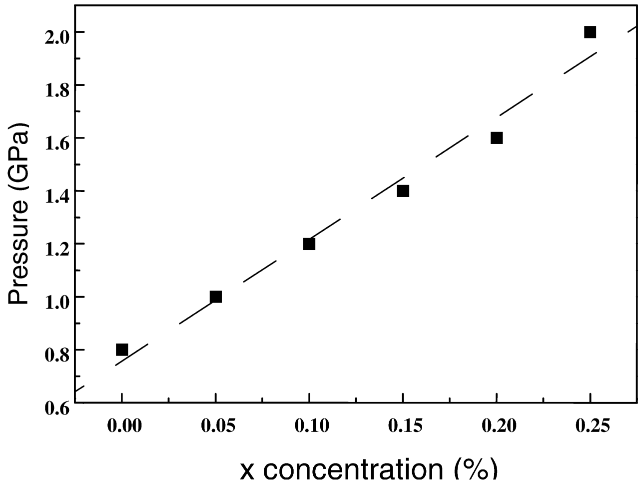

Fig. 4. The turning pressure dependence of doping *x* for the 202–040 *d*-spacing in the system $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ ($x=0$, 0.05, 0.1, 0.15, 0.2, 0.25).

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