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Transformation Kinetics of $Ba_2Ti_9O_{20}$ with ZrO_2 Additive

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Pure $Ba_2Ti_9O_{20}$ (BT29) was synthesized by a solid-state reaction in one step with various amounts of ZrO_2 powder additive. The transformation kinetics of BT29 were investigated by quantitative X-ray diffractometry (XRD). The results show that stoichiometric powder mixtures transform to the BT29 phase by nucleation and growth mechanism between 1200° and 1300°C with 1.0 mol% ZrO_2. The activation energy of the transformation was found to be 620±60 kJ/mol, but decreases to 515±30 kJ/mol when doped with 1.0 mol% ZrO_2. The addition of ZrO_2 possibly changes the phase transformation mechanism of BT29 from diffusion controlled to interface controlled.

I. Introduction

Pure $Ba_2Ti_9O_{20}$ (BT29) is an important material used for high-frequency resonators. A resonator requires a material with a high dielectric constant (ε_r), high quality factor (Q), and low temperature coefficient (τ_f).[1,2] However, there are many other TiO_2-rich compounds in the BaO–TiO_2 system possibly co-existing with BT29. The presence of these phases, $BaTi_4O_9$ (BT14), $BaTi_5O_{11}$ (BT15), and $Ba_4Ti_{13}O_{30}$, lowers the dielectric properties of the material. Therefore, the synthesis of a highly pure $Ba_2Ti_9O_{20}$ phase is of primary importance.

Early works reported by O'Bryan and Thomson,[2] and others[3,4] have pointed out the possibility of the synthesis of single-phase BT29 in a large quantity. The reported methods used foreign oxide additives, such as ZrO_2, B_2O_3, and SnO_2, to trigger the formation of BT29. The additives used in commercial $Ba_2Ti_9O_{20}$ powders usually contain some other spurious phase, such as BT14 and TiO_2. Jonker and Kwestro[5] reported that single-phase BT29 cannot be formed without SnO_2 and ZrO_2 additions. However, no conclusive description on the formation mechanism has been reported in previous studies.

We selected ZrO_2 as the typical additive to synthesize single-phase BT29 phase via a solid-state reaction. The formation of BT29 was quantitatively investigated by X-ray diffractometry (XRD) and electron microscopy in order to understand the phase transformation kinetics and related phenomena.

II. Experimental Procedure

The starting materials were $BaCO_3$ (99.9% pure, −325 mesh, CERAC Company, Taipei, Taiwan, ROC), TiO_2 powder (average size 400 nm, 99.97% pure, CR-EL, Ishihara Sangyo Kaisha Ltd., Tokyo, Japan) and ZrO_2 (average size 0.1 μm, 99.9% pure, m-phase, Z-Tech). Stoichiometric BT29 was prepared from a mixture of $BaCO_3$ and TiO_2 in the ratio 1:4.5. The doping level of the ZrO_2 powder was varied up to 10.0 mol%.

The analysis of BT29 phase was conducted by X-ray diffractometry (Philips PW1830, Philips Instrument, Amsterdam, the Netherlands) using Cu$K\alpha$ radiation with an applied voltage and current of 30 kV and 20 mA, respectively. The scan speed was 0.3°/min in a step of 0.01°. The XRD spectra of two typical samples are shown in Fig. 1, illustrating a pure BT29 and a mixture of BT29+BT14+TiO_2. Because the strongest three peaks of the diffraction patterns of BT29 and BT14 nearly overlap, the other three peaks ($\bar{4}\,3\,1$), (222) and ($\bar{4}\,0\,2$) of the BT29 spectrum in the vicinity of 32.21° were integrated (Fig. 2(a)) and compared with the (130) peak of BT14 (Fig. 2(b)).

In order to prepare standard samples for a QXRD test, BT29 with 2 mol% ZrO_2 was synthesized by a solid-state reaction calcined at 1200°C for 30 h. Figure 3 shows the calibration curve of the integrated XRD intensity as a function of the molar ratio of BT29 versus BT14. The best-fitting curve in Fig. 3 shows a 99.5% confidence with a standard deviation of about ±2%.

III. Results and Discussion

Additives, such as B_2O_3,[4] ZrO_2,[5,6] SnO_2,[5,6] Al_2O_3,[7–9] Bi_2O_3,[7,9] Mn,[10] GeO_2,[11] and Nd_2O_3,[12] can influence the formation of BT29 phases. Jonker and Kwestro[5] stated that the influence of Sn and Zr is the substitution of Ti, so as to increase the unit cell dimensions of BT29.

From the viewpoints of crystal structure, BT14 is orthorhombic and BT29 has a triclinic structure with less symmetry. When

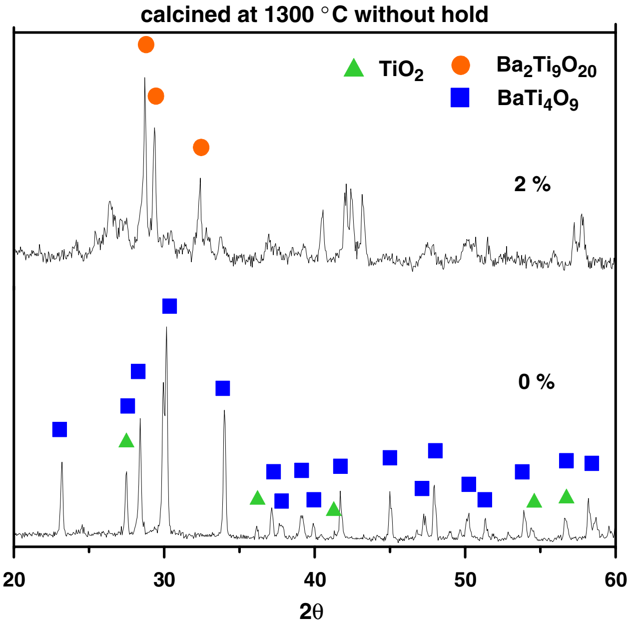

Fig. 1. X-ray diffractometry spectra of sintered mixtures of $BaCO_3$ and TiO_2 in a 1:4.5 molar ratio (top) doped with 2 mol% ZrO_2, and (bottom) without ZrO_2 calcined by continuously heating to 1300°C without holding.

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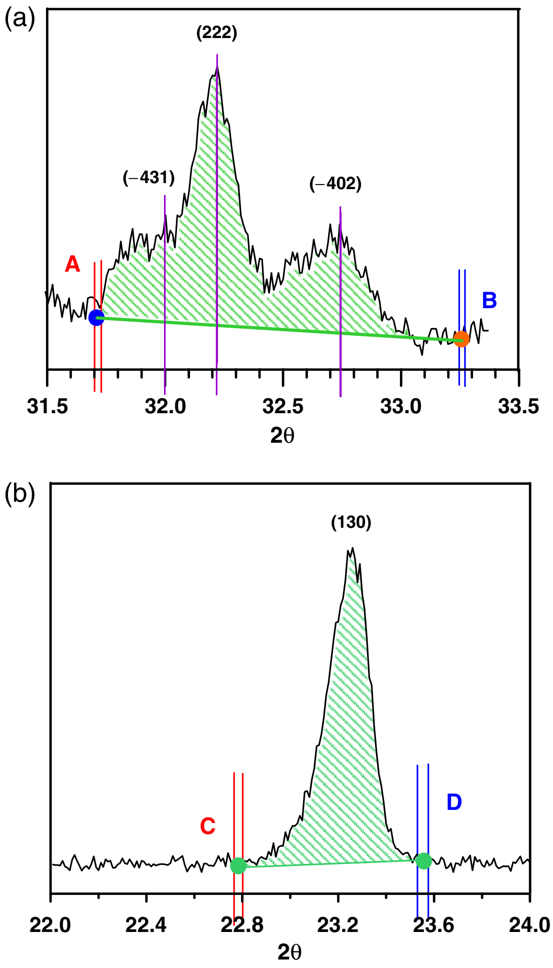

Fig. 2. Quantification of (a) $Ba_2Ti_9O_{20}$ peaks including (−4 3 1), (222) and $(\bar{4}\,\mathbf{0}\,\mathbf{2})$, and (b) (130) peak of $BaTi_4O_9$.

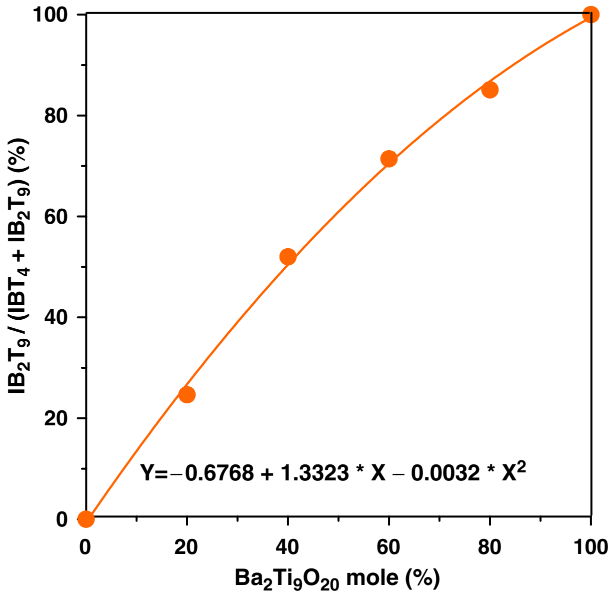

Fig. 3. Calibration curve of quantitative analysis of $Ba_2Ti_9O_{20}$ versus $BaTi_4O_9$ phase.

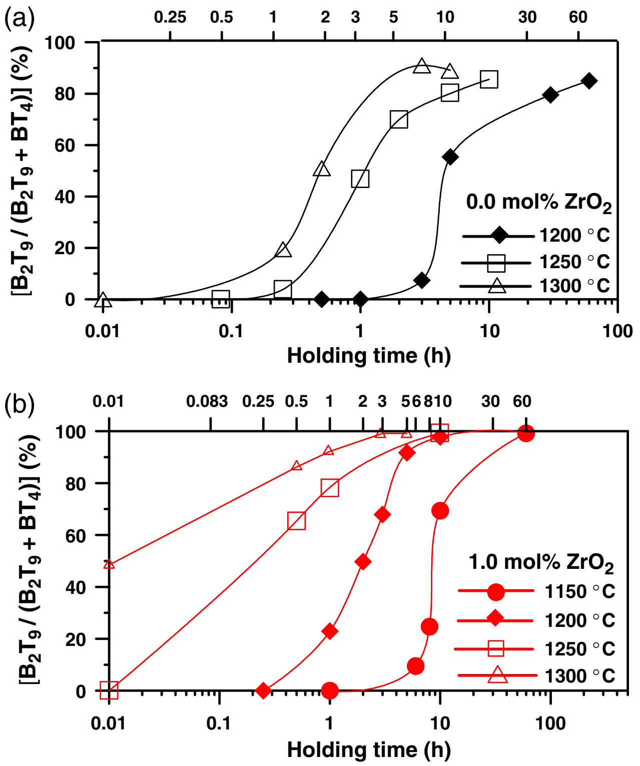

Fig. 4. Amount of $Ba_2Ti_9O_{20}$ plotted against holding time. The samples were calcined at 1150°–1300°C and doped with various amounts of ZrO_2 (a) 0 mol% or (b) 1.0 mol%.

the Zr ions substitute the Ti ions, the BT14 crystal structure is distorted because of the difference in size of the Zr and Ti ions. The radius of Zr^{4+} is about 0.084 nm, and that of Ti^{4+} is about 0.061 nm.[13] Therefore, the BT14 with a highly symmetric crystal structure cannot transform to BT29 without the presence of ZrO_2. The details are discussed below.

A plot of the phase transformation of BT29 versus transformation time is shown in Fig. 4, which illustrates that the data points can be fitted by sigmoidal-shaped curves. The transformation of the ceramic system can be described by a nucleation-and-growth (*N&G*) mechanism.

$$TiO_2 + 2BT14 \rightarrow BT29 \tag{1}$$

The sigmoidal curve and nucleation of BT29 in BT14 grain isothermally is the evidence of an *N&G* process. The isothermal phase transformation kinetics are usually expressed by the Johnson–Mehl–Avrami (JMA) equation.[14,15]

$$X = 1 - \exp\{-k^*(\dot{N}, \dot{G})t_m^n\} \tag{2}$$

where X is the molar fraction of a phase transformation; n is the time exponent that reflects the characteristics of nucleation and growth process. $k^*(\dot{N}, \dot{G})$is the rate constant, which is dependent on temperature and is a function of the nucleation and growth rates ($\dot{N}\dot{G}$). In this study, *N&G* rates are considered as remaining constant in the temperature range. t_m is equal to (t–τ_o), where τ_o is the temperature-dependent incubation time. Therefore, the term k^* can be expressed as an Arrhenius equation:

$$k^* = A\exp\left(\frac{-Q}{RT}\right) \tag{3}$$

where A is the frequency factor and Q is the activation energy of growth.

Figure 4 implies that all the transformations may proceed with an incubation period. The kinetic data of Fig. 4 can be fitted to Eq. (2) in a linear form:

$$\ln[-\ln(1 - X)] = \ln k^* + n \ \ln \ t_m \tag{4}$$

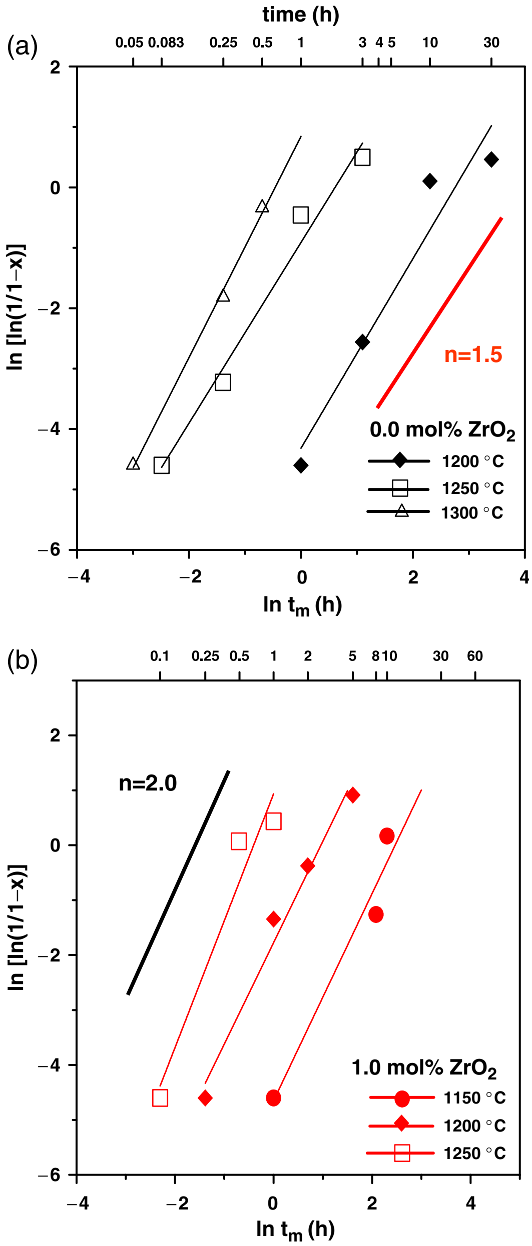

Fig. 5. Kinetic data expressed by Eq. (4). The samples doped with (a) 0.0% or (b) 1.0 mol% ZrO_2.

According to the above equation, the value of n and k^* can be calculated from the slope of the fitted curve, as shown in Fig. 5. The incubation times for the samples without and with doping ZrO_2 are estimated from the figure. The n values in each temperature for the samples doped with 0.0 and 1.0 mol% ZrO_2 are 1.6 and 2.0, respectively.

Comparing the n values with those reported in the literature,[16] the controlling mechanism of the sample without doping ZrO_2 may be a mixture of diffusion and interface control. For the sample doped with 1.0 mol% ZrO_2 ($n \sim 2.0$), the mechanism is interface controlled, implying that the controlling mechanism becomes interface controlled because of the solid solution of ZrO_2.

Because the incubation time is dependent on the processing temperature, the incubation time can be plotted against the reciprocal Kelvin temperature, as shown in Fig. 6. The activation energy of the nucleation is about 630 ± 60 and 515 ± 30 kJ/mol for the samples doped with 0.0 and 1.0 mol% ZrO_2, respectively. The addition of ZrO_2 reduces the incubation energy (ΔG) in 115 kJ/mol.

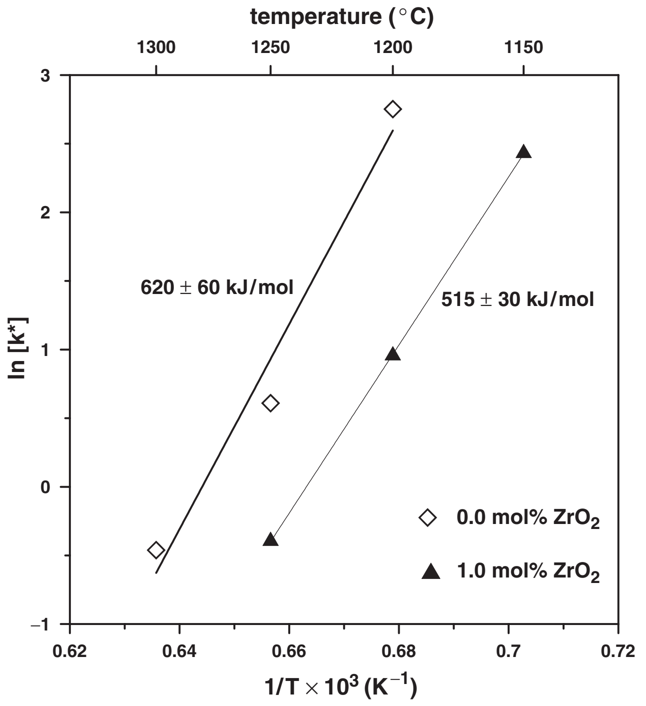

Fig. 6. Arrhenius plot of the rate constant k^* versus the reciprocal Kelvin temperature of BT samples with either 0% or 1.0 mol% ZrO_2.

Our TEM work[17] has illustrated the dissolution of a Zr element in a BT29 sample doped with ZrO_2. The Zr ions diffused into the BT29 lattice at the processing temperature (1300°C). The amount of ZrO_2 in BT29 was nearly constant: ca. 2.8 at.%. The result showed that there was no additional phase found at the ZrO_2 and BT29 interface. The other aspect, the nucleation of BT29 taking place at the highly stressed position, was proposed.[18,19] The residual stresses only induced from the difference of the thermal expansion coefficient between ZrO_2 and matrix act at room temperature, not at transformation temperatures ($\geq$ 1200°C). Can the stresses induce a nucleate site and promote the formation of BT29?

Monoclinic-phase ZrO_2 was used as the raw material. During heat treatment, phase transformation occurs between the m phase and t phase. Without a phase stabilizer, the t-phase ZrO_2 would transform back to the m phase during cooling. Meanwhile, the volume of the unit cell expands by about 4 vol% and the twin formed in the residual ZrO_2. Consequently, residual compressive stress is exerted during cooling. There is evidence[17] that residual ZrO_2 inclusions indeed exist in BT29 grains. The ZrO_2 inclusion also showed the twinning features, which were formed under shear stress and often nucleated at highly strained positions. However, Fang *et al.*[19] proposed that the stressed matrix of BT14 grain impinged the formation of the BT29 phase. In order to release the stress, the mixture was re-ground and re-calcined at 1200°C for another 3 h, whereby a pure BT29 was obtained. Additional ZrO_2 is harmful for the formation of BT29.

IV. Conclusions

This work can be summarized as follows:

(1) ZrO_2 addition aids the formation of BT29. Pure, single BT29 phase by doping 1–2 mol% ZrO_2 after calcined at 1300°C for 30 min can be obtained. Without ZrO_2 addition, the BT14 phase is retained in the mixture even after calcination at 1200°C for 60 h.

(2) The formation of BT29 goes through the nucleation and growth mechanism. The kinetic curves of BT29 formation can be formulated by the Avrami equation, showing that the activation energy of the formation of BT29 is 620 ± 60 kJ/mol. It

decreases to 515 ± 30 kJ/mol if doped with 1.0 mol% ZrO_2 particles.

(3) The addition of ZrO_2 enhances the interface-control transformation, which is due to the dissolution of ZrO_2 in BT29 grains.

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