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Structural stability of multiferroics $BiMnO_3$ under high pressure

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Abstract Multiferroics $BiMnO_3$ was fabricated via high pressure of 4 GPa. The crystal structure of as-prepared specimen was determined by x-ray diffraction to be highly distorted monoclinic perovskite with space group of *C*2. Multiferroism (or ferroelectromagnetism, i.e., coexistence of ferromagnetism and ferroelectricity) in as-prepared specimen has been reported in the recently published paper (Z.H. Chi, C.J. Xiao, S.M. Feng, F.Y. Li, C.Q. Jin, J. Appl. Phys. **98**:103519, 2005). Structural toughness of as-prepared specimen under high pressure was studied in diamond-anvil cell (DAC) combined with synchrotron radiation x-ray diffraction. No structural phase transition was detected up to the maximum pressure of 27 GPa, indicating a compact and low compressibility of monoclinically distorted perovskite structure of $BiMnO_3$. The bulk modulus B_0=141 GPa ($B_0^{'} = 4$) was derived from Birch–Murnaghan equation of state (EOS).

Keywords Multiferroics · DAC · Synchrotron radiation · Bulk modulus · Equation of state

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1 Introduction

Magnetoelectric multiferroics, sometimes termed as ferroelectromagnet, exhibiting ferroelectricity and ferromagnetism simultaneously, i.e., being both magnetically and electrically polarized, has stimulated a great deal of research interest during the very recent years [2–15]. Apart from the tremendous application perspective based on the mutual control of polarization and magnetization via magnetoelectric effect, i.e., the induction of electric polarization by means of magnetic field or vice versa, the fundamental physics behind is fascinating. Unfortunately, the number of ferroelectromagnet is dramatically reduced to very few cases with respect to pure ferroelectrics or ferromagnetics due to the incompatibility between magnetism and ferroelectricity in both electronic and crystal structure requirements. It is well established that magnetism and ferroelectricity are involved with local spins and off-center structural distortion, respectively. Through first principles calculation, Hill et al. [6] has pointed out that partially occupied orbital of transition metal *d* electron which is prerequisite for magnetism reduces the tendency for off-center structural distortion which is the origin of ferroelectricity. Thus, an additional structural driving force must be present to engender the concurrence of ferroelectricity and ferromagnetism. Lone pair of electrons has proven to play a pivotal rule in inducing structural distortion and ferroelectricity in typical ferroelectric $PbTiO_3$ [7], which exhibits an entirely different polarization mechanism in comparison with homologous $BaTiO_3$ due to the stereochemical activity of lone pair on Pb^{2+} cation. Homologous candidate ferroelectric $PbVO_3$ [8] with gigantic spontaneous polarization surpassing that of $PbTiO_3$ as a result of larger tetragonality has been fabricated by high pressure–high temperature synthesis technique. Like Pb^{2+}, Bi^{3+} with $6s^2$ lone pair is the key factor in triggering

ferroelectricity in perovskite multiferroics $BiFeO_3$ [9]. Very recently, $BiMnO_3$ was unraveled to be a new supplement to the scarce multiferroics family, in which magnetocapacitance effect (MC) has been verified [10]. Due to the fairly strong covalent character of $6s^2$ lone pair, $BiMnO_3$ can only be synthesized at high pressure of at least 3 GPa [11] to stabilize the highly distorted perovskite structure. Once quenched from high temperature–high pressure state, it survives as a metastable phase with *C*2 monoclinic structure at ambient condition [12]. Multiferroism (or ferroelectromagnetism) with ferroelectric Curie temperature T_E at 773 K and ferromagnetic Curie temperature T_M at 105 K in $BiMnO_3$ has been widely recognized. So far, investigation on structural feature of $BiMnO_3$ has been focused on temperature dependence only [13]. Structural evolution of $BiMnO_3$ when subjected to external pressure still remains open question. In this paper, we investigated the stability of non-centrosymmetric polar structure of $BiMnO_3$ under high pressure up to nearly 27 GPa.

2 Experimental

Polycrystalline $BiMnO_3$ ceramic was fabricated via a high pressure–high temperature synthesis route. Stoichiometric mixture of Bi_2O_3 (Alfa Aesar, 99.99%) and Mn_2O_3 (Alfa Aesar, 98%) reagents was intimately ground, pelletized and enveloped with gold foil to circumvent contamination from the ambience. The ultimate synthesis was conducted in a cubic anvil-type apparatus by keeping the specimen at 1,273 K and 4 GPa for 30 min. Pressure was released slowly after quenching the specimen to room temperature.

Angle-resolved powder x-ray diffraction pattern was recorded with Cu Kα radiation (λ=1.54050 Å) at M18AHF diffractometer (MAC SCIENCE, JAPAN). Data processing and structure refinement were performed employing *Powder X* software packet [14].

High-pressure synchrotron x-ray diffraction experiment was performed on 3W1A high-pressure beamline at Beijing Synchrotron Radiation Facility (BSRF). The diffraction pattern was recorded with white synchrotron radiation in an energy-dispersive mode. Finely ground powder of $BiMnO_3$ together with a tiny piece of ruby crystal for calibrating the inner pressure was loaded in a minute hole with diameter of 250 μm, which serving as sample chamber was drilled in the gasket made of T301 stainless steel. Then mixture of methanol and ethanol (4:1) as pressure-transmitting medium was injected into the chamber to ensure better quasi-hydrostatic pressure condition. The inner pressure in the chamber was monitored via the shift of the fluorescence bands of Cr^{3+} in the ruby crystal. Polychromatic radiation was collimated to a spot with size of 30×20 μm^2 in area. High pressure was generated in DAC (diamond-anvil cell) with diamond culet size of 500 μm. Germanium detector was located at a fixed angle of 7.45° with respect to the incident synchrotron radiation. The d spacing of different reflection (*h k l*) of $BiMnO_3$ specimen was calculated according to the Bragg law expressed as following:

$$E * d = \frac{6.19925}{\sin\theta} \tag{1}$$

3 Results and discussion

Figure 1 exhibits the angle-resolved powder XRD pattern of as-prepared specimen recorded at room temperature. Impurities including $Bi_2O_2CO_3$ and A-type Bi_2O_3 were detected despite enormous efforts made by changing stoichiometry of starting oxides, reaction pressure, reaction temperature and reaction time to improve the purity. The main peaks in the pattern can be indexed on the basis of *C2* monoclinic structure exclusive of peaks from impurities, in good accordance with the conclusion of neutron and electron diffraction [12].

In situ high-pressure energy-dispersive synchrotron X-ray diffraction spectra of $BiMnO_3$ are displayed in Fig. 2. The spectra were collected at pressures ranging between atmospheric and 26.8 GPa. Through deliberate analysis, nine diffraction peaks with corresponding indices of (111), (−113), (−311), (004), (−404), (222), (−315), (313) and (115) can be assigned to the *C2* monoclinic phase of $BiMnO_3$ in spite of poor profile and intensity of peaks. It is very explicit that all the diffraction peaks of *C2* phase of $BiMnO_3$ shift to the higher energy side with increasing pressure, which coincides well with the Bragg law (1). Neither new diffraction peaks emerge nor original peaks

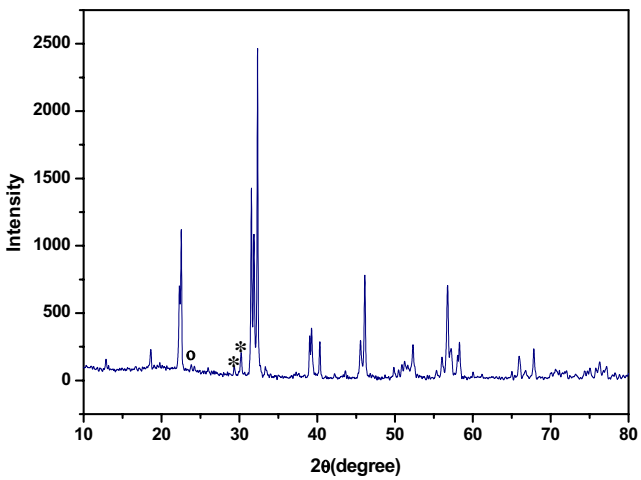

Fig. 1 Angle-resolution powder X-ray diffraction pattern of as-prepared $BiMnO_3$ ceramic recorded by Cu Kα radiation at room temperature (*asterisk* and *open circle* denote A-type Bi_2O_3 and $Bi_2O_2CO_3$ impurity, respectively)

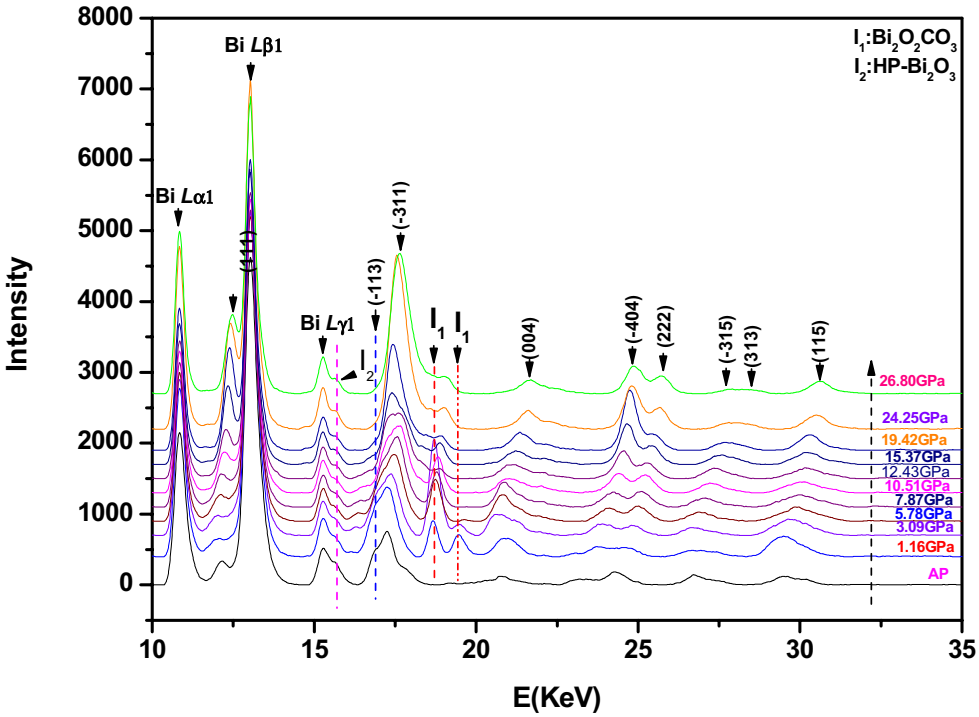

Fig. 2 In situ high-pressure energy-dispersive x-ray diffraction pattern of as-prepared $BiMnO_3$ ceramic recorded by white synchrotron radiation at room temperature (Bi $L_{\alpha 1}$, Bi $L_{\beta 1}$ and Bi $L_{\gamma 1}$ indicate the fluorescent peaks of element Bi, respectively)

disappear in the full pressure range, indicating no structural phase transition takes place during the compression process.

Lattice parameters of *C2* phase of $BiMnO_3$ with increasing pressure were calculated by virtue of modification of *d* spacing of detectable diffraction peaks. The calculated lattice parameter was plotted as a function of pressure in Fig. 3. As shown in the plot, lattice parameters along three fundamental axes change not monotonically but with sizable fluctuation, this can be attributed to the non isotropic compression as a result of poor hydrostatic condition.

In order to obtain an evaluation of the compressibility, volume compression ratio of V/V_0 as a function of pressure was plotted in Fig. 4. The scattered dot was fitted nonlinearly with Birch–Murnaghan equation of state (EOS):

$$P(\mathrm{GPa}) = \frac{3}{2} * B_0 * \left[(V_0/V)^{7/3} - (V_0/V)^{5/3}\right] * \left\{1 - \left(3 - 3 * B_0'/4\right) * \left[(V_0/V)^{2/3} - 1\right]\right\} \quad (2)$$

Supposing the first-order derivative $B_0' = 4$, we obtain the bulk modulus $B_0 = 141 \pm 4$ GPa, which is comparable to most oxide ceramics.

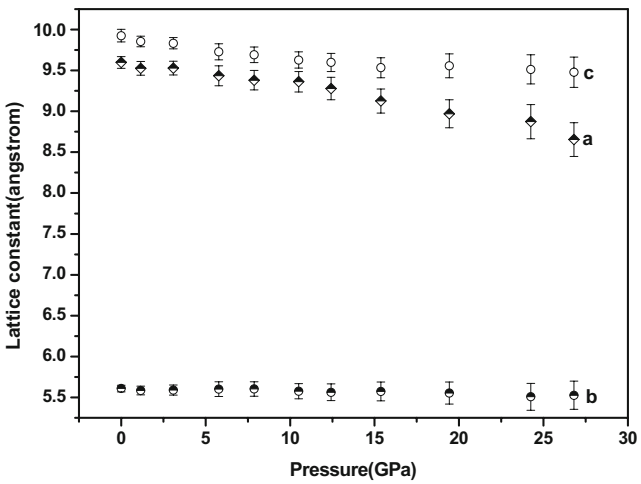

Fig. 3 Pressure dependence of lattice parameters of as-prepared $BiMnO_3$ ceramic

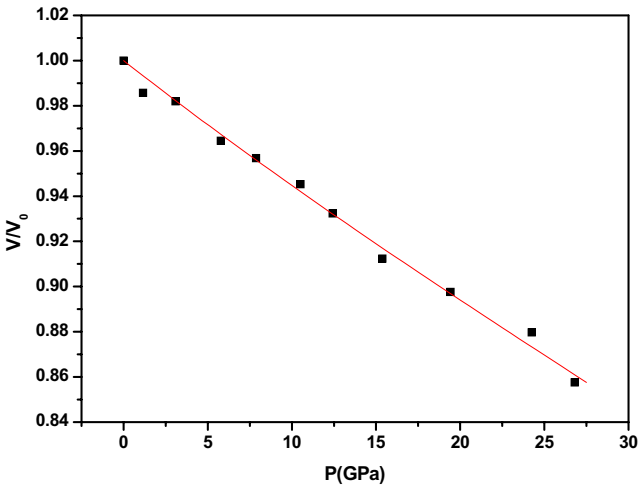

Fig. 4 Pressure dependence of volume compression ratio of as-prepared $BiMnO_3$ ceramic

4 Conclusion

Multiferroics $BiMnO_3$ ceramic with a highly distorted perovskite structure was synthesized and studied under high pressure. It is inferred that the *C2* monoclinic structure is stable up to nearly 27 GPa. Bulk modulus B_0 was calculated to be 141 GPa from Birch–Murnaghan equation of state.

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