Study of the ferroelectricity in $Bi_2Ti_2O_7$ by infrared spectroscopic ellipsometry

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Using infrared spectroscopic ellipsometry, the dielectric functions of (111) oriented $Bi_2Ti_2O_7$ thin films with pyrochlore structure prepared on $Pt/Ti/SiO_2/Si$ substrate were determined in the temperature range of 20–70 °C. It is demonstrated that there is a phase transition that appears near 40 °C in terms of static effective charge as a function of temperature calculated from the infrared spectroscopic ellipsometric data of $Bi_2Ti_2O_7$ thin films. It suggests that the static effective charge is related to the structural distortion, which can facilitate the polarization of $Bi_2Ti_2O_7$. Accordingly, ferroelectricity in $Bi_2Ti_2O_7$ is proved by analyzing the infrared dielectric function. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1875755]

Pyrochlore oxides with the general formula $A_2B_2O_7$ have been extensively studied for several decades. The pyrochlore structure was first determined to belong to the space group $Fd\bar{3}m(O_h^7)$ by von Gaertner[1] in 1930. The formula $A_2B_2O_7$ is usually expressed as $B_2O_6 \cdot A_2O'$ to emphasize the interpenetrating networks of B_2O_6 sublattice formed by BO_6 octahedra sharing corners and A_2O' sublattice.[2] In 1953, the discovery of ferroelectricity in oxides of face-centered cubic structure (pyrochlore $Cd_2Nb_2O_7$) was reported by Cook and Jaffe.[3] Recently, Sergienko *et al.*[4] reported the metallic "ferroelectricity" in the pyrochlore $Cd_2Re_2O_7$, which was revealed by the analysis of the elastic moduli. Moreover, some studies indicated that there is a close relationship between the physical properties and structure of the pyrochlore oxides.[5]

$Bi_2Ti_2O_7$ is one of various phases in the Bi_2O_3–TiO_2 system. It has the properties of relatively high dielectric constant and good insulating property. Recently, much attention has been paid to $Bi_2Ti_2O_7$ in the field of microelectronics.[6–8] In addition, $Bi_2Ti_2O_7$ crystals exhibit photocatalytic activity.[9] It was reported that both $Bi_2Ti_2O_7$ pyrochlore structure and a stacking-fault-induced structure appear in the recrystallization course from amorphous $Bi_4Ti_3O_{12}$, which can be explained by the valence fluctuation on Bi.[10] Many researchers had done much to clarify the nature of $Bi_2Ti_2O_7$, the focus of which was to see if $Bi_2Ti_2O_7$ has ferroelectricity. Yordanov, Ivanov, and Carapanov[11] had verified that $Bi_2Ti_2O_7$ is a ferroelectric material through the study of dielectric properties. They observed hysteresis loops in $Bi_2Ti_2O_7$ ceramics. Besides, Jiang, Hu, and Zhang[12] suggested that $(La_xBi_{1-x})_2Ti_2O_7$ also belongs to a ferroelectric material, as there is an obvious dielectric peak. And we have reported the dielectric and ferroelectric properties of the nanocrystalline $Bi_2Ti_2O_7$.[8]

Owing to the research and development of $Bi_2Ti_2O_7$ nanocrystals and ceramics, the investigation of $Bi_2Ti_2O_7$ thin films has become a subject of not only theoretical but also practical importance. If $Bi_2Ti_2O_7$ has ferroelectricity, the optical response of $Bi_2Ti_2O_7$ will appear a detectable variation near the phase transition temperature. In the present letter, we report the investigation of optical properties of $Bi_2Ti_2O_7$ thin films to prove the ferroelectricity by infrared spectroscopic ellipsometry (IRSE).

The $Bi_2Ti_2O_7$ thin films were prepared on $Pt/Ti/SiO_2/Si$ substrate by metalorganic decomposition method. We selected bismuth nitrate and titanium butoxide as starting materials. The resultant films were treated at 550 °C by rapid thermal annealing. The detailed procedure was reported in our previous work.[13] The crystallization of the $Bi_2Ti_2O_7$ films was studied by x-ray diffraction (XRD). The optical responses of $Bi_2Ti_2O_7$ thin films were investigated by IRSE in the temperature range of 20–70 °C.

Spectroscopic ellipsometry is a powerful technique to investigate the optical response of materials, as well as to measure the thickness and the dielectric function of a multilayer system simultaneously.[14] We use a classical dispersion formula to describe the dielectric function of $Bi_2Ti_2O_7$ thin films, and assume a three-layer model (ambient/$Bi_2Ti_2O_7$/Pt) for the $Bi_2Ti_2O_7$ thin films on platinized silicon substrates. A good fit of the model to the measured data of IRSE has been obtained by using this model.[15] The ellipsometric measurements were carried out by a variable-angle infrared spectroscopic ellipsometer (PhE-104) by synchronously rotating the polarizer and analyzer with a speed ratio of 1:1. The accuracy was better than 1% for $\tan\Psi$ and $\cos\Delta$ in the measurement. The incident angle was 70° for the samples. In the experimental measurement range of 2.5–12.6 μm wavelength, the corresponding energy is higher than the phonon frequencies, but much lower than the band gap energy of the $Bi_2Ti_2O_7$ thin films. The complex dielectric function $\varepsilon=\varepsilon_1+i\varepsilon_2$ of the $Bi_2Ti_2O_7$ thin films is described as follows:[15]

$$\varepsilon_1 = \varepsilon_\infty - \frac{Nq^2}{M^*\varepsilon_0}\frac{\tau^2}{1+\omega^2\tau^2}, \quad \varepsilon_2 = \frac{Nq^2}{M^*\varepsilon_0}\frac{\tau}{\omega(1+\omega^2\tau^2)}, \quad (1)$$

where N is the cell number per unit volume, q is the ionic average effective charge, $1/M^*=1/M_+ + 1/M_-$ the reduced mass of cations M_+ and anions M_- in a unit cell, τ an energy-independent relaxation time, and ω the light frequency, ε_∞ and ε_0 are the high frequency dielectric constant and dielectric constant in vacuum, respectively.

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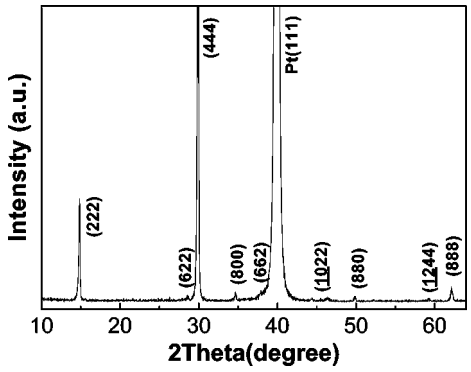

FIG. 1. XRD pattern of $Bi_2Ti_2O_7$ thin films on $Pt/Ti/SiO_2/Si$ substrate.

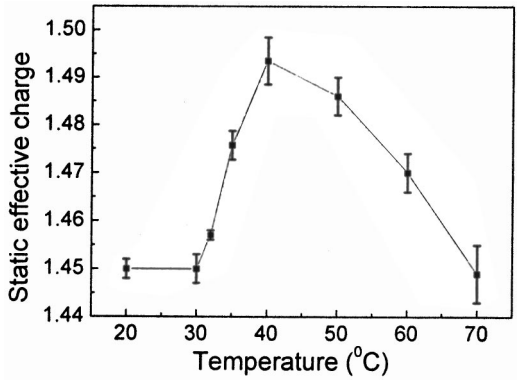

FIG. 3. The plot of static effective charge as a function of temperature.

Figure 1 shows a typical XRD pattern of $Bi_2Ti_2O_7$ thin films deposited on $Pt/Ti/SiO_2/Si$ substrate by annealing at 550 °C. It can be seen that the films show good crystallization with a preferential (111) orientation. And the *d* values of the peaks in the XRD pattern are consistent with those given in the Joint Committee on Powder Diffraction Standards data cards for $Bi_2Ti_2O_7$ (32-118), which is pyrochlore structure type. The XRD pattern indicates that highly (111) oriented $Bi_2Ti_2O_7$ thin films have been grown on $Pt/Ti/SiO_2/Si$ substrate.

We have reported the polarization versus electric field hysteresis loop of the $Bi_2Ti_2O_7$ films.[13] The hysteresis loop measured from the $Pt/Bi_2Ti_2O_7/Pt$ capacitor suggests that $Bi_2Ti_2O_7$ might have ferroelectricity. Furthermore, $Bi_2Ti_2O_7$ is prone to transform into $Bi_4Ti_3O_{12}$ at higher temperature,[16,17] so the IRSE investigation for phase transition of $Bi_2Ti_2O_7$ should be carried out at lower temperature in order to eliminate the influence of $Bi_4Ti_3O_{12}$. As a phase transition at 35 °C was observed in terms of the results of dielectric and thermal response for pressed nanocrystalline $Bi_2Ti_2O_7$,[8] we study the characteristics of $Bi_2Ti_2O_7$ films by IRSE in the temperature range of 20–70 °C.

Figure 2 shows the dielectric function spectra ε_1 and ε_2 for the $Bi_2Ti_2O_7$ thin films in the temperature range of 20–70 °C, which are derived from model fitting the experimental spectroscopic ellipsometric data. The optical constants of Pt in the fitting are taken from Ref. 18. The thickness of $Bi_2Ti_2O_7$ sample is about 240 nm. It can be seen from Fig. 2 that the values of ε_1 decrease as the wavelength increases and approach unity, while the values of ε_2 increase as the wavelength increases. As the temperature rises from 20 to 30 °C, the changes of ε_1 and ε_2 are so little that the curves of

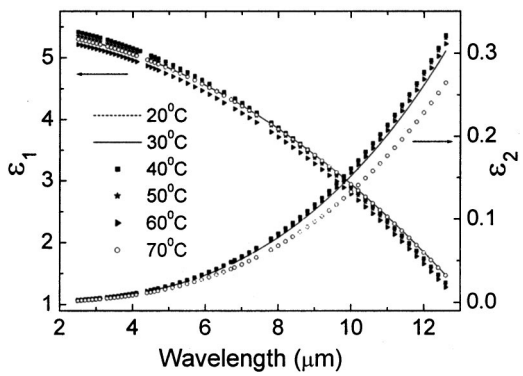

FIG. 2. The dielectric function spectra for $Bi_2Ti_2O_7$ thin films in the temperature range of 20–70 °C.

20 and 30 °C are almost overlapped. When the temperature is up to 40 °C, the difference of dielectric function can be observed. From Fig. 2, in the entirely measured wavelength range, as the temperature increases from 20 to 40 °C, the value of ε_2 reaches a maximum near 40 °C, and then reduces with the increase of temperature from 40 to 70 °C. It is noted that ε_2 relates to the mechanism of absorption, which reflects the change of electron density of states. The change of static effective charge can represent the change of density of states. So the maximum of ε_2 near 40 °C means that static effective charge will have a maximum near 40 °C similarly.

From the fitting results $\sqrt{Nq^2/M^*\varepsilon_0}$ at the temperature range of 20–70 °C, we calculate the static effective charges. The obtained static effective charge, which is an intuitive concept usually based on partitioning the ground state electronic density into contributions attributed to different atoms, is derived from $Nq^2/M^*\varepsilon_0$ in Eq. (1). Figure 3 shows the plot of the static effective charges as a function of temperature. The obtained static effective charge at 20 °C is $|q|=1.450\pm0.002\ e$. As expected, the nominal charges in a purely ionic material for $Bi_2Ti_2O_7$ are +3 for Bi, +4 for Ti, and −2 for O, which means the charge transfer is not completed. $Bi_2Ti_2O_7$ belongs to a mixed ionic-covalent compound.

In general, the phase transition is accompanied by a dramatic change in the dielectric function. Optical dielectric function spectra can reflect the structural phase transition of material effectively. Moreover, it suggests that the polarization originates from the static effective charge transfer. The effective charges can be used to predict the polarization for ferroelectric materials.[19,20] Thus, the peak of static effective charges derived from the data of dielectric function will represent the obvious change of polarization, where a phase transition occurs. From Fig. 3, the static effective charge reaches a maximum at 40 °C in the temperature range of 20–70 °C, which means that there is obviously a phase transition near 40 °C for $Bi_2Ti_2O_7$.

It is worthy of note that the result of phase transition near 40 °C consists with the results of dielectric and thermal response for pressed nanocrystalline $Bi_2Ti_2O_7$ essentially, in which a phase transition at 35 °C was observed.[8]

Ferroelectric materials are characterized by polarization, which is related to its structure. The ideal pyrochlore structure for $Bi_2Ti_2O_7$ is: Bi at (0, 0, 0), Ti at $\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$, O at $\left(\frac{1}{8},\frac{1}{8},x\right)$, and O′ at $\left(\frac{1}{8},\frac{1}{8},\frac{1}{8}\right)$ in space group $Fd\bar{3}m$.[21] However, $Bi_2Ti_2O_7$ has a pyrochlore structure with static bismuth displacements and probable domains of static O′ displacements.

The disorder of Bi and O′ ions is attributed to static displacements in pyrochlore where the Bi^{3+} cations have an active lone pair.[22] As Bi is an easily polarizable cation, oxygen-vacancy ordering accompanied by Bi^{3+} displacement can occur.[5] Bi^{3+} cations are often displaced off the threefold axis in a disordered manner, and besides, a small distortion from an octahedron is indicated by the O–Ti–O angles.[23] These will lead materials to be ferroelectric in the sense of symmetry breaking involved.

The phase transition in ferroelectrics occurs as a result of a delicate balance between long-range Coulomb interactions and short-range forces, and the former makes the ferroelectric instability sensitive to domain structure, defects, and boundary conditions.[24] Ferroelectricity will occur possibly involving symmetry breaking that can be reflected by the changes of static effective charges, which will result in polarization for small distortions. Therefore, the structural distortions sensitively affect the properties of pyrochlore oxides, such as the electrical and optical properties of materials. As the phase transition can lead to variation of optical response, the peak of static effective charge near 40 °C obtained from IRSE data suggests that $Bi_2Ti_2O_7$ has ferroelectricity because of the structural distortions.

In summary, the dielectric functions of $Bi_2Ti_2O_7$ films on $Pt/Ti/SiO_2/Si$ substrate have been investigated using IRSE in the temperature range of 20–70 °C. The temperature dependence of the static effective charge has also been derived. It is found that there is a peak in the curve of static effective charge as a function of temperature. The peak at about 40 °C is coincident with the phase transition observed in pressed nanocrystalline $Bi_2Ti_2O_7$ samples. The ferroelectricity in the pyrochlore $Bi_2Ti_2O_7$ has been confirmed by the investigation of static effective charge, which is related to the polarization of $Bi_2Ti_2O_7$.

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文章题目：用红外椭圆偏振光谱研究 $\mathbf{Bi_2Ti_2O_7}$ 的铁电性

中文摘要：

用红外椭圆偏振光谱在 20-70℃温度范围内确定了在 $Pt/Ti/SiO_2/Si$ 衬底上制备的（111）取向焦绿石结构 $Bi_2Ti_2O_7$ 薄膜的介电函数。从 $Bi_2Ti_2O_7$ 薄膜的红外椭圆偏振光谱数据计算得出的静态有效电荷随时间的变化证实了在 40℃附近有一个相变。静态有效电荷与结构形变相关，从而导致了 $Bi_2Ti_2O_7$ 的极化。因此 $Bi_2Ti_2O_7$ 的铁电性通过分析红外介电函数被证实。