Temperature and pressure effects of multiferroic Bi$_2$NiTiO$_6$ compound

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Bi$_2$NiTiO$_6$ compound which shows both magnetic ($T_M = 58$ K) and ferroelectric properties ($T_C = 513$ K) was synthesized under high pressure of 5 GPa and temperature of 1273 K. The crystal structure, as determined by X-ray powder diffraction and neutron powder diffraction, is a distorted A(B$_1$B$_2$)O$_3$ type perovskite with space group $Pn_2_1$.$a$. Structural evolution of multiferroic Bi$_2$NiTiO$_6$ shows that there are two isostructural phase transitions at $\sim$2 GPa and $\sim$15 GPa under high pressure and at room temperature and indicates that isostructural phase transitions occurred with temperature higher than 823 K under ambient condition. All the isostructural phase transitions come from the Bi ion discontinuous shift, which identifies the phase transition at $\sim$15 GPa and at temperature higher than 823 K are the same. Using a modified high-T Birch-Murnaghan equation of state and a thermal-pressure approach, we have derived the thermelastic parameters of high pressure phase Bi$_2$NiTiO$_6$, including the ambient bulk modulus $K_0$, temperature derivative of bulk modulus at constant pressure, volumetric thermal expansivity, pressure derivative of thermal expansion, and temperature derivative of bulk modulus at constant volume. © 2013 AIP Publishing LLC

I. INTRODUCTION

Multiferroic compounds with coexisting magnetic and ferroelectric orders and magnetoelectric interaction are a class of electronic functional materials. Such materials are highly interesting from both fundamental and technological points of view. Although early attempts to combine ferromagnetic and ferroelectric ordering states in a single material can be traced back to 1960s,1,2 the research has not received growing attention until 2000s while strong magnetic and electric coupling was observed in transition metal oxides.3,4 Ferroelectricity and ferromagnetism usually exclude each other.5,6 To polarize a crystal, the structure needs to be non-centrosymmetric such that it prefers non-magnetic ions. On the other hand, ferromagnetism is commonly occurs in materials containing transition metal ions with unpaired outer shell electrons. As a result, single-phase multiferroic compounds are to date quite scarce. Bi- and Pb-based ferroelectric compounds have received much attention in recent years due to their superior properties for technological applications.3,4,7 It is believed that the spontaneous polarization in these compounds mainly results from the $ns^2$ lone pair. As it has been reported by Azuma et al.,7 a classical way to obtain multiferroic properties in ABO$_3$ system is to have Bi$^{3+}$ and Pb$^{2+}$ at A site and magnetic transition metal ions at B site. Until now, the most studied Bi-based multiferroic perovskites are BiMnO$_3$ [Refs. 9–15] and BiFeO$_3$ [Refs. 16 and 17] with magnetic Mn or Fe ions at B site. However, those compounds usually show large leakage current partially caused by the presence of $d$ electrons, which leads to high density of states near the Fermi surface and improved conductivity with narrow band gaps. BaTiO$_3$ represents another type of classic ferroelectric compound in which the covalent bonding between non-magnetic Ti$^{4+}$ and O$^{2-}$ enhances the spontaneous polarization.18 Therefore, a common strategy to formulate new multiferroic compounds is to incorporate both magnetic and non-magnetic ions at B sites in favor of ferroelectricity.

Here we report the multiferroic compound Bi$_2$NiTiO$_6$, which has been studied as ferroelectric materials recently,19–21 has successfully been synthesized by means of high pressure sintering. The crystal structure, as determined by powder X-ray and neutron diffraction methods, is a La$_2$CuTiO$_6$-type$^{22}$ double perovskite with non-centrosymmetric space group $Pn_2_1$.$a$. We studied structural stability and equation of state of this multiferroic compound by synchrotron X-ray diffraction at elevated pressures and temperatures.

II. EXPERIMENTAL SECTION

The bulk sample of Bi$_2$NiTiO$_6$ was prepared at 5 GPa in a cubic anvil-type high-pressure apparatus at 1273 K for 30 min. The powder X-ray diffraction (XRD) experiments at ambient conditions were performed with an M18AHF...
dифрактометром (MAC SCIENCE, Japan) используя Cu Kα1 излучение в шаговом сканировании (3 с усреднительного времени для Δ2θ = 0.02°). Неоновый рентгеновский дифрактометр был выполнен в Центре для нейтронной исследовательской, Национальный Институт стандартов и технологии, Gaithersburg, Maryland с длиной волны λ = 1.5403 Å. Магнитная проницаемость была измерена с помощью суперпроводящего квантового интерферометра (SQUID) магнетометра (Quantum Design MPMS XL) в магнитных полях 100 Oe, 1000 Oe, 1 T, 3 T, 5 T, и 7 T. Диэлектрическая константа была измерена с помощью HP4294A иономера анализатора при температурах между 300 K и 600 K. Высокое-давление синхротронный угловой-дисперсионный рентгеновский дифрактометр (AD-XRD) эксперимент был выполнен при комнатной температуре на синхротронной линии 3W1A высокого давления в синхротронной радиации (BSRF), с длиной волны 0.6199. Загрузка образца в камеру была сделана в образец 0.3 мм в диаметре и 2.0 мм длиной. Пресс-жидкость была использована в качестве препарата для достижения высокой температуры. Пресс-жидкость использовалась как материал для нагрева до высокой температуры. Микстура аморфного бора и эпоксидной смолы была использована для получения высокой температуры. 

III. RESULTS AND DISCUSSION

A. Multi-scale characterization of as-prepared sample

The Bi2NiTiO6 sample recovered from high P-T synthesis is fully dense and well crystallized with a grain size of several microns, as revealed by scanning electron microscope (SEM) observations. Energy dispersive X-ray spectroscopy (EDX) measurement on a single grain of as-prepared sample shows atomic ratios of Bi:Ti:Ni:O = 2:0.9:1:1.61. Within the error of EDX analysis, our sample has the ideal composition of Bi2NiTiO6. These combined properties indicate that the as-prepared sample is a good candidate for ferroelectric property measurement.

Figure 1(a) shows the XRD pattern collected for Bi2NiTiO6 at room temperature. All reflections can well be indexed to an orthorhombic structure with space group Pn21a.

The final R factors of the refinement are Rwp = 10.37% and Rp = 8.37%. Inset of Figure 1(a) shows the simulated crystal structure. Note that Pn21a is a subgroup of Pnma. To further resolve this distinction, we collected neutron powder diffraction data on the same specimen, as shown Figure 1(b), which are more sensitive to XRD to the atomic positions of oxygen in crystal structure. The refinement with space group Pn21a gives Rwp = 10.8%, Rp = 8.24%, and χ² = 2.57. The refined lattice parameters are a = 5.61(±0.01) Å, b = 7.85(±0.01) Å, and c = 5.58(±0.01) Å. The site occupancies of Ti and Ni cations were also refined. The site occupancies of Bi cation and O anions are slight off the ideal 1 (less than 1%) and therefore fixed during the refinement. The impurity phases NiO and TiO were also refined in the neutron diffraction data. The fractional coordinates, site occupancies, and thermal parameters (Uiso) as well as the fractions of impurity phases from the refinement of neutron diffraction data are listed in Table I. It can be seen that Bi, Ni, and Ti ions are all shifted away from the positions of (0, 0.25, 0), (0, 0, 0.5), and (0, 0, 0.5) in Pnma space group. Alternatively, when we refine the diffraction data with Pnma, the thermal parameters for Bi are
nonisotropic with an abnormally large $U_{11}$ value, suggesting that Bi ion shifts away from the ideal position in $Pnma$ group. Because Bi$_2$NiTiO$_6$ is ferroelectric, another argument that favors $Pn2_1a$ is that this space group does not possess a center of symmetry whereas $Pnma$ is centrosymmetric and thus intrinsically prohibits ferroelectricity.

Figure 2 shows dielectric constant and dielectric loss ($\tan \delta$) measured at a frequency of 100 kHz. Dielectric anomalies with significant hysteresis between heating and cooling cycles are clearly revealed, indicating a classical, first-ordered ferroelectric phase transition at a temperature around $T_C = 513$ K. Figure 3(a) displays zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibilities of Bi$_2$NiTiO$_6$ measured at $H = 100$ Oe and $T = 5$–300 K. The ZFC and FC susceptibility curves start splitting below 60 K, with the ZFC susceptibility peaked at $T_M = 58$ K. The inverse ZFC susceptibilities are displayed in the inset of Figure 3(a), including a Curie-Weiss law fitting, $\chi = C/(T - T_0)$, of the data above 165 K. The values of Curie-Weiss temperature $T_0$ and effective magnetic moment $\mu_{eff}$ are $-242.7$ K and $2.28 \mu_B$/f.u., which reflect a strong antiferromagnetic interaction and magnetic frustration in this system. With increasing magnetic field, the anomalies are strongly depressed at $H = 7$ T, indicating a ferromagnetic-like, probably short ranged, magnetic contribution to the magnetization behavior, as shown in Figure 3(b). So in this Bi$_2$NiTiO$_6$ system, the magnetic interaction is complicated, showing a canted spin interaction and an inhomogeneous magnetic state.

### TABLE I. Refined fractional coordinates, occupation, and thermal parameters $U_{iso}$ as well as the fractions of impurity phases of NiO and TiO from neutron diffraction data.

<table>
<thead>
<tr>
<th>Coordinates of equivalent positions</th>
<th>Occupancy</th>
<th>$U_{iso}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>1.00</td>
<td>0.0448</td>
</tr>
<tr>
<td>Ni</td>
<td>0.502552</td>
<td>0.0016</td>
</tr>
<tr>
<td>Ti</td>
<td>0.526880</td>
<td>0.0016</td>
</tr>
<tr>
<td>O(1)</td>
<td>1.00</td>
<td>0.0648</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.270987</td>
<td>0.0016</td>
</tr>
<tr>
<td>O(3)</td>
<td>1.00</td>
<td>0.0791</td>
</tr>
</tbody>
</table>

Phase fractions

Bi$_2$NiTiO$_6$ 95(2) mol. %  TiO 1.4(1) mol. %  NiO 3.6(3) mol. %
isomorphous phase transition occurred at \( \sim 2 \text{ GPa} \), another phase transition at \( \sim 15 \text{ GPa} \).

Figure 5(b) shows the pressure dependency of the unit-cell volume for \( \text{Bi}_2\text{NiTiO}_6 \), where the solid lines are the fitting results for two isostructural phases using the second-order Birch equation of state (EOS)\(^{26}\)

\[
P(GPa) = \frac{3}{2} B_0 \left[ \left( \frac{V_0}{V} \right)^{7/3} - \left( \frac{V_0}{V} \right)^{5/3} \right] + \left\{ 1 - (3 - 3 \times B'_0/4) \times \left[ \left( V_0/V \right)^{2/3} - 1 \right] \right\}.
\]  

With \( B'_0 \) fixed at 4, we obtained the ambient isothermal bulk moduli of 94(7) GPa, 145(9) GPa, and 355(10) GPa, respectively, for the three phases. The fitted unit-cell volumes, \( V_0 \), of the three phases at ambient conditions are 244.6 \( \times 10^{-3} \) nm\(^3\), 244.4 \( \times 10^{-3} \) nm\(^3\), and 236.1 \( \times 10^{-3} \) nm\(^3\), respectively.

Temperature can also drive phase transitions in ferroelectric phase materials as what pressure can do. We performed \textit{in situ} high-temperature XRD experiments at atmospheric pressure. At temperatures above 823 K, a series of new diffraction peaks appears, and the diffraction pattern is similar to those observed at pressures higher than \( \sim 2 \text{ GPa} \), as shown in Figure 5(c). We refined all XRD patterns collected at different temperatures and pressures by using the GSAS program package. Figures 5(a) and 5(d) are the refined X and Z coordinates evolutions of Bi ions under different pressures and at different temperatures, respectively. The evolutions of Ni and Ti cations shifts as a function of high pressure are almost ignorable compared with Bi cation shifts and are not shown here. The pressure dependence of Bi ion positions is not continuous at \( \sim 2 \text{ GPa} \) and \( \sim 15 \text{ GPa} \), corresponding to the two isostructural phase transitions. The temperature dependence of Bi ion positions is not continuous at temperature higher than 823 K. Compared Figures 5(a) and 5(d), we conclude that the phase transition with temperature is identical with the isostructural phase transition at around 15 GPa. In Bi-based multiferroic, the \( 6s^2 \) lone pairs are thought to be the source of ferroelectric polarization. In the case of \( \text{Bi}_2\text{NiTiO}_6 \), it is conceivable based on the findings of this work that there may exist rich physical phenomena to be uncovered at elevated temperature and pressure.

C. Thermal equations of state of \( \text{Bi}_2\text{NiTiO}_6 \)

Figures 6 show the relations between unit-cell volumes and pressures at different temperatures for high pressure phase \( \text{Bi}_2\text{NiTiO}_6 \). We employ a modified high-\( T \) Birch-Murnaghan EOS\(^{27-31} \) truncated to third order, to derive the thermoelastic parameters based on the measured \( P-V-T \) data for \( \text{Bi}_2\text{NiTiO}_6 \). A general form of this modified EOS is formulated by

\[
P = 3K_T f \left( 1 + 2f \right)^{5/2} \left[ 1 - \frac{3}{2} \left( 4 - K' \right) f + \ldots \right],
\]  

where

\[
K_T = K_{T0} + \left( \frac{\partial K}{\partial T} \right)_P (T - 300),
\]

\[
K' = \left( \frac{\partial K}{\partial P} \right)_T,
\]

and

\[
f = \frac{1}{2} \left[ \left( V_T/V_{PT} \right)^{2/3} - 1 \right],
\]

\[
V_T = V_0 \exp \left( \alpha(0,T)dT \right).
\]

In Eq. (2), \( K_{T0} \) and \( K_T \) represent the isothermal bulk modulus at 300 K and a higher temperature \( T \), and \( \left( \partial K/\partial T \right)_P \) and \( \left( \partial K/\partial P \right)_T \) stand for the temperature and pressure derivatives of the bulk modulus, respectively. \( V_0 \), \( V_T \), and \( V_{PT} \) correspond to the unit-cell volumes at ambient conditions, at ambient pressure and temperature \( T \), and at high \( P-T \) conditions, respectively. \( \alpha(0,T) \) is the volumetric thermal expansion at atmospheric pressure, typically represented by

\[
\alpha(0,T) = a + bT - cT^2 \quad (T \text{ in Kelvin, see Ref. 32.})
\]

In the modified high-\( T \) Birch-Murnaghan EOS, the temperature effects are taken into account by replacing \( K_0 \) with \( K_T \) and substituting \( V_0/V_P \) with \( V_T/V_{PT} \) in the isothermal EOS.
Because of the limited pressure range that restricts an accurate constraint on $K'$, we assume $K' = 4$ for Bi$_2$NiTiO$_6$ in Eq. (2) throughout the data analysis. Similarly, we ignore the term of $c/T^2$ in $\chi(0,T)$ as well as higher-order terms and cross derivatives of the bulk modulus such as $\partial^2 K / \partial^2 T$ and $\partial^2 K / \partial P \partial T$. From least-squares fitting of the P-V-T data using Eq. (2), we obtain for the orthorhombic Bi$_2$NiTiO$_6$, $K_0 = 115(3)$ GPa, $\chi(0,T) = -0.017(7)$ GPa K$^{-1}$, and $\chi(0,T) = a + b/\theta$ with $a = 2.1(2) \times 10^{-5}$ K$^{-1}$ and $b = 2.25 \times 10^{-8}$ K$^{-2}$. Errors of these thermoelastic parameters were from those of Le Bail profile fitting; uncertainties in the P-V-T measurements were not included in the error estimation. For the high pressure orthorhombic Bi$_2$NiTiO$_6$, the bulk modulus obtained here (115(3) GPa) is slightly smaller than that fitted from the DAC data at room temperature. Because the presence of deviatoric stress in our DAC experiments, an important factor causing the $K_0$ discrepancy is the angle between the pressure loading direction and the diffraction plane ($\phi$), which is about 90$^\circ$ difference between our cubic anvil apparatus and the conventional DAC setup. In our experimental setup, the diffraction plane is almost perpendicular to the pressure loading direction. Thus the XRD data collected correspond to the maximum stress direction, which would result in smaller bulk modulus if no heating is applied to release the stress.

FIG. 5. (a) and (d) are the Bi ion X and Z position variations under different pressures and at different temperatures, respectively. The pressure dependence of Bi ion positions is not continuous at ~2 GPa and ~15 GPa, which is consistent with the unit cell parameters and volume anomalies under pressures and at different temperatures. (b) The volume variation under pressure and the two isomorphic phase transitions correspond to the Bi ion position discontinuity. (c) The XRD patterns as a function of temperature up to 823 K. The new peaks emerging temperature is consistent with the Bi ion position discontinuity.

FIG. 6. P-V-T data measured for high pressure phase Bi$_2$NiTiO$_6$. The curves represent results of the least-squares fitting using Eq. (2).
From the thermodynamic identity,
$$
(\partial \alpha / \partial P)_T = (\partial K / \partial T)_P K_0^{-2}. \tag{3}
$$

The pressure derivatives of the volume thermal expansivity, 
$(\partial \alpha / \partial P)_T$, are calculated to be $-1.3(6) \times 10^{-6} \text{K}^{-1} \text{GPa}^{-1}$ for $\text{Bi}_2(\text{NiTi})\text{O}_6$. The uncertainties in $(\partial \alpha / \partial P)_T$ are estimated from the error propagation of $K_0$ and $(\partial K / \partial T)_P$.

IV. CONCLUSIONS

In conclusion, the high pressure synthesized $\text{Bi}_2\text{NiTiO}_6$ multiferroic compound shows a first class ferroelectric phase transition $T_C$ at 513 K while heating and a typical canted-spin interaction with magnetic transition temperature $T_M$ at 58 K with complicated magnetic interactions. High-pressure XRD shows that there are two isostructural phase transitions one occurred at temperature higher than 823 K, which corresponds to the canting temperature, there is also an isostructural phase transition at 513 K while heating and a typical canted-spin interaction with magnetic transition temperature $T_M$ at 58 K with complicated magnetic interactions. High-pressure XRD shows that there are two isostructural phase transitions one occurred at temperature higher than 823 K, which corresponds to the canting temperature, there is also an isostructural phase transition at 513 K while heating and a typical canted-spin interaction with magnetic transition temperature $T_M$ at 58 K with complicated magnetic interactions.

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