On the formation mechanism of $BaTiO_3$-$BaZrO_3$ solid solution through solid-oxide reaction

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Abstract

The formation of solid solution composition $BaTi_{0.6}Zr_{0.4}O_3$, from $BaCO_3$, TiO_2 and ZrO_2 powders has been studied through solid-oxide reaction using TGA/DSC, XRD. $BaCO_3$ decomposes at much lower temperature in the mixture due to the presence of TiO_2. $BaTiO_3$ and $BaZrO_3$ start forming from the temperature range 700°-800°C without intermediate formation of BaO or other titanate/zirconate phases. Rate of $BaTiO_3$ formation is higher than $BaZrO_3$ formation due to the lower activation energy (34.3 kcal/mol) required for titanate formation than zirconate (48.4 kcal/mol). Solid solution then forms by diffusion of $BaTiO_3$ into $BaZrO_3$ from 1300°C onwards. Lattice parameter of initial SS-phase is higher, indicating the phase has a coherent interface with zirconate and higher in Zr-concentration than final product. Activation energy for the SS-formation (133 kcal/mole) indicates that Ba and/or O diffution through SS layer may limit the reaction.

Keywords: Perovskite; Ferroelectrics; Kinetics; $BaTiO_3$-$BaZrO_3$; Solid Solution

1. Introduction

Solid solution of $BaTiO_3$ with other perovskite type material offers a wide range of modification of its dielectric properties. For example the permittivity and the Curie temperature of $BaTiO_3$ can be varied in a large range by solid solution formation with $SrTiO_3$ [1]. Solid solution compositions in $BaTiO_3$ (BT)-$BaZrO_3$ (BZ) or BTZ-system have been established as one of the most important compositions for dielectrics in multilayer ceramic capacitors [2]. For composition $Ba(Ti_{1-x}Zr_x)O_3$, with x in the range $0.26<x<0.42$, the solid solution system showed some interesting relaxor like behaviors in the bulk materials [3-5]. This lead free relaxor material presents a great interest both for applications in the field of environmental protection and for fundamental studies. This inspired us to study the phase formation mechanism of the solid solution composition $BaTi_{0.6}Zr_{0.4}O_3$, formed through solid-oxide reaction route.

$BaTiO_3$-$BaZrO_3$ solid solution system is conventionally prepared by solid-state reaction between $BaCO_3$, TiO_2 and ZrO_2 [6]. Their fabrication usually involves a high temperature-processing step. The solid solution formation is governed by high temperature diffusional phase formation kinetics. W. Hacssler and co-authors [7] studied the system in the form of thin film grown by MOCVD. The study revealed that slightly Zr doped $BaTiO_3$ film adopt the tetragonal $BaTiO_3$ structure and for higher substitution rate the solid solution tends to a cubic structure. S.Gopalan and A.V. Virkar [8] examined the interdiffusion in doped BT-BZ sintered couples and a Kirkendall porosity formation was found indicating transport occurs on all sub-lattices in the system. Solid solution formation mechanism of the system from precursor powder is not available in details. Proper understanding of its formation mechanism is very useful for the synthesis and application of the system. In the present work, the composition $Ba(Ti_{0.6}Zr_{0.4})O_3$ was synthesized through mixed oxide reaction. The objective is to gain insight into the kinetics and mechanism of BTZ(ss) formation.

2. Experimental

BTZ-solid solution was prepared by solid-state reaction route from $BaCO_3$ (S.D. Fine Chem., Mumbai), TiO_2 (E. Merck India Ltd.) and ZrO_2 (Loba Chem., Mumbai). All the powders were having more than 99% purity. Particle size of starting raw materials, measured using Malvern Mastersizer, are: $BaCO_3$ [D(v,0.1)=0.25 μm, D(v,0.5)=2.09 μm, D(v,0.9)=13.20 μm], TiO_2 [D(v,0.1)=0.27 μm, D(v,0.5)=0.35 μm, D(v,0.9)=0.48 μm] and ZrO_2 [D(v,0.1)=0.42 μm, D(v,0.5)=10.27 μm, D(v,0.9)=15.48 μm]. The powders were thoroughly mixed in agate mortar using IPA. Decomposition behavior of raw mixture and $BaCO_3$ were investigated using NETZSCH Thermal Analyzer. Mixed powder was calcined at various temperatures in the range 700°C to 1600°C for 1 hour to study the phase formation behavior. The calcined powders were characterized with respect to phase identification, phase quantity measurement, crystallite size determination and lattice parameter measurement etc., all by using Cu-K_α XRD (PW-1830, Philips, Netherlands). For quantitative estimation of phases, calcined powders were uniformly mixed with an internal standard and the resulting mixture was analyzed using a step size of 0.02°, 2θ with 10 second/step. The relative weight fractions were quantified from the ratio of peak areas, according to the process described by S.Kumar & G.L.Messing [9]. On the basis of XRD line broadening at half maxima of the [110] peak, crystallite sizes of the phases were estimated using the Scherrer equation [10].

3. Results and Discussions

Figure 1 shows DSC-TG tracing of precursor. TG graph shows a continuous wt loss from about 500°C. There are two small DSC peak at 556°C and 728°C, corresponding ~1.4% and ~0.8% wt loss of the precursor. These weight losses may be attributed to the decomposition of very fine $BaCO_3$ particles present in the precursor. As stated previously, $BaCO_3$ raw material has finer particle fraction D(v,0.1)=0.25 μm and these fractions decomposes at lower temperature in presence of TiO_2. A sharp endothermic peak at 810°C corresponds to the polymorphic transformation of witherite to α-$BaCO_3$ [11], as there was no weight loss found under that peak for pure $BaCO_3$ decomposition. The 979°C huge endothermic peak corresponds to the major decomposition of $BaCO_3$ in the precursor. However, in pure $BaCO_3$ that peak occurs at about 1187^0C. This indicates that $BaCO_3$, which present in the precursor, decomposes at much lower temperature due to the presence of acidic TiO_2 in the mixture [12].

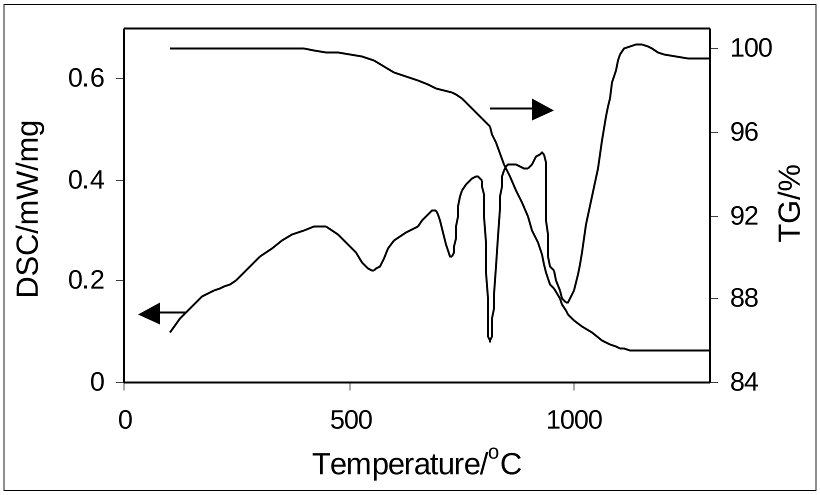

Fig. 1. TGA and DSC curve in air for the $BaCO_3$, TiO_2 and ZrO_2 powder mixture.

Figure 2 shows XRD pattern of precursor powder calcined at different temperature for 1 hour. It shows that BT and BZ form separately in the system and then BTZ(ss) forms by inter-diffusion between BT-BZ. Slow step scanning XRD analysis reveals that $BaTiO_3$ starts forming from 700°C and $BaZrO_3$ from 800°C.

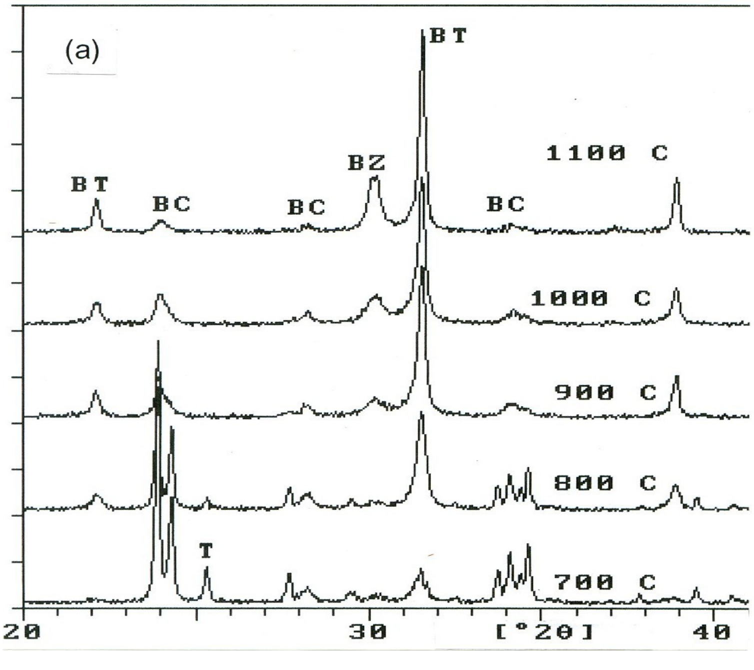

Fig. 2. XRD patterns of calcined precursor powder for 1 hour (a) at 700°, 800°, 900°, 1000° and 1100°C; (b) at 1200°, 1300°, 1400°, 1500° and 1600°C; with notations: BT=$BaTiO_3$, BZ= $BaZrO_3$, BC=$BaCO_3$, BTZ(ss)= $Ba(Ti_{0.6}Zr_{0.4})O_3$ and T=TiO_2

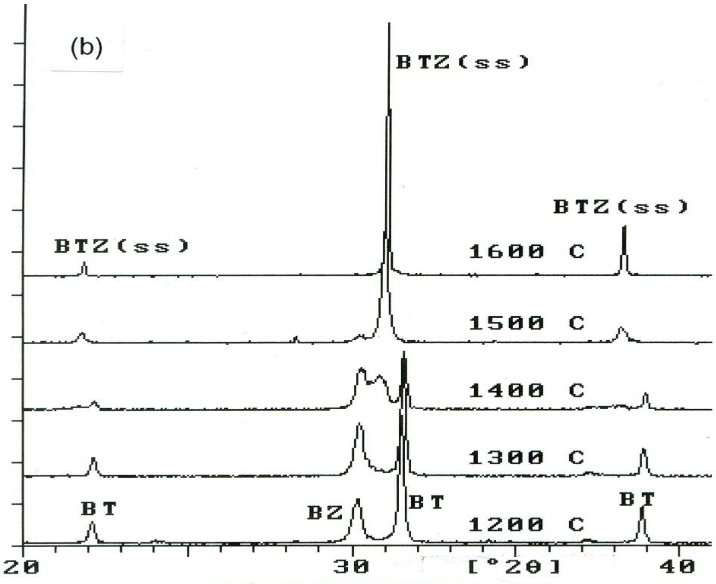

Fig. 2. (…continued)

Formation of intermediate BaO or other phases, like Ba_2ZrO_4, Ba_2TiO_4 or $BaTi_3O_7$, has not been observed within the detection limit of XRD. Consequently, BT and BZ are formed directly due to the reaction:

$$BaCO_3(s)+ZrO_2(s)+TiO_2(s)= BaTiO_3(s)+BaZrO_3(s)+CO_2\,(g) \quad (1)$$

The XRD patterns also suggest that the rate of $BaZrO_3$ formation is lower than that of $BaTiO_3$, which may be due to the (i) high average particle size of ZrO_2 (10.27 μm) than TiO_2 (0.35 μm) and/or (ii) higher ionic radius of Zr^{+4} (0.72 Å) than that of Ti^{+4} (0.61 Å). BTZ(ss) starts forming from 1300°C. Variation of their phase content with calcinations temperature is shown in Fig. 3. The quantity of BT is always higher than the quantity of BZ at any temperature up-to 1200°C. But after 1300°C, quantity of BT decreases quicker than BZ and the quantity of BTZ(ss) increases rapidly. These observations indicate that $BaTiO_3$ forms easily in the system through solid-state reaction between $BaCO_3$ and TiO_2 and the rate of BZ formation is relatively slower. However, quantity of BT increases slowly in the temperature range 900°C to 1100°C, which may be due to the decrease in the finer fraction of $BaCO_3$ and TiO_2 reactants, as they are used to form BT in the lower temperature range. These phase formations may be considered to follow a diminishing-core model. Diminishing cores are TiO_2 and ZrO_2. Above 1300°C, BTZ(ss) increases rapidly due to inter-diffusion between BT and BZ. To check the phase formation kinetics, concentration of the phases were used to measure the activation energy for their formation using the following relationship [13]:

$$[1- [(1-X_B)^{1/3}]^2 = 2Kt/R^2 \quad (2)$$

where $2K/R^2$ is essentially a reaction rate constant, X_B is the volume fraction reacted at time ' t '. Log (K/R^2) vs. 1/T plot represents Arrhenius expression and activation energy for the phase formation can be derived from the slope of the plot.

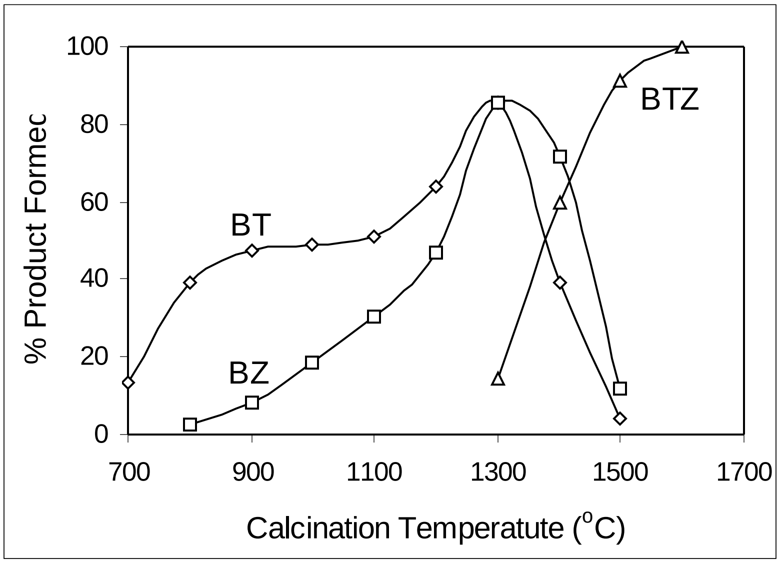

Fig.3. Non-isothermal transformation kinetics of precursor in static air.

Figure 4 shows temperature dependency of their phase formation reactions. They show Arrhenius type of linear temperature dependency. Activation energy measured from the slope shows that BT formation requires less activation energy (32.65 kcal/mol and 34.3 kcal/mol in the temperature range 700° to 900°C and 1100°C to 1300°C respectively) than that of BZ formation (48.4 kcal/mol). BT-formation activation energy in the temperature range 900°C to 1100°C, is not evaluated due to its temporary slow down in formation kinetics. Phases were formed in this system through solid-state interdiffusion between different particles. Interdiffusions take place with different ions limiting the speed of diffusion. Activation energy results show that phase formation reactions may be limited by the diffusion of Ti for BT and Zr for BZ formation respectively. In this case Ba and O are assumed to be immobile because their concentrations are spatially invariant. Since Zr^{+4} has higher ionic radius than Ti^{+4}, its diffusion requires higher energy than Ti^{+4} to form perovskite phase.

BTZ solid solution formation requires much high activation energy (133 kcal/mole), which is slightly higher than that (3.66 eV) reported by S.Gopalan and A.V.Virkar [8] for doped BT-BZ couples. In the present case, slight increase in activation energy may be due to the use of loose powders for reaction kinetics experiment in compared to sintered pellets and/or use of un-doped material. For BTZ(ss) formation reaction, the rate may be limited by the diffusion of Ba and/or O movement, which were proposed to be moveable during inter-diffusion experimental study in doped BT-BZ perovskites [8].

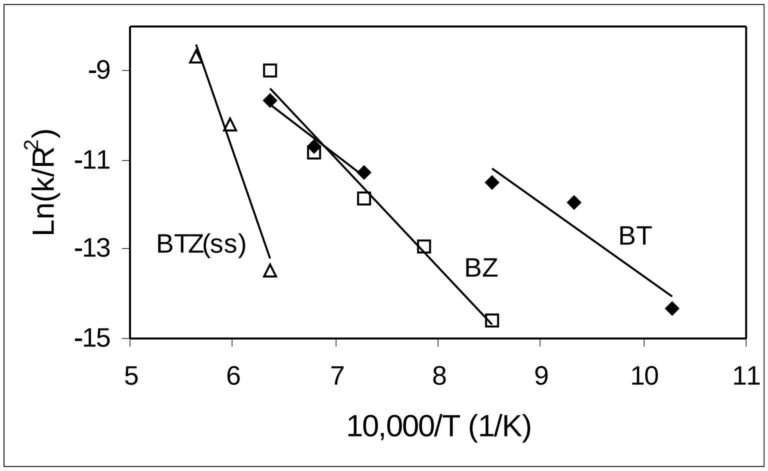

Fig. 4. Arrhenius dependence of reaction rate on calcination temperature for the transformation of precursor to $BaTiO_3$ (♦) and $BaZrO_3$ (□) and then to $BaTi_{0.6}Zr_{0.4}O_3$ solid solution (Δ).

The studies also indicate that solid-solution formation takes place by the diffusion of BT into BZ lattices, as BT decay more rapidly than BZ. Also from XRD data it is found that [110] peak of BZ shifted to higher angle with calcination temperature from 900°C to 1300°C, indicating the decrease in unit cell volume (Table-1) due to the incorporation of smaller Ti^{+4} ions. Where as, lattice parameter of BT remains almost same in the said temperature range (Table-1), indicating there is no diffusion of Zr^{+4} ion into BT lattices. Table 1 also shows that BTZ (ss) has higher lattice parameter at 1300°C than that at 1600°C, indicating that initial solid solution is higher in Zr^{+4} ion content than the final equilibrium one. So it may be considered that solid solution grows on BZ lattices having a coherent interface with BZ crystal. Here the diminishing core is BZ. This mechanism also suggests that the morphology of BTZ (ss) should be controlled by the morphology of BZ phase formed in the intermediate stage. Table 1 also shows the XRD crystallite sizes of BZ, BT and BTZ (ss) at different calcination temperature. Crystallite size of BT is always much higher than BZ, which again shows the easy formation of BT in the system.

Table 1
Variation of lattice parameter a_0 and XRD crystallite size (within first bracket) of BT, BZ and BTZ-solid solution with calcination temperature.

	Lattice parameter in Å (Crystallite size in nm)		
	900^0C	1300^0C	1600^0C
$BaTiO_3$	4.0094 (65.3)	4.0057 (232.4)	-----
$BaZrO_3$	4.1914 (39.1)	4.1696 (64.5)	-----
BTZ (ss)	-------	4.1216 (19.5)	4.0750 (180.2)

4. Conclusion

The formation kinetics of $BaTiO_3$-$BaZrO_3$ solid solution from mixture of $BaCO_3$, TiO_2 and ZrO_2 powders has been studied in air at 700°-1600°C using TGA/DSC and XRD. Based on non-isothermal kinetic analysis and on crystal structure, the reaction mechanism can be described by two-step process:

(1) During first step $BaTiO_3$ and $BaZrO_3$ phases are formed through direct solid-state reaction between $BaCO_3$ and TiO_2, ZrO_2, with latter two acting as diminishing cores. Formation of intermediate phases as Ba_2ZrO_4, Ba_2TiO_4 or $BaTi_3O_7$, etc has not been detected. $BaTiO_3$ formation activation energy, 34.3 kcal/mol, is lower than $BaZrO_3$ formation energy, 48.4 kcal/mol, may be due to the difference in their ionic radius.

(2) During the second step, $BaTiO_3$-$BaZrO_3$ solid solution is formed mainly by the diffusion of $BaTiO_3$ into the $BaZrO_3$ lattice, where latter phase acts as diminishing core. Activation energy for this step is 133 kcal/mole, may be due to the diffusion of Ba and/or O ions through solid solution interface.

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