

Influence of vanadium substitution on the conductivity of $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ and $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_{2.97}\text{V}_{0.03}\text{O}_{12}$ ceramics

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Abstract We have fabricated $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ and $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_{2.97}\text{V}_{0.03}\text{O}_{12}$ ceramics using the conventional solid-state reaction method. We measured their *dc* conductivity and analyzed the impedance spectroscopy in order to clarify the influence of vanadium substitution for titanium site on $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ ceramic. The vanadium substitution for titanium site in $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ can reduce the Bi cation and oxygen vacancies. Furthermore, the elimination of these defects, trapped in the grain boundary and grain-electrode interface, significantly reduces the influence of domain pinning, which would be responsible for the improvement in the ferroelectricity and piezoelectricity.

Keywords Conductivity · Impedance spectroscopy · Oxygen vacancies · Bismuth titanate

1 Introduction

In recent years, bismuth layer-structured ferroelectrics (BLSF) have been intensively investigated as novel ferroelectric materials to replace conventional Pb-based ferroelectrics (e.g., PbTiO_3 and $\text{Pb}(\text{Zr,Ti})\text{O}_3$) because of their excellent piezoelectric and ferroelectric properties. Bismuth titanate (BIT: $\text{Bi}_4\text{Ti}_3\text{O}_{12}$) are extensively studied materials of the BLSF family for their large spontaneous polarization along the *a*-axis ($\sim 50 \mu\text{C}/\text{cm}^2$), low processing temperature, high Curie temperature, and lead-free composition [1]. However,

in spite of prodigious efforts to integrate BIT into device application, the thin films and ceramics of BIT suffer from high leakage current and domain pinning due to defects leading to a low ferroelectricity and piezoelectricity [2, 3]. Recently, lanthanides-modified BIT ($\text{Bi}_{4-x}\text{Ln}_x\text{Ti}_3\text{O}_{12}$; Ln=La, Nd, Sm) films were reported to reveal relatively high ferroelectricity [4–6]. Noguchi et al. [3] reported that the ferroelectric properties in BIT ceramics were enhanced by the substitution of Ti^{4+} with higher valence ions such as V^{5+} or W^{6+} . According to our previous work [7, 8], lanthanum and vanadium-cosubstituted BIT ($\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_{2.97}\text{V}_{0.03}\text{O}_{12}$; BLaTV) ceramics exhibited relatively high electromechanical coupling factor ($k_t = 20\%$), quality factor ($Q_m = 5140$) and remnant polarization ($P_r = 11.7 \mu\text{C}/\text{cm}^2$). These values are higher than those of $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLaT) ceramics. Therefore, the small amount of vanadium substitution for titanium site on BLaT can help to improve in the ferroelectricity and piezoelectricity. In this work, a detailed analysis of conductivity and impedance spectroscopy has been carried out to characterize the conduction behaviors of BLaT and BLaTV ceramics in order to clarify the influence of vanadium substitution for titanium site on BLaT ceramic.

2 Experimental

Ceramic samples of $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLaT) and $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_{2.97}\text{V}_{0.03}\text{O}_{12}$ (BLaTV) were prepared by the conventional solid-state reaction method. Powders of Bi_2O_3 , La_2O_3 , TiO_2 , and V_2O_5 of 99.9% purity were mixed in methyl alcohol with zirconia balls and then calcined at 750°C for 2 hr. To fabricate ceramic samples, the calcined powders were pressed into disk-shaped pellets with 15 mm in diameter and approximately 1 ~ 3 mm in thickness, and sintered at $900 \sim 1150^\circ\text{C}$ for 2 hr in air atmosphere. X-ray

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diffraction (XRD) with Cu-K α radiation was used to determine the crystal structure. For electrical measurements, the specimen was lapped into 0.3 mm in thickness, and platinum electrodes were deposited on both sides of the specimens using dc sputtering. The ferroelectric P - E hysteresis loops were measured by a Sawyer-Tower circuit. The dc conductivity was measured over the temperature range of 30 ~ 500 °C by an impedance analyzer (HP4192A) and electrometer (KEITHLEY237), respectively. The impedance spectroscopy measurements were performed using HIOKI 3522-50 (0.1 Hz ~ 1 kHz) and HP4192A (1 kHz ~ 10 MHz).

3 Results and discussion

The crystal structure of BLaT and BLaTV ceramics were confirmed by XRD patterns. Figure 1 shows XRD patterns of BLaT and BLaTV ceramics. Both specimens were crystallized into an orthorhombic structure with a layered perovskite structure without a detectable secondary phase similar to that of BIT. There are no significant differences except a slight shift of XRD peaks.

Figure 2 shows P - E hysteresis loops of BLaT and BLaTV ceramics. The ferroelectric hysteresis loops were measured using a driven electric field of 80 kV/cm at a frequency of 60 Hz under room temperature. The capacitor is characterized by a well-saturated P - E hysteresis curve. But, the shape of the P - E hysteresis loop changes slightly with the doping of V ion. The remnant polarization value ($P_r = 11 \mu\text{C}/\text{cm}^2$) of BLaTV ceramic is larger than that of BLaT ($P_r = 7.5 \mu\text{C}/\text{cm}^2$) and a coercive field ($E_c = 42 \text{ kV}/\text{cm}$) is smaller than that of BLaT ($E_c = 56 \text{ kV}/\text{cm}$). The vanadium substitution for titanium site on BLaT mainly influenced the ferroelectric properties. Noguchi et al. [3] reported that the ferroelectric properties of BIT ceramics were enhanced by the substitution of Ti $^{4+}$ with higher valence ions such as V $^{5+}$ or W $^{6+}$. This is probably because of domain pinning due to residual vacancies. The oxygen vacancies generated

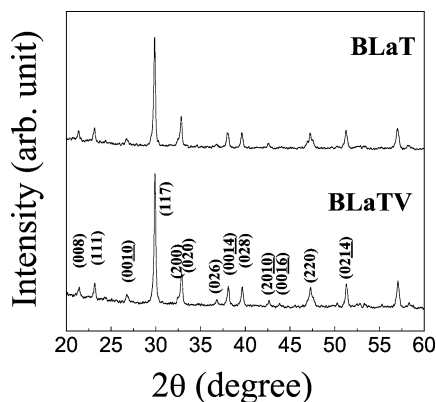


Fig. 1 XRD patterns of BLaT and BLaTV ceramics

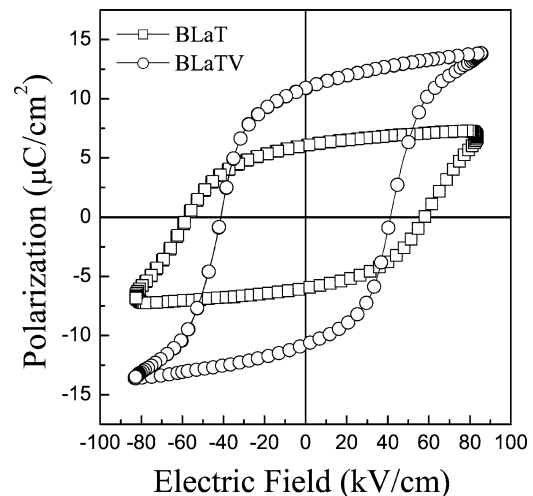


Fig. 2 P - E hysteresis loops of BLaT and BLaTV ceramics

by inevitable Bi cation vacancies would assemble at domain boundaries on the relatively high temperatures, leading to a strong domain pinning. Thus, the intrinsic ferroelectricity of BIT could not be drawn out in the form of thin films and bulk ceramics. In contrast, vanadium doping could be effective for a decrease in oxygen vacancies and significantly reduce the influence of domain pinning, which would be responsible for a larger P_r and smaller E_c found for vanadium-doped BIT.

In order to understand the influence of space charge density on ferroelectric properties of the BLaT and BLaTV ceramics, we performed the impedance analysis. The ac impedance analysis is known to be a powerful means to separate out the grain boundary and grain–electrode effects, which usually are the sites of trap for oxygen vacancies and other defects. It is also useful in establishing space charge polarization and its relaxation mechanism, by appropriately assigning different values of resistance and capacitance to the grain and grain boundary effects. A noteworthy aspect of the impedance analysis is the possibility of calculating the different contributions to the conductivity, namely, the grain, grain boundary, and grain–electrode contributions [9–11].

Figure 3(a) and (b) shows the Cole-Cole plots which were measured at 400 °C for BLaT and BLaTV ceramics, respectively. When a Cole-Cole plot is considered, the impedance response commonly shows a semicircular form. The real part (Z') vs imaginary part (Z'') of impedance curve of BLaT ceramic can be clearly divided into three kinds of semicircles (Fig. 3(a)). The 1st semicircle at high frequencies indicates the effect of the grain, 2nd semicircle at intermediate frequencies is influence of grain boundary effect and 3rd one at low frequencies is component of electrode effect.[9] On the other hand, the Cole–Cole plots of BLaTV is composed of two semicircles (Fig. 3(b)) which are not clearly separated.

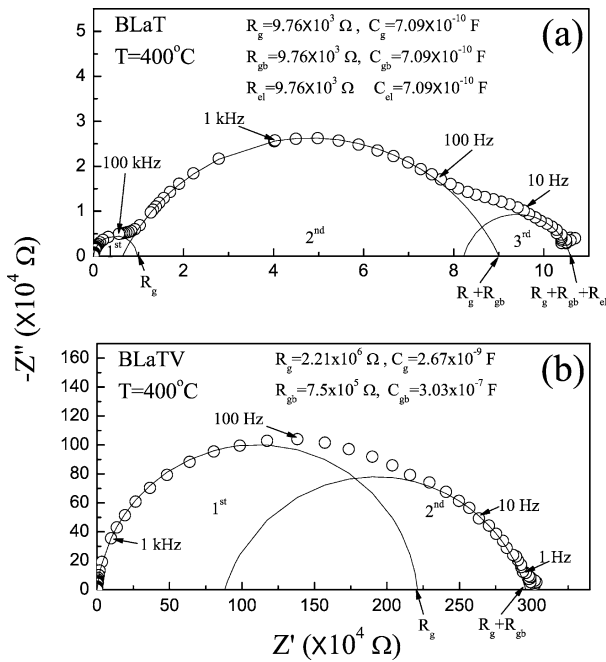


Fig. 3 Cole–Cole plots for (a) BLaT and (b) BLaTV ceramics

This indicates that the grain boundary and grain-electrode interface in BLaT ceramic serve as traps for space charges.

The intercept of the semicircle on the real axis (Z') gives the resistance of the corresponding component contributing towards the impedance of the samples. The values of the grain resistance (R_g), grain boundary resistance (R_{gb}) and grain-electrode resistance (R_{el}) are calculated and displayed in the figure. The capacitance of each component can be calculated using the formula $\omega\tau = 2\pi f_{max}RC = 1$ where f_{max} is the frequency of the maximum of semicircles.[12] The values of the grain resistance ($R_g = 2.21 \times 10^6 \Omega$) and the grain boundary resistance ($R_{gb} = 7.5 \times 10^5 \Omega$) of BLaTV are much higher than those of BLaT. The grain conductance calculated for BLaTV ($2.88 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$) is much smaller than that of BLaT ($1.38 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$). Therefore BLaTV appears to have a lower grain conductivity, which indicates a lower mobility of the carriers and a lower charge carrier density than those of BLaT.

Figure 4 shows the dc conductivity of BLaT and BLaTV ceramics as a function of temperatures with the conventional $\log\sigma$ vs $1000/T$ plot. As temperature increases, the conductivity of BLaT ceramic increases with different slopes in different temperature regions. This indicates that it has multiple activation processes with different energies. However, the activation energy of BLaTV ceramic is nearly constant in full temperature range. The activation energies are calculated using the Arrhenius equation $\sigma = \sigma_0 \exp(-E_a/k_B T)$, where k_B and E_a are Boltzmann constant and activation energy for electrical conduction, respectively. In BLaT, the value of activation energy at low temperature region ($<150^\circ\text{C}$) was

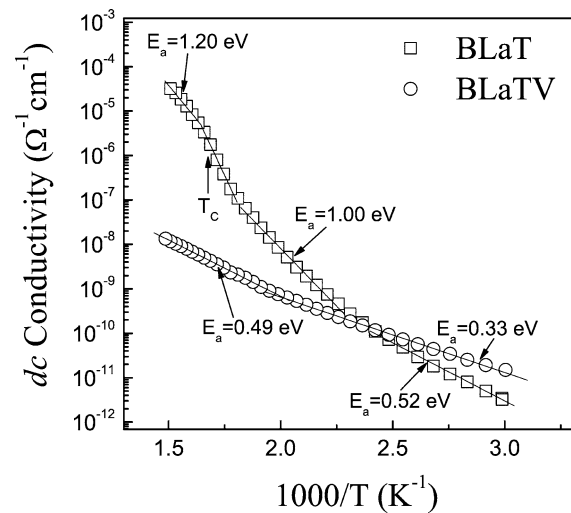


Fig. 4 The dc conductivity for BLaT and BLaTV samples as a function of temperatures.

0.52 eV, but it was changed to 1.00 ~ 1.20 eV at high temperature region ($>150^\circ\text{C}$), excluding near the T_c region. Typically, the activation energy for conduction behavior of oxygen vacancies in the octahedral any perovskite structure is ~ 1 eV, and that of cation vacancies is higher value [13–15]. Therefore, the conduction behavior of BLaT ceramic at high temperature region is due to volatile Bi cation and oxygen vacancies. On the other hand, the conductivity of BLaTV is much lower than that of BLaT at high temperature region. In addition to that, the activation energies of BLaTV ceramic were obtained low values (0.33 ~ 0.49 eV) over full temperature region. Z. S. Macedo et al. [16] reported that the calculated values of the activation energies at high, intermediate, and low frequencies in BIT ceramics were 0.39, 1.05, and 1.02 eV, respectively. The activation energies of BLaTV ceramics are similar to that of BIT ceramics at high frequencies region. The electrical properties at high frequencies region were influence of grain rather than grain boundary and grain-electrode effect. This indicates that the vanadium substitution for titanium site in BLaT can reduce the Bi cation and oxygen vacancies. Furthermore, the elimination of these defects, trapped in the grain boundary and grain-electrode interface, significantly reduces the influence of domain pinning, which would be responsible for the improvement in the ferroelectricity and piezoelectricity.

4 Conclusions

We have investigated dc conductivity and impedance spectroscopy of $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLaT) and $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_{2.97}\text{V}_{0.03}\text{O}_{12}$ (BLaTV) ceramics in order to clarify the influence of vanadium substitution for titanium site on BLaT ceramic. The Cole–Cole plot of BLaT ceramic

can be clearly divided into three kinds of semicircles. On the other hand, the Cole–Cole plot of BLaTV is composed of two semicircles which are not clearly separated. This indicates that the grain boundary and grain-electrode interface in BLaT ceramic serve as traps for space charges. The grain conductance of BLaTV ($2.88 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$) is much smaller than that of BLaT ($1.38 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$). Therefore BLaTV appears to have a lower grain conductivity, which indicates a lower mobility of the carriers and a lower charge carrier density than those of BLaT. At high temperature region ($>150^\circ\text{C}$), the activation energies of BLaT ceramic were obtained $1.00 \sim 1.20 \text{ eV}$, due to volatile Bi cation vacancies and oxygen vacancies, but those of BLaTV ceramic were obtained low values ($0.33 \sim 0.49 \text{ eV}$). This indicates that the vanadium substitution for titanium site in BLaT can reduce the Bi cation and oxygen vacancies. Furthermore, the elimination of these defects, trapped in the grain boundary and grain-electrode interface, significantly reduces the influence of domain pinning, which would be responsible for the improvement in the ferroelectricity and piezoelectricity.

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