A high-pressure study of phase stability in $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ by energy-dispersive x-ray diffraction

2002 J. Phys.: Condens. Matter 14 11115

(http://iopscience.iop.org/0953-8984/14/44/435)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **14** (2002) 11115–11118 PII: S0953-8984(02)37966-9

A high-pressure study of phase stability in $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ by energy-dispersive x-ray diffraction

Xin Wang[1,2,3], **Qiliang Cui**[1], **Yuewu Pan**[1] **and Guangtian Zou**[1]

[1] National Laboratory for Superhard Materials, Jilin University, Changchun 130023, People's Republic of China
[2] Institute of Physics, Chinese Academy of Sciences, PO Box 603, Beijing 100080, People's Republic of China

E-mail: xinwang@aphy.iphy.ac.cn

Received 11 June 2002
Published 25 October 2002

Abstract

Energy-dispersive x-ray diffraction studies are 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. The unusual expansion of the 202–040 *d*-spacing under pressure is observed, and the change of the Mn–O bond angle brings about the disappearance of the basal-plane Q_2 distortion mode. With doping content increasing, a shoulder peak appears in the observed main peak of $La_{0.25}Bi_{0.25}Ca_{0.5}MnO_3$ at 43.9 GPa. The pressure-enhanced interactions between charge, orbital, and coupling with the lattice distortion are discussed.

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]. For the hole doping concentration of $x \approx 1/3$, these compounds exhibit an insulator-to-metal transition that is intimately related to paramagnetic-to-ferromagnetic ordering. For other doping concentrations, the high-temperature phase is paramagnetic and the low-temperature phase can be antiferromagnetic, canted antiferromagnetic, spin-glass, or ferromagnetic. For one particular doping level, $x = 1/2$, the low-temperature magnetic structure was described as being of CE type, proposed originally by Wollan and Koehler [2] 40 years ago, in which Mn^{3+} and Mn^{4+} charge orders within the orthorombic chemical cell and form a magnetic structure that doubles the chemical cell in the *a* and *c* directions. In Goodenough's model, charge ordering is accompanied by orbital ordering, where the d_Z^2 Mn^{3+} orbitals (associated with long Mn^{3+}–O bonds in the Jahn–Teller distorted $Mn^{3+}O_6$ octahedra) would order and

---

[3] Author to whom any correspondence should be addressed.

Table 1. The high-pressure experimental conditions for $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ ($x = 0, 0.05, 0.1, 0.15, 0.2, 0.25$).

Composition x	Diameter of culet (μm)	Gasket	Diameter of sample chamber (μm)	Spot size of white x-ray beam (μm)	Pressure calibrant	Diffraction 2θ angle (deg)
0	350	T301	150	60 × 60	Au	16.026
0.05	500	L605	240	144 × 144	Au	17.323
0.1	500	T301	200	80 × 80	Pt	17.913
0.15	350	T301	140	60 × 60	Pt	17.976
0.2	350	T301	140	60 × 60	Au	16.571
0.25	500	L605	240	144 × 144	Au	17.174

form zig-zag chains in the *a–c* plane [3]. Structural anomalies between T_C and T_N have been evidenced, which are associated with the development of a strong Jahn–Teller type distortion of the MnO_6 octahedra with decreasing temperature [4]. While the studies of structural behaviours under high pressure would be of value for a better understanding in such a charge ordering system. In this paper, we carried out *in situ* high-pressure x-ray diffraction studies on $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ ($x = 0, 0.05, 0.1, 0.15, 0.2, 0.25$) with synchrotron radiation. The effects generated by the substitution of Bi^{3+} for La^{3+} and by the application of hydrostatic pressure are discussed.

2. Experimental details

Polycrystalline samples $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ were prepared by the conventional ceramic method using stoichiometric mixtures of oxides, and the synthesis procedure was described elsewhere [5].

All the high-pressure x-ray diffraction patterns that employed an energy-dispersive method were recorded on the wiggler beamline (3 W1A) of the Beijing Synchrotron Radiation Laboratory. 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. The pressure was determined from the (111) and (220) peaks of Au and Pt along with their respective equation of state. We can obtain the d values of the prepared specimens according to the energy dispersion equation: $Ed = \frac{0.619\,927}{\sin\theta}$ (keV nm). The storage ring was operated at 2.8 GeV. The diffracted beam was collected between 5 and 40 keV. The detailed experimental conditions under pressure are listed in table 1.

3. Results and discussion

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 our energy-dispersive runs, not all the diffraction peaks could be included and only four main peaks were chosen for examination, due to the narrow energy range involved (between 5 and 40 keV). 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, as shown in figure 1. However, it is unusual for the 202–040 d-spacing, which expands under compression and then contracts when further pressurized above a certain pressure. This abnormal change of the 202–040 d-spacing is related to the

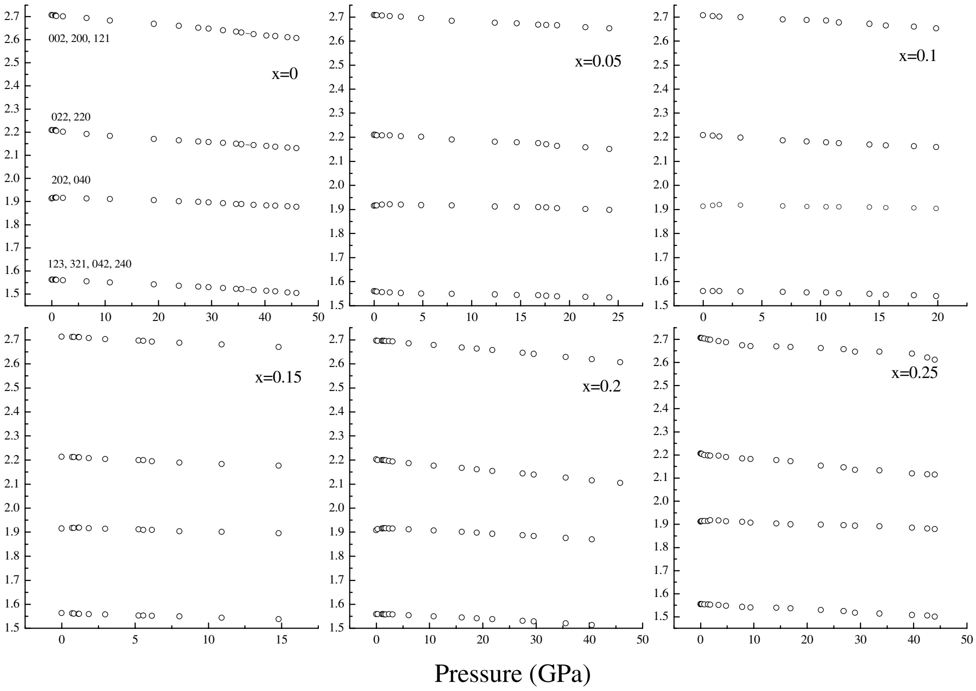

Figure 1. The effect of pressure on the observed d-spacings of $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ ($x = 0, 0.05, 0.1, 0.15, 0.2, 0.25$).

structural characteristics of the ABO_3 compounds, especially in the case of manganites. Mn^{3+} as a Jahn–Teller ion in the MnO_6 octahedra causes severely deformation to the crystal lattice, which can be described by a combination of the Q_2 and Q_3 octahedral stretching modes. Moreover, these deformed oxygen octahedra have been clearly evidenced in $LaMnO_3$ [3]. Our diffraction data give a clear insight into the behaviour of Jahn–Teller distortion under high pressure. The pressure dependence of the two distorted modes, Q_2 and Q_3, is different. At ambient pressure, one can assume that the stretch modes Q_2 and Q_3 in MnO_6 coexist due to Jahn–Teller distortion. Applying pressure favours the displacement of the basal plane oxygen atoms contracting and the apical oxygen atoms extending from their ideal positions in a Q_3 type way and it reflects on the change of 202–040 d-spacing. The Q_3 distorted mode becomes more dominant than the Q_2 mode in this process. When the pressure reaches a certain level, the basal-plane distortion Q_2 mode progressively vanishes.

On increasing the pressure up to a much higher region, a major change in the spectrum occurs around 45 GPa, as indicated by the appearance of the doublet around 15.5 keV for $La_{0.25}Bi_{0.25}Ca_{0.5}MnO_3$. Figure 2 compares the spectra between $La_{0.5}Ca_{0.5}MnO_3$ and $La_{0.25}Bi_{0.25}Ca_{0.5}MnO_3$. Since the only difference between the two samples is A-site chemical substitution, thus the effect of the substitution of Bi in place of La and the effect of pressure on it should be considered. The Bi cation that is shifted from the centre of the hexagon of the oxide anion has a tendency to cause a lowering of the symmetry of the whole structure, which behaves more prominently in the end member $BiMnO_3$ [6]. This is mainly due to the high-polarizability $6s^2$ lone-pair characteristic of the Bi^{3+} ion. The primary effect of the external pressure is to compress all the bond lengths (A–O and B–O), which thus enhances the A–O and the B–O interactions due to the increased overlap of oxygen orbitals with the A-site

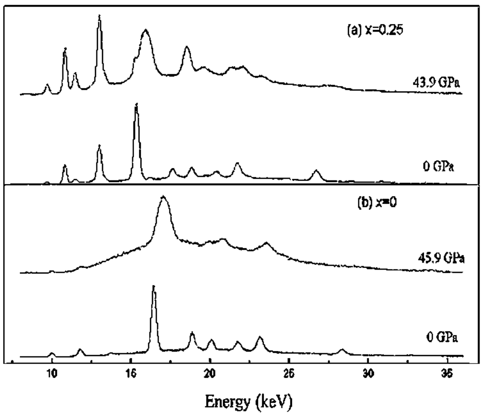

Figure 2. The spectrum comparison between $La_{0.5}Ca_{0.5}MnO_3$ and $La_{0.25}Bi_{0.25}Ca_{0.5}MnO_3$.

and the B-site orbitals. From a microstructural viewpoint, the disordered Bi and La ions with their neighbouring Mn and oxygen ions form a number of discrete clusters. Under external pressure, when the crystal field forces the Bi^{3+} ion into high symmetry, the clusters of Bi^{3+} with its neighbouring atoms would have a smaller volume than those of La^{3+} due to its lone-pair characteristics. Thus a local lattice distortion would be introduced by this difference. As the pressure increases, more dilute local deformations are introduced. Finally, this results in the doublet in the main peak of $La_{0.25}Bi_{0.25}Ca_{0.5}MnO_3$.

In conclusion, we have carried out an *in situ* x-ray diffraction study on the structural behaviour of $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ ($x = 0, 0.05, 0.1, 0.15, 0.2, 0.25$) using synchrotron radiation. The application of pressure brings about the competition between the two types of Jahn–Teller distortion, Q_2 and Q_3, in MnO_6. An abnormal change in the 202–040 d-spacing was observed and this lead to the suggestion of the disappearance of the Q_2 distortion mode within the a–c basal plane. This is consistent with the fact that applying external pressure can progressively reduce the Jahn–Teller split of the e_g band, which is related to the Q_2 distortion mode. Under higher pressure, a doublet appears in the main peak of the diffraction patterns in $La_{0.25}Bi_{0.25}Ca_{0.5}MnO_3$ and a possible explanation is given by the hypothesis suggesting that multiple phases are simultaneously present in the distorted domains.

Acknowledgments

This work was supported by the Basic Research Project of the Ministry of Science and Technology of China, the National Doctoral Foundation of the China Education Commission under grant no 89018316, and partially supported by the National Natural Science Foundation of China.

References

[1] Schiffer P, Ramirez A P, Bao W and Cheong S W 1995 *Phys. Rev. Lett.* **75** 3336
[2] Wollan E O and Koehler W C 1955 *Phys. Rev.* **100** 545
[3] Goodenough J B 1955 *Phys. Rev.* **100** 564
[4] Chen C H and Cheong S W 1996 *Phys. Rev. Lett.* **76** 4042
[5] Wang X, Cui Q L, Pan Y W, Gao W, Zhang J and Zou G T 2001 *J. Alloys. Comp.* **321** 72
[6] Atou T, Chiba H, Ohoyama K, Yamaguchi Y and Syono Y 1999 *J. Solid State Chem.* **145** 639