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A possible phase separation scenario observed in perovskite manganites under high pressure

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Abstract

Energy-dispersive x-ray diffraction measurements have been carried out in the perovskite $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and bismuth-doped $\text{La}_{0.25}\text{Bi}_{0.25}\text{Ca}_{0.5}\text{MnO}_3$ under hydrostatic pressure in a diamond cell. On the substitution of La^{3+} ion with Bi^{3+} ion, a shoulder peak appears in the observed main peak of $\text{La}_{0.25}\text{Bi}_{0.25}\text{Ca}_{0.5}\text{MnO}_3$ at 43.9 GPa, but not in that of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ with the pressure up to 45.9 GPa. This phenomenon can be explained by a number of discrete clusters that are simultaneously present in the sample, due to the pressure enhanced interactions between charge, orbital and coupling with the lattice distortion coming from the unique $6s^2$ lone-pair characteristics of Bi^{3+} .

1. Introduction

The mixed-valent manganites with a disordered distribution of Mn^{3+} and Mn^{4+} , which have a general formula $\text{Ln}_{1-x}\text{B}_x\text{MnO}_3$ (Ln = rare earth, B = Ca, Sr, Ba, or Pb), are well known and their physical properties are important and interesting in the field of material science [1]. The chemical composition $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ is particularly interesting, since it displays various magnetic transitions as a function of temperature and doping. Between $0.2 < x < 0.5$, the system undergoes a paramagnetic insulator to a ferromagnetic (FM) metal phase transition upon cooling and exhibits colossal magnetoresistance near the Curie temperature [2]. Recently, interest has been concentrated on the antiferromagnetic (AFM) insulating ground state observed in the system at a higher doping level ($x \geq 0.5$). In an intermediate doping regime typically near $x = 0.5$, where the energy scales of double exchange and charge ordering (CO) are comparable, one can obtain a metal–insulator transition between the conducting and CO ground states [3]. Several experiments have already reported coexisting metallic FM and insulating CO–AFM clusters for phase-separation tendencies

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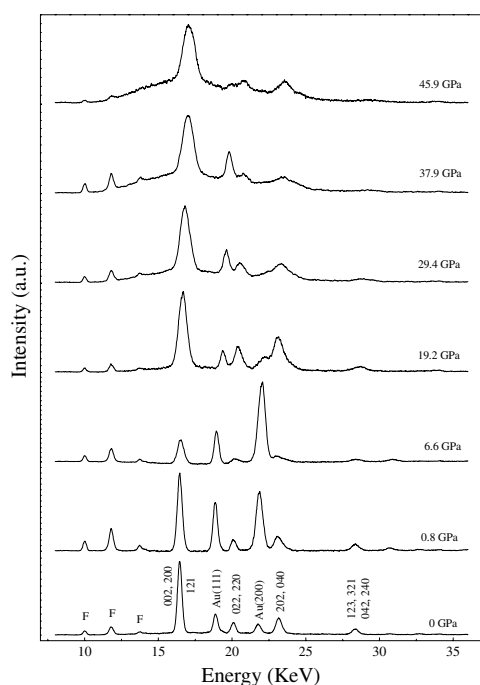


Figure 1. Energy-dispersive x-ray diffraction patterns of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ as a function of pressure. F is the x-ray emission line of Au. The 2θ angle between the direct beam and the detector was set at $\sim 16^\circ$.

in this region [4–6]. Also accompanied by the magnetic transitions, the observation of structural anomalies between T_C and T_N has been found by Radaelli *et al* [7], who ascribed the anomalies to four phase with the similar lattice parameters simultaneously present in the sample. Alternatively, recent theoretical analyses place more emphasis on the effect of the Jahn–Teller interaction inherent to the Mn^{3+}O_6 octahedron in these compounds [8]. Pressure as a fundamental thermodynamic variable can efficiently influence the interactions responsible for such electron–phonon coupling. In this paper, we carried out an *in situ* x-ray diffraction study on two perovskite-structured compounds: the orthorhombic $\text{La}_{0.25}\text{Bi}_{0.25}\text{Ca}_{0.5}\text{MnO}_3$ and $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, at room temperature and pressures up to 43.9 and 45.9 GPa, respectively, using a diamond anvil cell interfaced with synchrotron radiation. By replacing the La^{3+} ion with the Bi^{3+} ion, we can maintain the same ratio of Mn^{3+} to Mn^{4+} and the similar average ionic size of $\langle r_A \rangle$ for the samples ($\text{La}^{3+} \sim 1.22 \text{ \AA}$, $\text{Bi}^{3+} \sim 1.24 \text{ \AA}$, in nine-coordination). Therefore, we can investigate the net effect of substitution-induced lattice distortion and seek further understanding of the role of lattice distortion in manganites.

2. Experimental procedures

Polycrystalline samples of $\text{La}_{0.5-x}\text{Bi}_x\text{Ca}_{0.5}\text{MnO}_3$ with $x = 0, 0.25$ were prepared by the conventional ceramic method using stoichiometric mixtures of oxides. The synthesis procedure and energy-dispersive x-ray diffraction setup under high-pressure were described elsewhere [9].

3. Results and discussion

Powder x-ray diffraction patterns at ambient pressure revealed that the crystalline products were pure phase and had the orthorhombic structure reported by Bokov *et al* [10]. High-pressure x-ray diffraction measurements for $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and $\text{La}_{0.25}\text{Bi}_{0.25}\text{Ca}_{0.5}\text{MnO}_3$ were extended

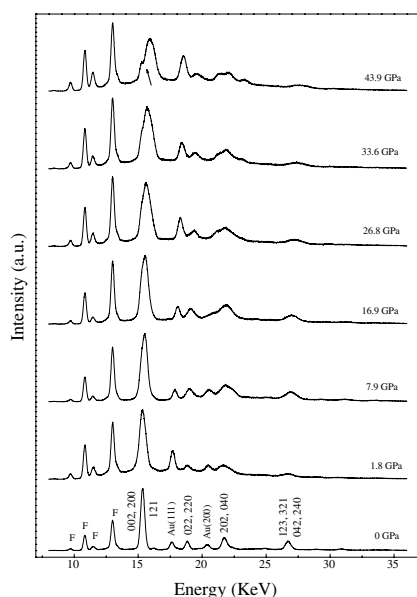


Figure 2. Energy-dispersive x-ray diffraction patterns of $\text{La}_{0.25}\text{Bi}_{0.25}\text{Ca}_{0.5}\text{MnO}_3$ as a function of pressure. F is the x-ray emission lines of Au and Bi. The 2θ angle between the direct beam and the detector was set at $\sim 17^\circ$. The arrow indicates the appearance of a doublet at 43.9 GPa.

to 45.9, and 43.9 GPa, respectively. Figure 1 shows the pressure dependence of the energy-dispersive x-ray diffraction patterns at selected pressures for $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. Increasing pressures leads to a decrease in the peak intensities and a general degradation of the peak-to-background ratio in the diffraction patterns, which is related to the strength of the materials. This is also the case for sample $\text{La}_{0.25}\text{Bi}_{0.25}\text{Ca}_{0.5}\text{MnO}_3$ as shown in figure 2. However, by comparing the energy-dispersive x-ray diffraction patterns of two samples under much higher pressures, a major change in the spectrum occurs around 45 GPa, as indicated by the appearance of the doublet around 15.5 keV for $\text{La}_{0.25}\text{Bi}_{0.25}\text{Ca}_{0.5}\text{MnO}_3$. Since the only difference between two samples is the chemical substitution in the A-site, the effect of Bi substitution as opposed to La substitution and the effect of pressure on it should also be considered.

Extensive studies on the perovskite-type ABO_3 compounds have shown that one is able to vary the dimensions of the unit cell by varying the A-site ion. Accompanying the changes in crystal dimensions, we may expect variations in the A–O and the B–O interactions, and thus the magnetic and transport properties can also be varied in these materials [11]. Alternatively, one of the key factors in these oxides is the Jahn–Teller distortion due to the Mn^{3+} ions, which has a $3d^4:t_{2g}^3e_g^1$ electron configuration [12]. However, in place of the La^{3+} ion, which has a similar ionic radius to the Bi^{3+} ion, the average ionic radii of A-site (r_A) and the contents of Mn^{3+} can be maintained. The effect from the Jahn–Teller distortions and $\langle r_A \rangle$ would be equal for both samples, and thus the appearance of this doublet for the bismuth-doped sample shown in figure 2 would be associated with the pressure dependence of the inherent characteristics of the Bi^{3+} ion. Previous research on the $x = 0$ end member of the solid solution has revealed that the high-polarizability $6s^2$ lone-pair characteristic of Bi^{3+} in BiMnO_3 is distinctly different to the LaMnO_3 in its physical properties [12, 13]. Therefore it is reasonable to consider that the behaviour of this unique characteristic under high pressure may be responsible for the appearance of the doublet in the spectrum, if the lone-pair characteristics of bismuth in the bismuth compounds is considered. When this characteristic is dominant, the Bi^{3+} compound is distorted, and the Bi^{3+} and La^{3+} counterparts will have approximately equal volumes. When Bi^{3+} is forced into high symmetry, a Bi^{3+} compound should have a smaller

volume than that of La^{3+} , and this characteristic becomes constrained [14]. The primary effect of the external pressure is to compress all the bond lengths (A–O and B–O) and thus the A–O and B–O interactions are enhanced due to the increased overlap of oxygen orbitals with the A- and B-site orbitals. From a microstructural viewpoint, the disordered bismuth and lanthanum ions with their neighbour manganese and oxygen ions will form a number of discrete clusters. Under external pressure, when the crystal field forces Bi^{3+} ion into high symmetry, the clusters of Bi^{3+} with its neighbour 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 and the cooperativity between local site deformations may be dynamic. The interplay among charge, spin and orbital is amenable to being changed by the variation of temperature, magnetic field and composition through a mixed-phases process in the perovskite manganites [4–6]. Early work has revealed that the effect of substitution of Bi in place of La would induce a structural phase transition from orthorhombic to monoclinic, with the doping $x > 0.3$ at ambient pressure [10]. As the pressure increases, the pressure dependence of the lone-pair characteristic of bismuth becomes constrained, and it introduces more dilute local deformations. With these deformations coupling with the enhanced charge, orbital interactions will form a number of discrete phases, which have a coherence length larger than the intrinsic coherence length for x-rays, that are simultaneously present in the sample. Their relative proportions vary with pressures, and the results are reflected by the asymmetrical peak shape during the course of the application of hydrostatic pressure. Under much higher pressures, cooperativity among the dynamic discrete phases can be enhanced, and this finally results in the appearance of the doublet as shown in the diffraction patterns of $\text{La}_{0.25}\text{Bi}_{0.25}\text{Ca}_{0.5}\text{MnO}_3$. Although the exact refinement of this unusual pattern is not yet available, a possible explanation is given by the hypothesis of the multiple distorted domains that are simultaneously present in the specimen. Further work needs to be done to clarify the mixed-phases process in detail.

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