Transformation Kinetics of Ba$_2$Ti$_9$O$_{20}$ with ZrO$_2$ Additive

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Pure Ba$_2$Ti$_9$O$_{20}$ (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°C 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$_2$Ti$_9$O$_{20}$ (BT29) is an important material used for high-frequency resonators. A resonator requires a material with a high dielectric constant ($\varepsilon_r$), high quality factor (Q), and low temperature coefficient ($\tau$). 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, Ba$_3$Ti$_5$O$_9$ (BT14), Ba$_3$Ti$_7$O$_{15}$ (BT15), and Ba$_4$Ti$_{13}$O$_{30}$, lowers the dielectric properties of the material. Therefore, the synthesis of a highly pure Ba$_2$Ti$_9$O$_{20}$ phase is of primary importance.

Early works reported by O’Bryan and Thomson, and others 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$_2$O$_3$, and SnO$_2$, to trigger the formation of BT29. The additives used in commercial Ba$_2$Ti$_9$O$_{20}$ powders usually contain some other spurious phase, such as BT14 and TiO$_2$. Jonker and Kwestro stated that the influence of Sn and Zr is the substitution of Ti, so as to increase the unit cell dimensions of BT29.

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 CuKα 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 (4 3 1), (2 2 2) and (0 2 0) 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$_2$O$_3$, ZrO$_2$, SnO$_2$, Al$_2$O$_3$, Bi$_2$O$_3$, M$n$, GeO$_2$, and Nd$_2$O$_3$, can influence the formation of BT29 phases. Jonker and Kwestro 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.
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.

\[
\text{TiO}_2 + 2\text{BT14} \rightarrow \text{BT29} \tag{1}
\]

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

\[
X = 1 - \exp\left(-k^* (N, G) t_m^n\right) \tag{2}
\]

where \(X\) is the molar fraction of a phase transformation; \(n\) is the time exponent that reflects the characteristics of nucleation and growth process. \(k^* (N, G)\) is the rate constant, which is dependent on temperature and is a function of the nucleation and growth rates \((N, G)\). In this study, N\&G rates are considered as remaining constant in the temperature range. \(t_m\) is equal to \((t - t_0)\), where \(t_0\) 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:

\[
\ln[-\ln(1 - X)] = \ln k^* + n \ln t_m \tag{4}
\]
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$_2$ ($n = 2.0$), 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 $620 \pm 60$ 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 ($\Delta G$) in 115 kJ/mol.

**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 $620 \pm 60$ kJ/mol. It
decreases to $515 \pm 30$ 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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References
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