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Structure, ferroelectric and dielectric properties of Bi_2WO_6 with different bismuth content*

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This paper reports that the Bi_2WO_6 ferroelectric ceramics with excess Bi_2O_3 of 0.0, 2.0, 3.5 and 5.0 wt.% of the stoichiometric composition are prepared by the conventional solid-state reaction method. Their microstructure, ferroelectric properties, the concentration and mobility of the defects have been analysed systematically. With increasing Bi content, the remnant polarization decreases, and the broken-down voltage increases. The optimum Bi excess, 3.5, lowers the oxygen vacancy concentration, while further Bi-addition brings about more defects. The activation energies fitted from cole-cole plots are 0.97 eV, 1.07 eV, 1.18 eV, and 1.33 eV, respectively. This suggests that the mobility of the defects is weakened by Bi-addition, which may be due to the increase of the ratio of the number of Bi_2O_2 layers to that of the perovskite blocks.

Keywords: ferroelectric ceramics, Bi_2WO_6, oxygen vacancy, x-ray photoemission spectroscopy
PACC: 7780, 7700, 7790

1. Introduction

In recent years, the Aurivillius family of layered bismuth oxides, one of the most important classes of ferroelectric material, has been extensively studied in particular for their potential in the information storage systems.[1,2] Structurally they are generally formulated as $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$, where A represents a mono-, bi- or trivalent ion, B denotes a tetra-, penta- or hexavalent ion, and m is the number of BO_6 octahedra in each pseudo-perovskite block (m = 1, 2, 3, 4, 5...). The pseudo-perovskite blocks $(A_{m-1}B_mO_{3m+1})^{2-}$ are interleaved with bismuth oxide layers $(Bi_2O_2)^{2+}$ along the c-axis.[3]

Among those oxides, Bi_2WO_6(BW, $m = 1$) is the simplest member. Its perovskite block consists of an infinite two-dimensional array of corner-linked WO_6 octahedra. It is prospective for high temperature devices because of its high Curie temperature around 940°C,[4] and it is also one of the promising bismuth layer structure ferroelectric (BLSF) materials for application due to its low dielectric constant and low processing temperature.[4,5] Obviously, understanding the structure and the properties of this simplest BLSF material will be helpful to explore the characters of other BLSF materials possessing more complicated structure.[6,7] However, the investigation on BW is far from enough. Previously, Tabata *et al* reported the preparation of epitaxially growth c-axis-oriented BW thin films by pulsed laser deposition method, and presented their dielectric properties.[8] Ishikawa *et al* prepared BW thin films with (00l)-orientation by metalorganic chemical vapour deposition method, and found the remnant polarization ($2P_r$) is as low as 0.17 μC/cm^2.[5] The low $2P_r$ is attributed to its high c-axis orientation because it is usually acknowledged that the polarization is almost exclusively along the a or b axis for BLSF materials. Thus, it is necessary to investigate on the ferroelectric and dielectric behaviours of the bulk BW with random orientation. In addition, due to the volatility of Bi, the oxygen vacancies will be generated accompanying with the Bi vacancies. These oxygen vacancies act as defects, deteriorating the ferroelectric and fatigue properties of BLSF materials. In BW, the Bi^{3+} ions at A sites are shared with the Bi_2O_2 layers, and the volatiliza-

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tion of bismuth will have more significant influence on its properties. Based on these considerations, different excesses of Bi_2O_3 were added to compensate for the loss of Bi as the ceramic samples were synthesized. Their microstructure, ferroelectric and dielectric properties, the concentration and the mobility of the oxygen vacancies are investigated in order to find out the optimum value of Bi excess.

2. Experiment

The BW bulk samples were prepared with the conventional solid-state reaction method using powders of Bi_2O_3 (99.00% purity) and WO_3 (99.00% purity). Excess Bi_2O_3 of 0.0 wt.%, 2.0 wt.%, 3.5 wt.%, and 5.0 wt.% of the stoichiometric composition were added to the starting powders to compensate for the volatilization of bismuth. The four samples are denoted as BW-0.0, BW-2.0, BW-3.5, and BW-5.0, respectively. The raw materials were firstly mixed by ball-milling for 24 h. After drying, the mixed powders were calcined at 650°C∼ 680°C for 8 h, then pressed into disc-shaped samples with a diameter of 12 mm and a thickness of about 1 mm. The samples were finally sintered at 820°C∼ 870°C in air for 4 h followed with the furnace cooling. To confirm the compound formation, the crystalline structure was characterized by the x-ray diffraction method (XRD) using an M03XHF$_{22}$ diffractometry (Cu $K_\alpha, \lambda = 1.54056$Å, 1Å = 0.1 nm). The chemical composition investigations were carried out by x-ray fluorescence (XRF) (ARL9800x). The ferroelectric properties were measured with a Precision LC ferroelectric analyser. To study the conductive property relating to the defects such as oxygen vacancy, AC impedance spectroscope was measured with a low-frequency impedance analyser (HP-4192A). Since x-ray photoemission spectroscopy (XPS), a non-destructive method, is sensitive to local electronic structure and can present the binding energies of constituent atoms, an ESCALB MK-II spectroscope with Mg K_α radiation was used for XPS measurements to probe the chemical nature of the BW samples.[9]

3. Results and discussion

3.1. Structure and composition

Figure 1 shows the powder XRD patterns of the BW ceramic samples with different Bi content. The peaks are indexed according to the standard powder diffraction data of Bi_2WO_6. The samples of BW-0.0, BW-2.0 and BW-3.5 are of single phase of bismuth-layered perovskite structure. As for BW-5.0, it is found that there are two additional weak peaks at the positions with 2θ of 27.5° and 45.8°, respectively. The emergence of the second phase may imply that excessive Bi_2O_3 of 5.0 wt.% is too much for Bi_2WO_6 prepared with the present condition.

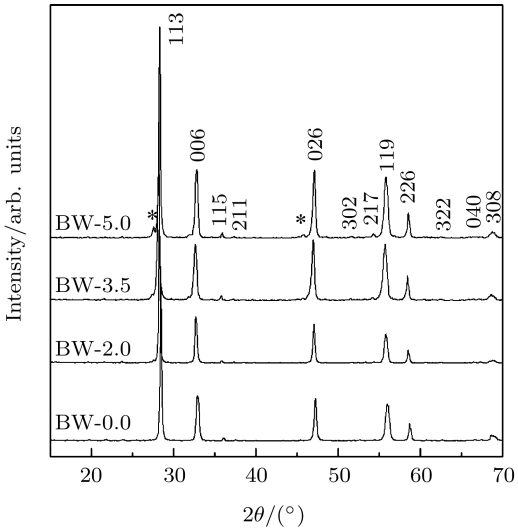


Fig.1. x-ray diffraction patterns of the Bi excess (0.0–5.0 wt.%) Bi_2WO_6 ceramics.

The variation of the lattice parameters a, b, and c as a function of the value of Bi excess is shown in Fig.2. The a, b of all the samples, and c of BW-0.0, 2.0, and 3.5 are nearly unaffected as the Bi excess content increases. However, the c of BW-5.0 increases obviously. The Bi excess of 5.0 wt.% is too much for BW at present preparing condition. The excess Bi

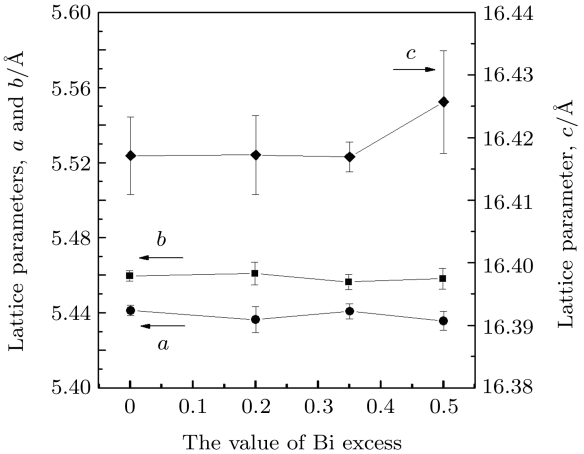


Fig.2. The lattice parameters (a, b and c) of the samples as a function of Bi excess. 1Å = 0.1 nm.

may create the extra Bi_2O_2 layers which result in the jump of the lattice parameter c of BW-5.0.

The mole ratios of Bi to W of four samples determined by XRF are presented in Table 1. The Bi/W mole ratio of the ceramic samples shows a linear dependence on the value of Bi excess in the starting materials, as depicted in Fig.3. The linear relation suggests the identical influence of preparing condition on the composition. Among the samples, it is obvious that the Bi/W mole ratio of BW-3.5 is proximal to the stoichiometric composition.

Table 1. Bi/W mole ratio of the BW ceramic samples.

The value of Bi excess (wt.%)	0.0	2.0	3.5	5.0
Bi/W mole ratio	1.34	1.73	2.09	2.25

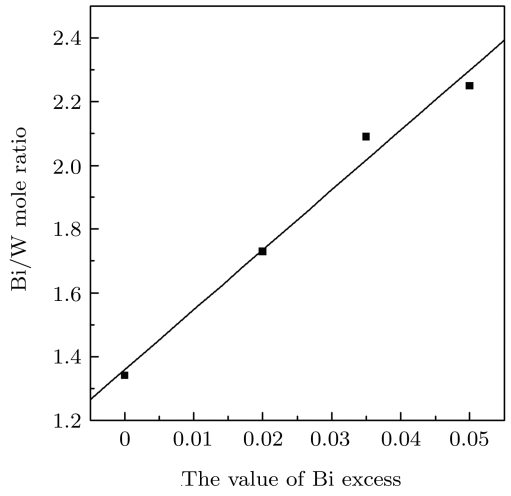


Fig.3. Bi/W mole ratio of BW as a function of Bi excess.

3.2. Ferroelectric properties

Figure 4(a) illustrates the remnant polarization ($2P_r$) versus the maximum field (E_m) measured at room temperature. As the E_m is higher than 50 kV/cm, the increase of the $2P_r$ of BW-0.0 becomes significant. While for BW-2.0 and BW-3.5, the significant increase of $2P_r$ starts at the E_m of about 120 kV/cm and 200 kV/cm, respectively. However, the value of $2P_r$ of BW-5.0 is almost zero, and the polarization hysteresis loop is almost a straight line as the electric field is as high as 400 kV/cm. In the ferroelectric materials, as the electric field reaches an adequately high value, the domains start to switch, leading to the apparent increase of $2P_r$. The adding of bismuth notably increases the applied electric field required for the switching of the ferroelectric domains of the BW samples. It can also be concluded from Fig.4(a) that the broken electric voltage increases with the Bi content. The sample of BW-0.0 is electrically broken down at the applied field of 210 kV/cm, while BW-2.0 is broken down at the E_m of 230 kV/cm. As the Bi excess is 3.5 wt.%, the broken down electric field is increased to 290 kV/cm, while for BW-5.0, the broken down field is 600 kV/cm. Therefore the perfect hysteresis loop can be obtained, which is depicted in the insert of Fig.4(b). The $2P_r$ of Bi-5.0 is as large as 22.5 μC/cm^2 as E_m = 600 kV/cm. Ferroelectric hysteresis loops of the samples under the same electric field of 200 kV/cm are shown in the Fig.4(b). It can be seen that the $2P_r$ of BW-0.0 is the largest of four samples. And the loop of BW-0.0 appears distorted,

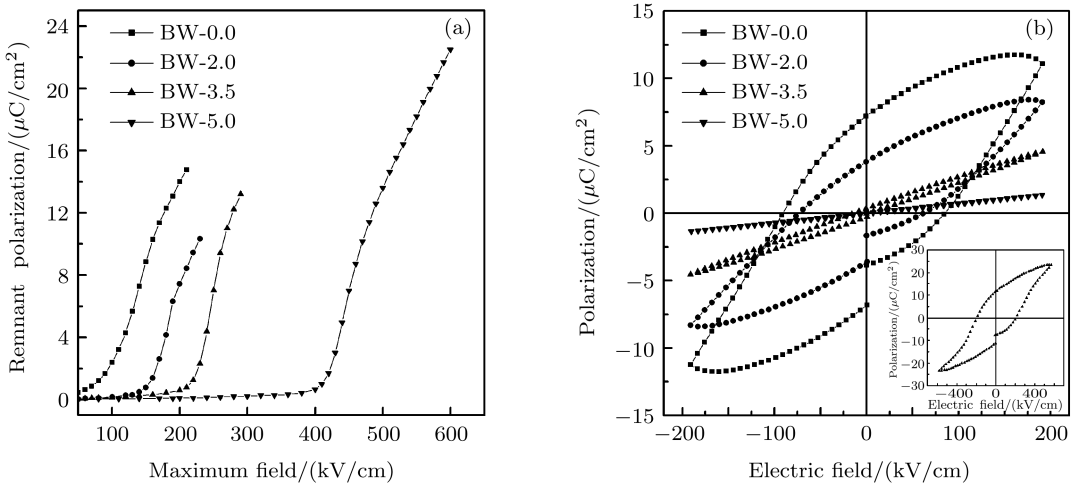


Fig.4. (a) Maximum electric field dependence of remnant polarization measured at room temperature; (b) Polarization hysteresis loops at E_m of 200 kV/cm (the inset figure is the ferroelectric hysteresis loop of BW-5.0 at 600 kV/cm).

which may be due to its high leakage current. The $2P_r$ of BW-5.0 is the lowest and the loop is almost a line.

It is well-known that the Bi_2O_2 layers in BLSF materials play the role of insulating layers, and have a very important influence on the broken down voltage and the leakage current.[10−15] As for BW-0.0, the Bi/W mole ratio is rather lower than the stoichiometric value of 2. Bismuth deficiency will cause the deficiency or destruction of Bi_2O_2 layers, and the insulating effect is weakened. So the broken down field is as low as 210 kV/cm, and the high leakage current is also obvious from the ferroelectric hysteresis loop. With the increase of Bismuth content, the broken down voltage increases and the leakage current decreases. When the Bi content increases to 5.0 wt.%, the E_m is rapidly increased to 600 kV/cm, and the ferroelectric loop is well saturated. This must be related to the increment of the insulating effect of Bi_2O_2 layers. Thus the point of view that the extra Bi_2O_2 layers may appear due to the excess of Bi content is completely reasonable.

3.3. XPS spectra of BW samples

Figure 5 presents the XPS spectra of Bi 4f and W 4f. The calibration of the binding energy scale was controlled by using the C 1s line that appears in the photoelectron spectra of the as-received samples due to the usual carbon contamination. Any binding energy shift due to the sample charging was corrected by the C 1s (284.6 eV) peak as an internal reference.[16−18] It is seen that the binding energy of Bi 4f is 158.40, 158.85, 158.90, and 158.60 eV for the BW-0.0, 2.0, 3.5, and 5.0, respectively. As for W 4f, the binding energy for the four samples is 34.70, 35.05, 35.05, and 34.75 eV, respectively. As the Bi excess is 3.5 wt.%, the binding energies of Bi 4f and W 4f maximize, which are increased by 0.50 and 0.35 eV in comparison with those of BW-0.0. However, with the further increasing of Bi content to 5.0 wt.%, the binding energies are decreased. Especially for W 4f of BW-5.0, its binding energy is near the value of BW-0.0. Due to the oxygen vacancies in the vicinity of Bi and W, the Bi and W may be in the $(+3-x)$ and $(+6-y)$ valence state (x and y are positive), and the binding energies will be lower than those in Bi_2O_3 (∼163 eV) and WO_3 (∼35.8 eV). As the oxygen vacancy is restrained, the chemical valence of Bi and W will be increased, which corresponds to the increase of the binding energy.[18] Thus, the variation of the binding energies of the BW samples implies that the oxygen vacancies are obviously suppressed by the addition of bismuth with the content of 3.5 wt.%. And the addition of more bismuth increases the oxygen vacancy concentration, which may be due to the producing of the extra Bi_2O_2 layers. And it is consistent with the obvious increase of the lattice parameters c for BW-5.0. If so, there exist two kinds of Bi atoms in the Bi_2O_2 layers. One is the original Bi_2O_2 layers, in which Bi is in the +3 valance state, the other is the additional Bi–O layer, in which the Bi may approach the +2 valance state to meet the restriction of the charge neutrality. So the average binding energy of Bi decreases with the emergence of the additional Bi–O layers.

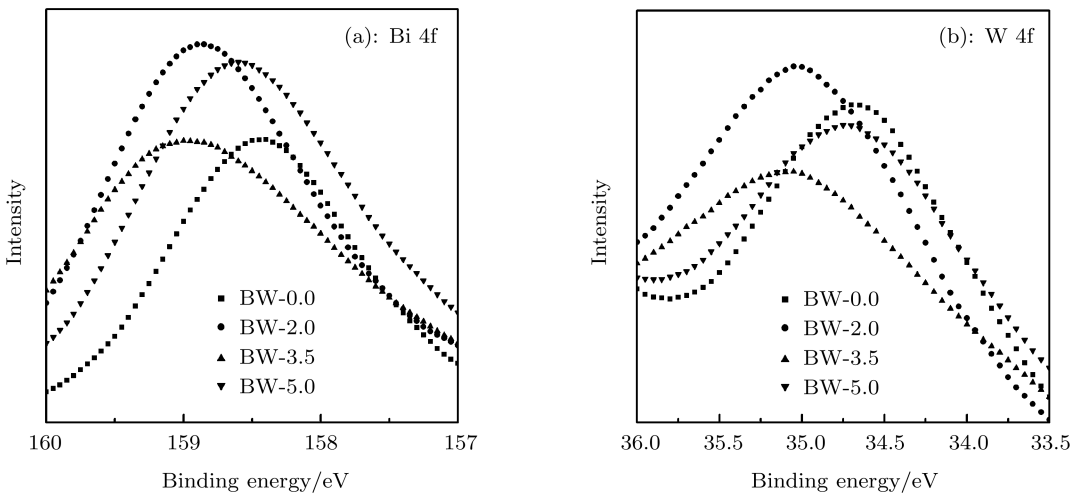


Fig.5. x-ray photoemission spectra of Bi 4f and W 4f. (a): Bi 4f, (b): W 4f.

3.4. Conductivity measurements

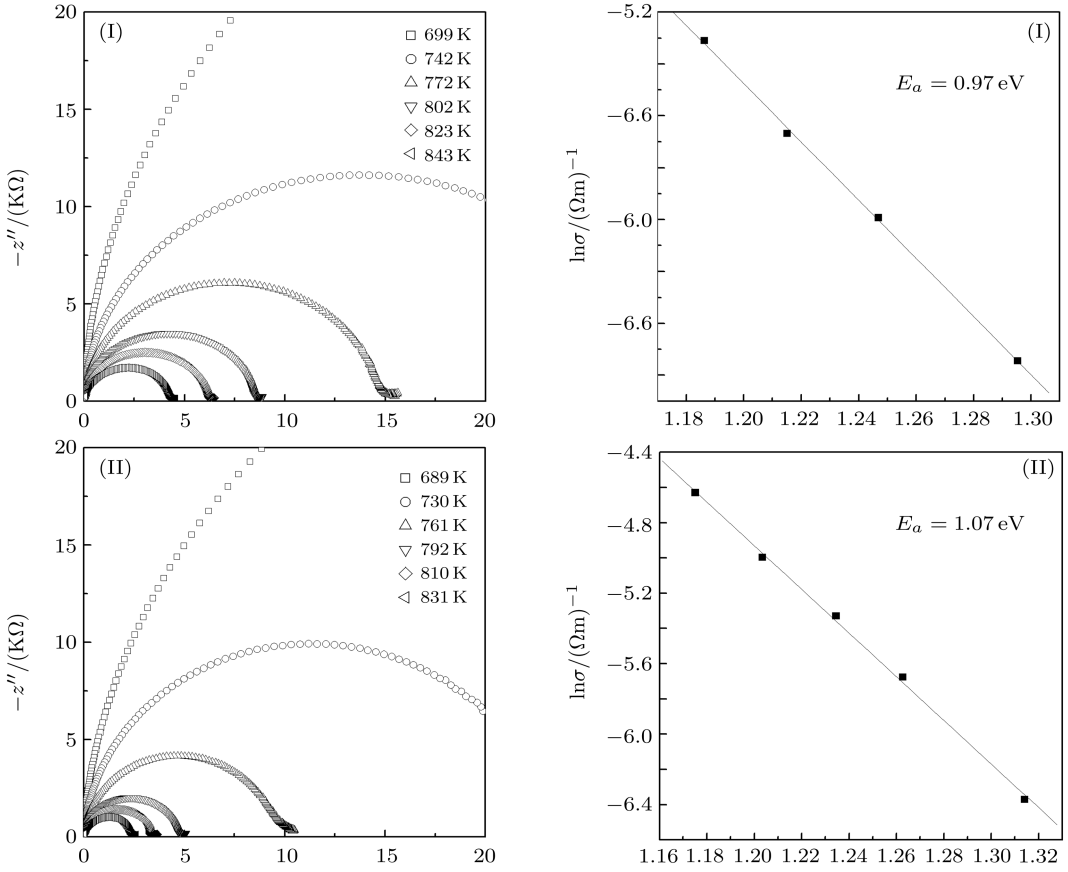
Figure 6(a) (I–IV) presents the variation of real and imaginary parts of the impedance for the BW ceramic samples as a function of temperature and frequency in the form of cole–cole plots. At low temperature, only an arc is present, while semicircles are observed in high temperature region, and there is a tail appears at low frequencies at each semicircle.

The electrical conductivity of the specimen increases with the temperature and can be calculated from the interceptions of the observed semicircles on the real axis of cole–cole plots. The electric conductivity follows the Arrhenius law

$$\sigma = \sigma_0 \exp\left(-E_a/kT\right), \tag{1}$$

where σ_0 is a pre-exponential factor, E_α presents the activation energy for conduction, k is Boltzmann constant, and T is the absolute temperature. Figure 6(b) (I–IV) shows the Arrhenius plots of $\ln\sigma$ versus $1000/T$ for the specimen in the temperature region between 760 K and 860 K. The activation energies for four samples were calculated to be around 0.97 eV, 1.07 eV, 1.18 eV, and 1.33 eV, respectively. And the electric conductivity is in the order of 10^{-3} S/cm at a temperature of 773 K.

The activation energy of oxygen vacancy in $SrTiO_3$ was 1.0∼1.1 eV, while that in $PbTiO_3$- based materials was 0.9∼1.1 eV.[19−21] The value of E_a observed in the Bi_2WO_6 ceramic samples is consistent with the activation energy of oxygen vacancy in perovskite materials. The variation of the activation energy suggests that the mobility of the oxygen vacancy decreases with the increasing addition of the excess Bi in the BW samples. In BLSF material, it is accepted that the Bi_2O_2 layers act as the insulating layers and are self regulated to compensate for space charge, and have a very important influence on the properties of BLSF material.[22−24] In BW-0.0, the Bi/W mole ratio is lower than the stoichiometric value as shown in Fig.3. Bismuth deficiency will cause the deficiency or structural destruction of Bi_2O_2 layers, and then weaken the insulating effect. So the oxygen vacancies need rather low energy to migrate. This is consistent with the distorted loops and the low broken voltage of the BW-0.0. On the contrary, in the BW-5.0 the extra Bi_2O_2 layers may appear between two WO_6octahedra



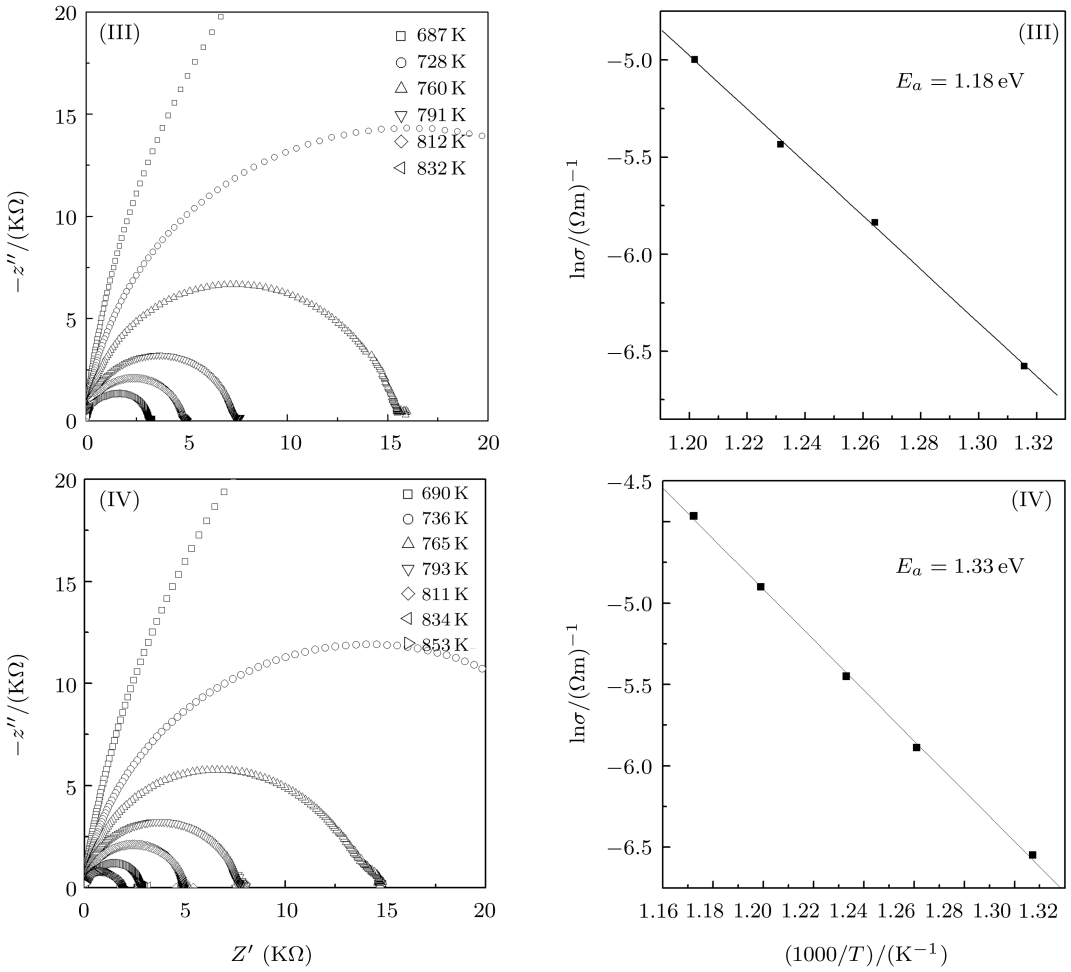


Fig.6. (a) Complex impedance curves for four samples at various temperatures. (b) Arrhenius plots of electric conductivity of BW ceramics. (I): BW-0.0, (II): BW-2.0, (III): BW-3.5, (IV): BW-5.0.

due to the richness of Bi. The extra insulation layers hinder the migration of defects, leading to the enhancement of the activation energy.

From the results of various measurements above, we can have a conclusion to explain our viewpoint that extra Bi_2O_2 layers may appear between two WO_6 octahedra when the Bi content increases to 5.0 wt.%. First, the obvious jump of the lattice parameter c for BW-5.0 is the most direct witness. Second, as for BW-5.0, the broken down voltage increases obviously and the ferroelectric loop is well saturated. These behaviours have direct relationship with the enhancement of insulating effect which is eventually due to the appearance of the extra Bi_2O_2 layers. Third, the XPS spectra show that the binding energy of Bi 4f is decreased for BW-5.0 in comparison with BW-2.0 and BW-3.5. It implies that the oxygen vacancy increases and the chemical valence of Bi decreases. If the extra Bi_2O_2 layers do exist, the average valence of Bi will decrease. So this is another powerful proof of our viewpoint. At last, from the variation of the activation energies for four samples, the consistency is also presented.

Thus, the variation of the ferroelectric properties can be concluded. As for BW-0.0, the concentration of the oxygen vacancies is the highest according to the XPS spectra, while their low activation energy enables them to overcome the potential barrier to diffuse through the perovskite layers easily. These cause the distorted loops and the low broken voltage of BW-0.0. And the relative number of perovskite layers is higher than the stoichiometric value due to the Bi deficiency. Because the polarization of BLSF material mainly originates from the octahedra rather than the Bi_2O_2 blocks, much perovskite slabs will induce the large remnant polarization. As the Bi content increases to 2.0 wt.%, the concentration of the oxygen vacancies is decreased and their migration becomes difficult, so the ferroelectric loops become saturated and the broken voltage is enhanced. Although the

variation of the concentration and mobility of the defects will helpful for the improvement of ferroelectric properties, the decrease of octahedron number will be predominant, which decreases the remnant polarization. Due to the same cause, the $2P_r$ of BW-3.5 decreases further and the broken voltage increases. As for BW-5.0, because the hopping of oxygen vacancies is hindered by the extra Bi_2O_2 layers, the ferroelectric loop is well saturated in spite of the slight increase of the defect concentration. The extra Bi_2O_2 layers bring about the enhancement of the broken-down voltage and the decrease of the ferroelectric property.

4. Conclusions

The different Bi additions to the starting materials cause the different microstructure and properties of the Bi_2WO_6. Among the present samples, the Bi addition content optimizes at the value of 3.5 wt.%, and more or less Bi additions induced the high oxygen vacancy concentration. The residual Bi in the samples produced the extra Bi_2O_2 layers, which hinder the movement of the defects, leading to the well saturated hysteresis loop and higher broken-down voltage. And the extra Bi_2O_2 layers with no polarization deteriorate the ferroelectric properties of the samples.

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