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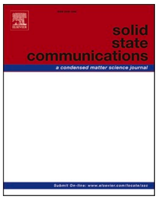

The strange case of enhancing the resistivity by extended sintering time in $(Bi_{0.5}Na_{0.5})TiO_3$–$BaTiO_3$ solid solution

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ABSTRACT

With the presence of volatile elements in the composition of a ceramic material, longer sintering time presumably creates more vacancies. In the case of $(Bi_{0.5}Na_{0.5})TiO_3$–$BaTiO_3$ lead-free piezoelectric ceramics and when batched and calcined with a Bi_2O_3 deficient stoichiometry, there can be a surprising increase in resistivity with increasing sintering time. It is deduced that the extended sintering time reduces the concentration of bismuth vacancies (and the ionically compensating oxygen vacancies). This is also associated with a decrease of depolarization temperature, T_d, and possibly a change in dielectric polarization phenomena from normal to relaxor ferroelectric. These observations do not occur in pure $(Bi_{0.5}Na_{0.5})TiO_3$, suggesting that they are actually facilitated by the Ba^{2+} content in the solid solution BNT−BT. Microstructural observations indicate the formation of $BaTi_2O_5$ secondary phase which considerably grows as sintering goes on. With more Ti^{4+} being incorporated to the secondary phase, the stoichiometry of the solid solution can be restored, so is the resistivity and the observed trends in decreased T_d.

1. Introduction

Sintering is the diffusion-controlled densification process of a ceramic sample from compacted powders. Temperature and time are two fundamental sintering conditions essential to the quality of the product [1,2]. Sintering temperature is often paid more attention as it affects the performance more critically and sometimes even modifies the phase composition [3,4]. At a given temperature, however, sintering for different dwell time can lead to variations in grain size [5]. When volatile species are involved, such as PbO in $Pb(Zr,Ti)O_3$, K_2O in $(K_{0.5}Na_{0.5})NbO_3$ or Bi_2O_3 in $(Bi_{0.5}Na_{0.5})TiO_3$, longer sintering time presumably allows more evaporation, therefore creates more metal vacancies in the sample. In $(Bi_{0.5}Na_{0.5})TiO_3$ (BNT), for instance, bismuth vacancies need to be ionically compensated by oxygen vacancies, Eq. (1). Here we use the Kroger-Vink notation, and "a" is the activity of the Bi_2O_3. Migration of the oxygen vacancies gives rise to ionic conduction in BNT, of which the magnitude is proportional to the concentration [6]. Supposedly, extended sintering will increase the ionic conductivity in BNT by creating larger amount of point defects of both Bi vacancies and the compensating oxygen vacancies.

$$2Bi_{Bi}^{\times} + 3O_O^{\times} \xrightarrow{BNT} 2V_{Bi}^{'''} + 3V_O^{\bullet\bullet} + a(Bi_2O_3) \qquad (1)$$

In this paper, we are going to show an unusual scenario in the $(Bi_{0.5}Na_{0.5})TiO_3$–$BaTiO_3$ (BNT−BT) solid solution, where longer sintering time decreases the conductivity. Pure BNT, at room temperature, is nonergodic relaxor phase with the depolarization temperature (T_d) around 150 °C [7]. By forming solid solution with BT, T_d changes, as well as the nature of the polarization. In BNT−15%BT, the T_d increases to ~210 °C while the normal ferroelectric domains dominate at lower temperatures [8]. Besides the ferroelectric properties, the conduction behavior is also modified by BT content. Ionic conduction is the major mechanism in pure BNT, with a low activation energy ~0.4 eV. However, BNT−15%BT features electronic conduction, as suggested by the activation energy ~1.4 eV [9]. The ionic conductivity in BNT−15%BT can be promoted by the Bi deficiency on A site (Eq. (1)) or through an acceptor dopant on B site (Eq. 2) [10]. In both cases, sintering time is found to have similar impacts on the conductivity and the ferroelectric property, that is enhancing the resistivity while decreasing the T_d. Microstructural examinations will be conducted in the Bi deficiency samples to reveal the mechanisms behind the sintering time effects.

$$MgO \xrightarrow{BNT} Mg_{Ti}^{''} + O_O^{\times} + V_O^{\bullet\bullet} \qquad (2)$$

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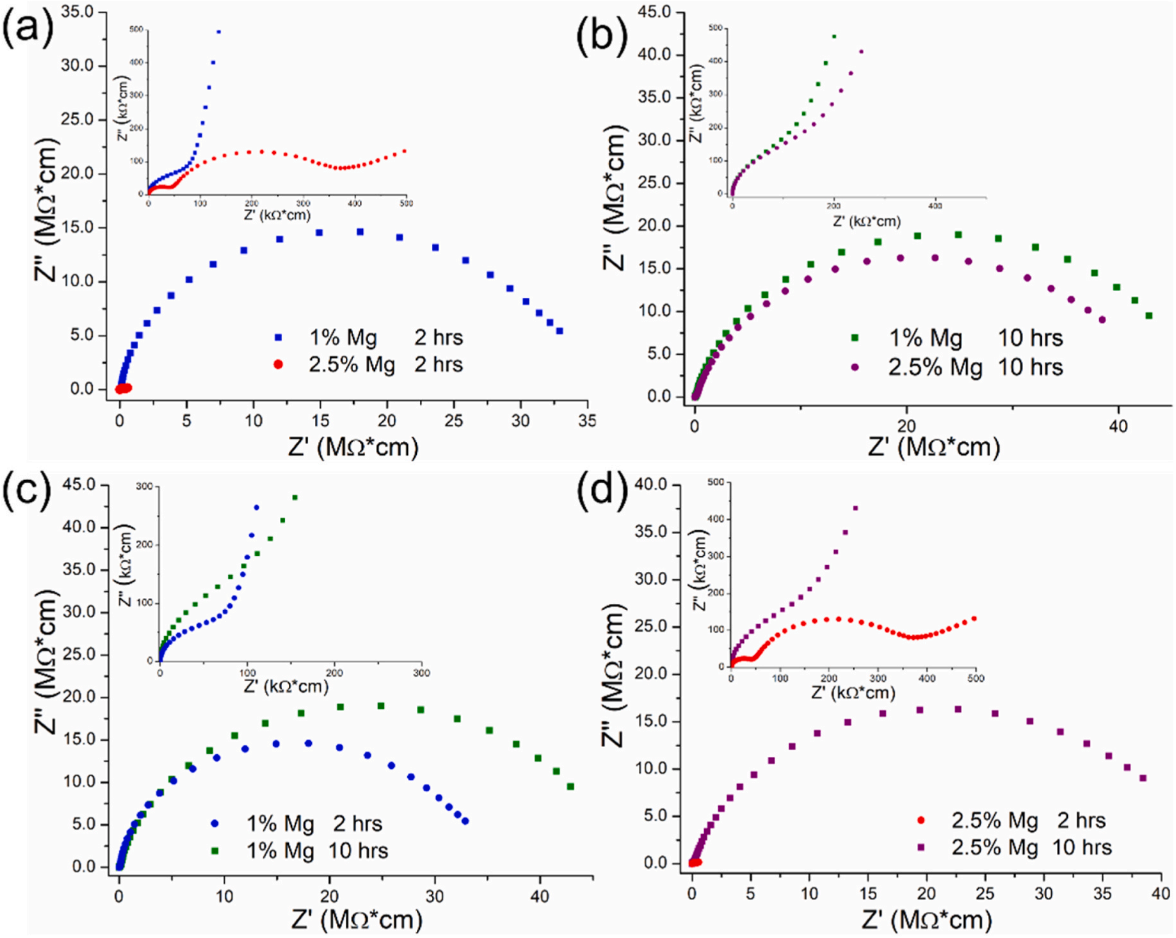

Fig. 1. Impedance spectroscopy in (a) 1Mg(2h) and 2.5Mg(2h); (b) 1Mg(10h) and 2.5Mg(10h); (c) 1Mg (2h) and 1Mg(10h); (d) 2.5Mg(2h) and 2.5Mg(10h).

2. Experimental methods

The BNT−15%BT (with or without Mg^{2+} doping to partially substitute Ti^{4+}) ceramics were fabricated using conventional solid state reaction method, with starting powders of Bi_2O_3 (>99.9%), Na_2CO_3 (>99.95%), TiO_2 (>99.9%), $BaCO_3$ (>99.8%) and MgO (>99.99%) weighted according to the stoichiometry. The samples with 1.2% Bi_2O_3 deficiency are hereafter called 1.2Bi, while the Mg^{2+} doped samples are named xMg (x% is the doping concentration). The mixed powders were ball milled in ethanol both before and after the 2 h calcination at 900 °C. The calcined powder, mixed with 1.5 wt% Acryloid binder, was pressed into a 15 mm diameter disk. The binder was then burned out at 600 °C for 2 h. The sintering was conducted at 1200 °C with a 5 °C/min heating and cooling rate, while the dwelling times are subject to change as will be explained in detail. The sintering time is also indicated in the sample's nomenclature, e.g., 1.2Bi(20min) or 1Mg (10h). The as-sintered pellets were polished to ~1 mm in thickness prior to sputtering the platinum electrodes. The impedance spectroscopy was performed at elevated temperatures in a computer-controlled furnace with a Solartron ModuLab XM impedance analyzer from 0.1 Hz to 1 MHz. The polarization-field (P-E) hysteresis loop was recorded using a Sawyer-Tower circuit with a Trek Model 30/20 high voltage amplifier system (Trek, Inc., Lockport, NY). The depolarization temperature, T_d, was measured via the pyroelectric measurement based on a modified Byer and Roundy setup equiped with a pA meter (4140B, Hewlett Packard). The microstructure of the ceramics was checked with Transmission Electron Microscopy (TEM) on Talos F200× (FEI). The secondary phase was identified through quantifying the Energy Dispersive X-Ray spectroscopy (EDS) data acquired by a SuperX EDX detector. The TEM specimens were prepared by focused ion beam (Scios, FEI).

3. Results and discussion

According to Eq. (2), Mg^{2+} doping tends to increase the conductivity in BNT−15%BT. Fig. 1 compares the impedance spectroscopy measured from BNT−15%BT−x%Mg ceramics. Two semi-circles are present at high and low frequencies, representing grain and grain boundary contributions respectively [11]. 1Mg(2h), as shown in Fig. 1a, has a more resistive grain boundary than the grain. If the doping level is raised to 2.5% and still sintered for 2 h, the conductivity, especially the grain boundary conductivity, is obviously increased (Fig. 1a). However, if the samples are sintered for 10 h, 1Mg(10h) and 2.5Mg(10h) show equal conductivity (Fig. 1b). By extending the sintering time from 2 h to 10 h, the resistivity of the studied compositions is always enhanced. The difference is that the enhancement in 2.5Mg (Fig. 1d) is much more significant than in 1Mg (Fig. 1c).

The impacts of sintering time on the ferroelectric properties in BNT−15%BT−x%Mg are studied. Acceptor doping is always less effective than donor doping in terms of shifting the depolarization temperature [12–14]. Fig. 2a shows that 1Mg maintains the T_d of 0Mg, while 2Mg and 2.5Mg have it decreased. If the ceramics are sintered for 10 h, compared with the 2 h sintered ones, T_d becomes lower in all four samples, among which 0Mg and 1Mg see very minor change in contrast to the >20 °C drop in the more heavily doped cases. Coincidentally, the resistivity enhancement in 1Mg by extended sintering time is not as substantial as that in 2.5Mg (Fig. 1c&d). The Cann group recently discovered a similar coincidence in a BNT-BKT solid solution [15]. The exact mechanism is not thoroughly elaborated yet. It is known that

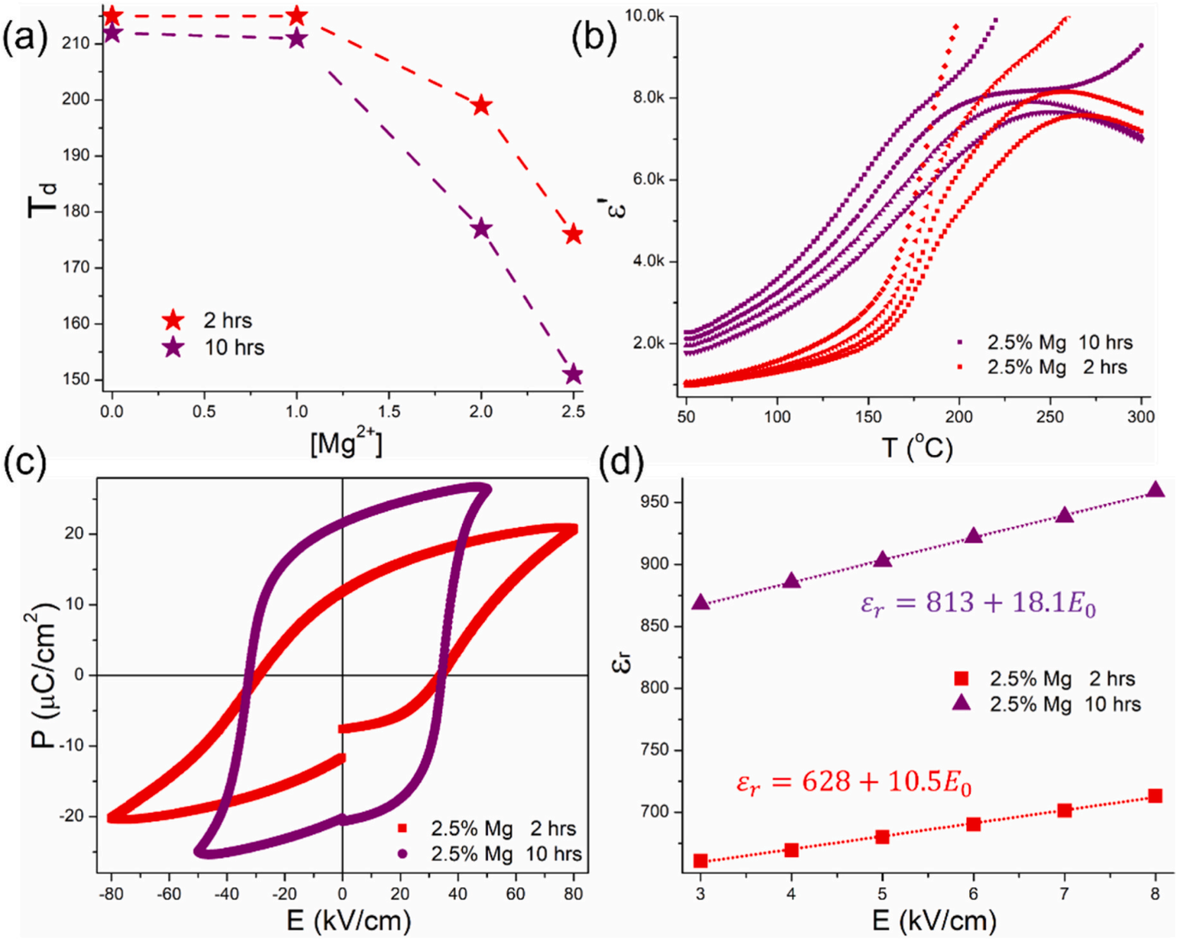

Fig. 2. (a) Depolarization temperature as a function of Mg^{2+} doping and the dependence on sintering time. (b) Temperature dependent dielectric permittivity of 2.5Mg(2h) and 2.5Mg(10h) at different frequencies. (c) P-E loops measured in 2.5Mg(2h) and 2.5Mg(10h). (d) Rayleigh analysis conducted in the poled 2.5Mg(2h) and 2.5Mg(10h).

longer sintering time facilitates the grain growth. The Ranjan group controlled the grain size on purpose by post-annealing the as-sintered BNT ceramics at different temperatures but for equal time [16]. They found that T_d is higher in the samples with larger grain size. However, our result shows the opposite trend, which means that the grain size effect, if any, plays only a marginal role.

In 2.5Mg(2h), the temperature dependent dielectric permittivity undergoes a rapid rise at around 180 °C, suggesting the normal ferroelectric phase at room temperatures undergoing a phase transformation at T_d. On the contrary, no such anomaly is observed in 2.5Mg(10h), and this is indicative of the room temperature FE phase transitioning to nonergodic relaxor induced by extended sintering time (Fig. 2b). Such transition is also learnt from the comparably more noticeable frequency dispersion in the dielectric permittivity near room temperature in 2.5Mg (10h) than 2.5Mg(2h), whereas the frequency dispersion observed in both samples at higher temperatures is due to thermally activated space charges. Owing to the more random configuration of ferroelectric domain structures, coupling between the spontaneous polarization and the defect dipoles is weaker in relaxor than in normal ferroelectric phase [17]. Accordingly, the switchability of polarization is improved in 2.5Mg(10h) (Fig. 2c). However, the doubled remanent polarization in 2.5Mg(10h) is not enough to account for the difference in the piezoelectric coefficients, which are ~ 90 and ~25 pC/N in 2.5Mg(10h) and 2.5Mg(2h) respectively. The Rayleigh analysis is utilized to separate the extrinsic contribution to the piezoelectric coefficient (Fig. 2d) [18]. Since the polarization nature are different in two samples, the Rayleigh analysis is carried out in the poled state in order to rule out the contribution from the field induced relaxor to ferroelectric phase transition [19]. The Rayleigh coefficient of 2.5Mg(2h) is approximately 42% lower, suggesting a stronger pinning force against the irreversible domain wall motion by the point defects, which is consistent with its higher conductivity than 2.5Mg(10h).

According to Eq. (1), introducing Bi_2O_3 deficiency on A site also creates oxygen vacancies through the aforementioned ionic compensation. With 1.2% Bi_2O_3 deficiency, 1.2Bi(2h) is indeed more conductive than the stoichiometric BNT−15%BT. However, if the sintering time is extended to 10 h, the resistivity is remarkably "restored" to nearly equal to the stoichiometric sample (Fig. 3a). If the sintering time is reduced to 20 min, the conductivity can be raised by another order of magnitude relative to 1.2Bi(2 h) (Fig. 3b). Meanwhile, T_d drops with sintering time, from ~236 °C in 1.2Bi(20min) to ~226 °C in 1.2Bi(2 h) to ~210 °C in 1.2Bi(10 h). Note that the T_d in stoichiometric BNT−15%BT is exactly 210 °C [8]. It means that a sufficiently long sintering likely "restores" not only the resistivity, but also the ferroelectric property of the solid solution.

Electric modulus spectroscopy enables a clear distinction between relaxation processes with various capacitance [20]. In 1.2Bi(20min), the major peak is at high frequency (relaxation #2), with a shoulder on the low frequency side (Fig. 3c). In 1.2Bi(2 h), the peak for relaxation #1 moves toward lower frequency whereas the intensity reduces, representing an increase in the corresponding resistance and capacitance. In the meantime, the shoulder in 1.2Bi(20min) develops into an isolated peak (relaxation #2). In 1.2Bi(10 h), the peak for relaxation #2 appears at very low frequency while becomes taller, suggesting that the

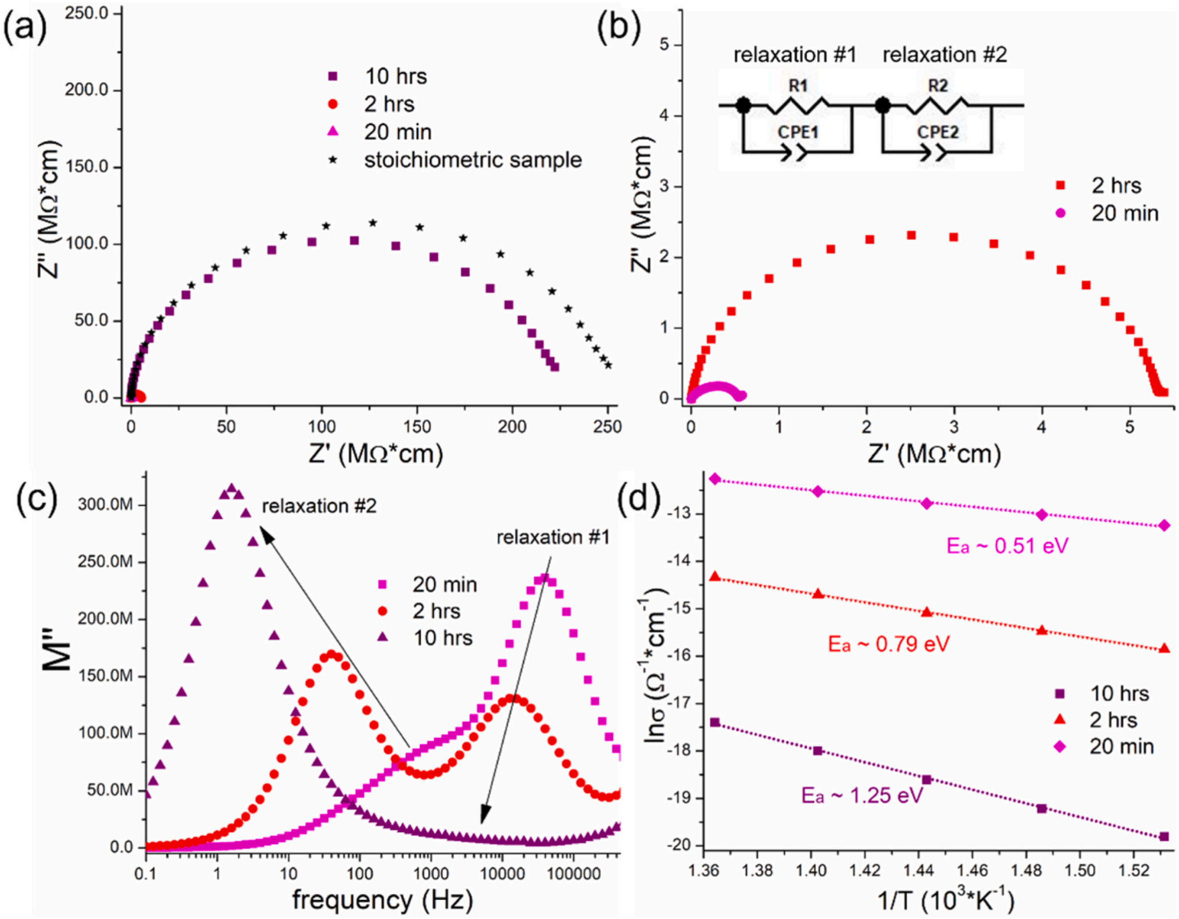

Fig. 3. (a), (b) The impedance of 1.2Bi sintered for different dwelling time and the comparison with the stoichiometric BNT−15%BT. (c) The electric modulus plot highlights the evolution of relaxation #1 and #2 with sintering time. (d) The activation energies associated with relaxation #2 in three samples.

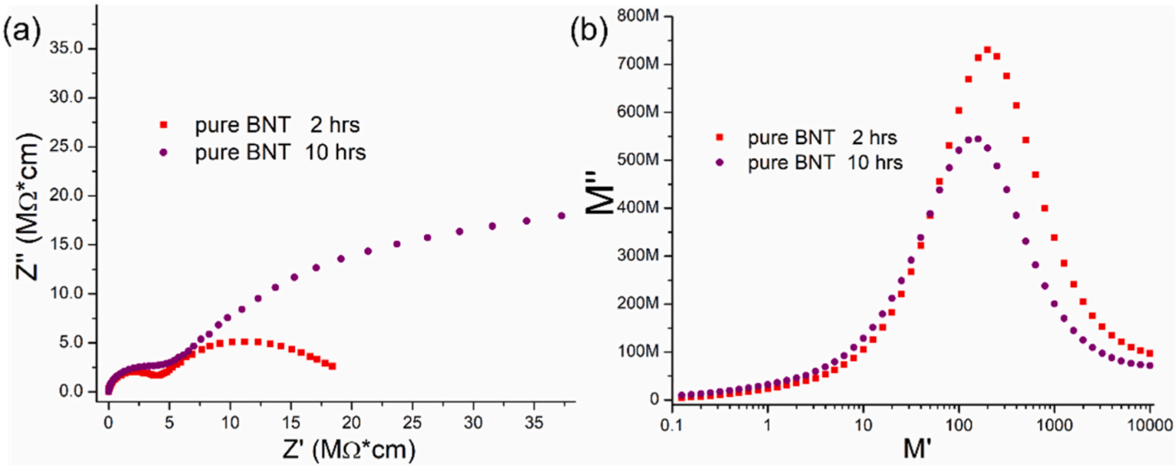

Fig. 4. The (a) impedance and (b) modulus spectroscopy measured in pure BNT sintered for two or 10 h.

corresponding resistance increases and the capacitance decreases. More importantly, relaxation #1 is now completely suppressed. So, with extended sintering time, the overall resistance enhances, while relaxation #2 takes over relaxation #1 as the predominant portion. This could be regarded as the shell growth in a grain with core-shell structure at the cost of the core, inferred from the capacitance values of the two relaxations in each sample. To fit the electric modulus data, the equivalent circuit containing two R–C elements in series is used, see inset of Fig. 3b. Admitting that the particular equivalent circuit has been usually adopted to distinguish grain and grain boundary conductivity, we are inclined to assign core and shell to the two relaxations in our case, which will be still referred to as relaxation #1 and #2 to avoid controversy. Since relaxation #1 is absent in 1.2Bi(10 h), only relaxation #2 of the three samples are compared. As revealed by the Arrhenius plot in Fig. 3d, the activation energy continuously increases from ~0.5 eV in 1.2Bi(20min) to ~0.8 eV in 1.2Bi(2 h) to ~1.25 eV in 1.2Bi(10 h). It

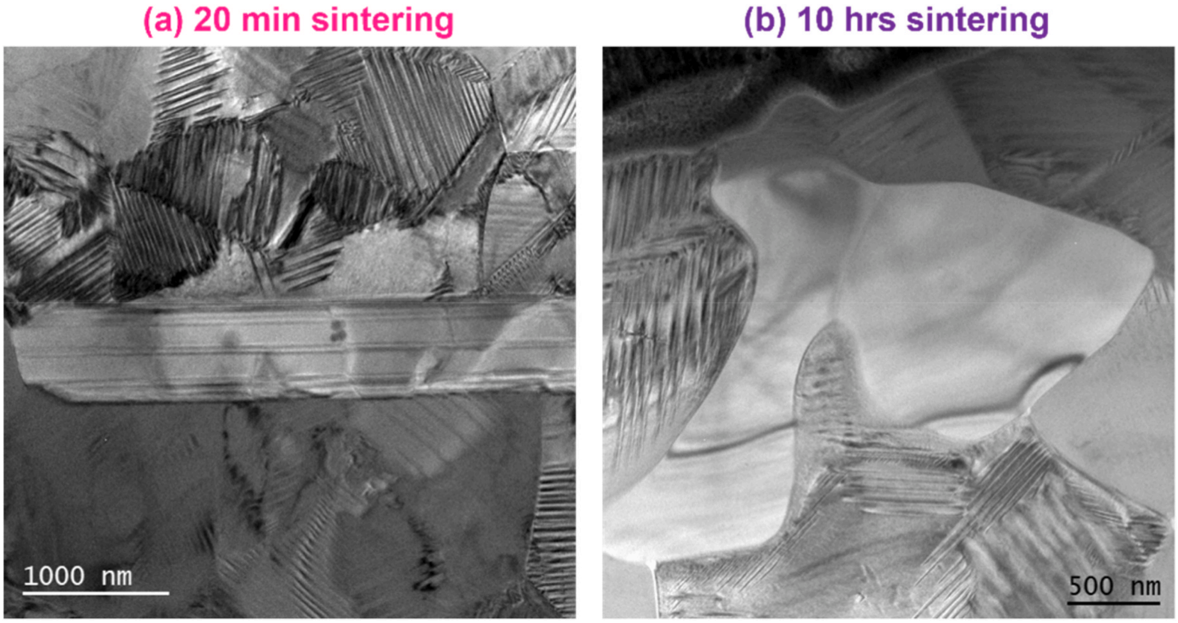

Fig. 5. TEM bright field micrographs of the $BaTi_2O_5$ secondary phase in (a) 1.2Bi(20min) and (b) 1.2Bi(10 h).

demonstrates that the enhancement of resistivity is essentially due to the evolution of the mixed conduction mechanism, from ionic to electronic, as a function of the sintering time. Till 1.2Bi(10 h), the ionic conduction is almost gone. Recall that, longer sintering time enhances the resistivity of heavily Mg^{2+} doped samples too, but ionic conduction is always the major conduction mechanism, and the enhanced resistivity cannot surpass 1Mg (Fig. 1). It implies that the Bi_2O_3 deficiency on A site can be “corrected” by extended sintering but Mg^{2+} doping on B site cannot.

What “corrects” the Bi_2O_3 deficiency, and how? We sintered the pure BNT ceramics for two or ten hours. As seen in Fig. 4, the resistivity is almost invariant (Fig. 4a), and dominated by the same single relaxation (Fig. 4b). According to Sinclair et al., pure BNT is naturally deficient in Bi_2O_3 due to volatility [6]. However, the resistivity cannot be “restored” by extended sintering time unless excessive Bi_2O_3 is batched [21]. Therefore, the Ba^{2+} content must be necessary for the observed sintering time effect in BNT−15%BT solid solution. Fig. 5 exhibits the representative microstructure of 1.2Bi(20min) and 1.2Bi(10h). The secondary phase, $BaTi_2O_5$ (BT2), always exists regardless of the sintering time. However, the morphology changes completely. In 1.2Bi(20min), the BT2 is in needle-shape with an aspect ratio over ten. Note that the grown BT2 crystals naturally adopt the needle-shape [22,23]. In 1.2Bi(10 h), however, the BT2 secondary phase grows into chunky shape, despite keeping the same composition.

The observation of BT2 and its growth with sintering time appropriately explains the conduction behaviors in 1.2Bi. BT2 secondary phase reduces the Ti^{4+} content on B site in BNT−15%BT, which is equivalent to “correcting” the Bi^{3+} deficiency on A site [24]. When the sintering time is short, oversaturated bismuth vacancies are still preserved in the solid solution, giving rise to the ionic conduction (Eq. (1)). Once the sintering time is sufficiently long and the equilibrium between the solid solution and the BT2 secondary phase is reached, bismuth vacancies are eliminated from the solid solution, so is the ionic conduction. Our previous work has elucidated that bismuth vacancy increases T_d in BNT−15%BT [8], but in this case with BT2 secondary phase there is a change in BT compositions. According to the BNT−x% BT phase diagram, T_d monotonically drops as BT% decreases from 15% to 11%, namely approaching the morphotropic phase boundary from the high BT% side [25]. Thus, having less BT% remaining in the grains, longer sintering time lowers the T_d.

4. Conclusions

In BNT−15%BT solid solutions with either Bi_2O_3 deficiency or Mg^{2+} doping, extended sintering time enhances the resistivity and decreases the depolarization temperature. The mechanism is related to the formation of Ti-rich secondary phase and its growth during sintering. Bismuth vacancies on A site are eliminated from the solid solution as the consequence of the Ti^{4+} on B site being incorporated into the secondary phase. The resistivity and T_d are accordingly changed due to the sintering induced compositional modification in the solid solution.

Declarations

The authors have no conflict of interest.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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