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Study on phase formation and sintering kinetics of BaTi_{0.6}Zr_{0.4}O₃ powder synthesized through modified chemical route

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Abstract

BaTi_{0.6}Zr_{0.4}O₃ powder was prepared from barium oxalate hydrate, zirconium oxy-hydroxide and titanium dioxide precursors. Barium oxalate hydrate and zirconium oxy-hydroxide were precipitated from nitrate solution onto the surface of suspended TiO₂. Phase formation behaviour of the materials was extensively studied using XRD. BaTiO₃ (BT) and BaZrO₃ (BZ) start forming separately in the system upon calcinations in the temperature range 600°C–700°C. BT-BZ solid solution then forms by diffusion of BT into BZ from 1050°C onwards. The precursor completely transforms into BaTi_{0.6}Zr_{0.4}O₃ (BTZ) at 1200°C for 2 hours calcination. The activation energy of BT (134 kJ mol⁻¹) formation was found to be less than that of BZ (167.5 kJ mol⁻¹) formation. BTZ formation requires 503.6 kJ mol⁻¹ of energy. The sintering kinetics of the powder was studied using thermal analyzer. The mean activation energy for sintering was found to be 550 kJ mol⁻¹.

Keywords: A. Ceramics; A. Ferroelectrics; B. Precipitation; B. Sintering; D. X-ray diffraction

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1. Introduction

Solid solutions of BaTiO₃ (BT) with other perovskites-type materials offer a large range of possible modification of the dielectric properties. For example, the Curie temperature (T_c) and the dielectric permittivity (ϵ) can be tuned in a large range in the BaTiO₃–SrTiO₃ solid solution [1, 2]. A study on the BaTiO₃–BaZrO₃ (BT–BZ) solid solution has shown some interesting relaxor-like behaviour in the composition BaTi_{1-x}Zr_xO₃ (BTZ) with x in the range 0.26-0.42 [3-5]. This lead free relaxor materials would be particularly interesting for environmental-friendly applications as lead-based relaxor perovskites are presently avoided because of its toxic nature [6].

The BT–BZ solid solutions were conventionally synthesized through solid oxide route [7-9]. Chemical solution methods are also used to produce more homogeneous, finer particle size and low impurity level powders than that produced by the solid-oxide method [10-12]. On the other hand, the solid-oxide synthesis has advantages with respect to the use of relatively low-cost raw materials and simple processing steps. In the present synthesis Ba(NO₃)₂, ZrOCl₂.8H₂O solutions and TiO₂ powder are used for the preparation of BTZ to get some of the benefits of both the solid-oxide and chemical route. Use of TiO₂ powder, instead of its organometallic salt, can effectively reduce the powder synthesis cost. Aqueous solution of Ba(NO₃)₂ and ZrOCl₂.8H₂O are used to precipitate barium oxalate hydrate and zirconium oxy-hydroxide onto the surface of suspended TiO₂ particles by adding oxalic acid, to get more homogeneous mixing of raw materials than that obtained in solid powder mixing.

This type of powder synthesis has been reported earlier in the literature especially for SrTiO₃ and BaTiO₃ [13, 14]. Reports on BTZ phase formation from barium oxalate hydrate, titanium dioxide and zirconium oxy-hydroxide precursor mixture is not available in the literature. In the present work, the Ba(Ti_{0.6}Zr_{0.4})O₃ powder was synthesized from the precursor containing solution precipitated barium oxalate hydrate, zirconium oxy-hydroxide and TiO₂. The decomposition behavior of precursor was investigated. The BTZ solid solution formation mechanism and its kinetics were studied. Finally, the sintering kinetics of the powder was investigated.

2. Experimental procedure

The basic materials used in the present work include; Ba(NO₃)₂ (Assay >99%, Merck India Ltd.), TiO₂ (Anatase, Assay >99%, Merck India Ltd., particle size: d₁₀ = 0.27 μm, d₅₀ = 0.35 μm, d₉₀ = 0.48 μm), ZrOCl₂.8H₂O (Assay >99%, Loba Chemie Pvt. Ltd.) and (COOH)₂.2H₂O (Assay >99%, Merck India Ltd.). An aqueous solution of 0.12 M barium nitrate was prepared using deionized water. The exact molarity of the solution was determined by the chemical analysis. Required amount of ZrOCl₂.8H₂O was dissolved in the above barium nitrate solution. Appropriate amount of TiO₂ was added to 0.15 M oxalic acid solution with continuous stirring to form a suspension. The suspension was treated in ultrasonic bath for 10 min to break soft agglomerates. The solution containing barium nitrate and zirconium oxy-chloride was added drop-wise into the suspension of TiO₂ in oxalic acid solution under vigorous stirring. Finally, the pH of the resultant mixture was adjusted to 8 by adding ammonia solution. This process precipitates barium oxalate hydrate & ZrO(OH)₂ on the surface of fine TiO₂ (acting as seed) particles by heterogeneous nucleation. The resulting

precipitate was filtered out and then washed repeatedly using deionized water and isopropyl alcohol, followed by drying at 50 °C for 24 h.

The decomposition behavior of precursor was characterized using thermo-gravimetric (TG) analysis and differential scanning calorimetry (DSC), at a heating rate of 10 °C/min from room temperature up to 1300 °C in air. The precursor was calcined in air for 2h at various temperatures in the range of 600 °C to 1200 °C followed by phase identification, phase quantity measurement and lattice parameter measurement using Cu (K_α) X-ray Diffractometer (PW-1830, Philips, Netherlands). For quantitative estimation of phases, the calcined powders were uniformly mixed with an internal standard and the resulting mixture was analyzed by XRD of step scanning with the 10s irradiation every 2theta = 0.02 ° step. The relative weight fractions were quantified from the ratio of peak areas, according to the process described by S. Kumar et.al. [15]. The calcined (1200 °C for 2 hours) powder was ball milled for 24 hours using zirconia balls. The milled powder was then uniaxially pressed to disk-shaped pellet (15 mm diameter) at 3.5 tonne pressure. The sintering kinetics of the powder was studied on pellet sample using NETZSCH Thermal Analyzer (Model no DIL 402 C, Germany).

3. Results and discussion

Fig.1 shows the DSC-TG tracing of the precursor as a function of temperature. TG graph shows the weight loss in various stages. The first major weight loss, of about 2.9% within the temperature range 100 °C-300 °C, corresponds to an endothermic reaction in the DSC curve. This weight loss may be attributed to the decomposition of BaC₂O₄.xH₂O to BaC₂O₄.

The second weight loss of about 2.4% appearing in the temperature range 300°C-425°C, corresponds to a small endothermic reaction in the DSC curve. This weight loss may be attributed to the dehydration of ZrO(OH)₂ to ZrO₂. The third major weight loss of about 8.7% is found in the temperature range 425°C-600°C, which corresponds to an exothermic reaction in the DSC curve. This weight loss may be attributed to the decomposition of barium oxalate to barium carbonate as per the reactions:

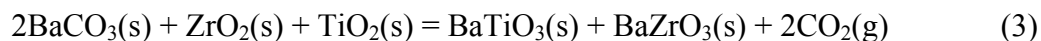


Reaction (1) is an endothermic one. However, at the same time CO is converted exothermically to CO₂, taking oxygen from air. The huge exothermic peak appears at 508°C is due to the reaction (2), which suppresses the endothermic peak of reaction (1). A sharp endothermic peak at 811°C corresponds to the polymorphic transformation of whitrite to α-BaCO₃ [7]. The fourth major weight loss of about 14%, started from around 700°C, is due to the decomposition of BaCO₃ and formation of BT & BZ. The figure also shows that the BaCO₃ decomposition completed up to 1000°C. However, in pure BaCO₃ the decomposition peak occurs at about 1187°C. This indicates that BaCO₃, which formed intermediately in the precursor, decomposes at lower temperature due to the presence of acidic TiO₂, fine particle size and better homogeneity in the mixture [14].

To understand the fundamental issues of BTZ formation, the precursors were heated in air at different temperatures and then were analyzed by XRD. Fig. 2 shows the XRD patterns of the precursor heated at different temperatures. The analysis of raw powder shows the presence of BaC₂O₄.0.5H₂O (PDF No. 20-0134) and TiO₂ (Fig. 2a). The presence of ZrO₂C₂O₄.xH₂O type phases in the precursor had not been detected within the limit of XRD.

BaC₂O₄·0.5H₂O was converted to BaC₂O₄ (PDF No. 37-0674) upon calcination at 400°C (Fig. 2b). This confirms the first weight loss in TG analysis is due to the loss of crystalline water of barium oxalate hydrate. The presence of ZrO(OH)₂ as well as ZrO₂ was not detected by XRD analysis. It is supposed that both of them remain in amorphous state. The 700°C calcined precursor shows the presence of BaCO₃ and TiO₂. The material in the final product (1200°C/4h) was identified (Fig. 2d) as BTZ by comparing with standard pattern for Ba(Ti_{0.75}Zr_{0.25})O₃ (PDF No. 36-0019).

To study the phase transformation behavior and reaction kinetics, the precursor powder was calcined at different temperatures for 2 hours. Fig. 3 shows the XRD pattern of calcined product, which suggests that BT and BZ form separately in the system and then BTZ forms by interdiffusion between BT and BZ. Slow step scanning XRD analysis reveals that BT and BZ starts forming simultaneously in the temperature range 600°C-700°C by the reaction:



Formation of intermediate BaO or other phases, like Ba₂ZrO₄, Ba₂TiO₄ or BaTi₃O₇ had not been observed within the detection limit of XRD. The precursor was completely transformed into single phase, cubic structure BTZ (a₀ = 4.0832(37) Å) at 1200°C for 2h calcinations.

The variation of phase content with calcination temperatures is presented in Fig. 4. As may be seen from the figure, the rate of decomposition of barium carbonate is higher in the temperature range 600°C-800°C. It also shows that the amount of BZ formation is less than that of BT at initial stage. This may be due to the higher reactivity of BaCO₃ with TiO₂, as Ti is more electronegative than Zr. At the later stage (850°C–1000°C), the amount of BZ formation exceeds that of BT, which is in contrast to the result reported earlier for the mixed oxide route BTZ synthesis [7]. The reason behind this is (a) high reactivity of very fine

homogeneously mixed ZrO₂ particles as it was formed through solution precipitation-dehydroxylation and (b) finishing of the lower size particle fraction of TiO₂ in the mixture. However, the rate of BT formation increases rapidly higher than 1000^oC. The amount of BZ decreases slightly at 1050^oC, which may be due to the formation of BTZ. The BTZ starts forming from 1050^oC onwards. The amount of BT and BZ decreases sharply above 1100^oC and formation of BTZ increases rapidly due to inter diffusion reaction between BT and BZ.

To check the phase formation kinetics, the concentrations of phases were used to measure the activation energy for their formation using the following relationship [16]:

$$k = \left(\frac{2.303}{t} \right) \log \left(\frac{a}{a-x} \right) \quad (4)$$

where k is the velocity constant of first order reaction, t is the time in second, a is the initial concentration and x is the concentration after time t . The activation energy (Q) for different phase formation reactions were derived using:

$$\log k = \left(\frac{-Q}{2.303R} \right) \frac{1}{T} + \log A \quad (5)$$

Where T is the temperature in Kelvin, and A is a constant called the frequency factor. Log k versus $1/T$, plot as shown in Fig. 5, represents Arrhenius type dependency of reaction rate on calcination temperature for BT, BZ and BTZ formation. It shows that BT formation requires less activation energy 134 KJ mol⁻¹ in the temperature range 950^oC to 1100^oC, than that of BZ formation (167.5 KJ mol⁻¹ in range 800^oC to 1000^oC). BT-formation activation energy in the temperature range 700^oC to 950^oC is not evaluated here due to its temporary slow down in formation kinetics. Phases were formed in this system through interdiffusion between

different particles. Inter-diffusions take place with different ions limiting the speed of diffusion. The 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. That is, two reactions are occurring in the same environment of BaCO₃. Since, Zr⁴⁺ has higher ionic radius than Ti⁴⁺, its diffusion requires higher energy to form perovskite phase. BTZ solid solution formation requires much higher activation energy 503.6 KJ mol⁻¹. However, that is less than 556.8 KJ mol⁻¹ reported earlier by J. Bera *et al* [7] for solid-state synthesis route. For BTZ formation reaction, the rate may be limited by the diffusion of Ba and/or O movement, which were proposed to be moveable during interdiffusion experimental study in doped BT–BZ perovskites [9].

The lattice parameter of BT ($a_0 = 4.0161 \pm 10$) remains more or less constant in all temperature ranges up to 1150°C. In case of BZ, it is almost constant ($a_0 = 4.182 \pm 08$) up to 1000°C and decreases ($a_0 = 4.1382$) as the temperature increases to 1150°C. It is supposed that titanium from BT inter-diffuses in to BZ after 1050°C, which is responsible for this decrease in lattice parameter. From the XRD, it is found that [110] peak of BZ shifts to higher angle with increase in calcinations temperature from 1050°C to 1150°C. It indicates the decrease in unit cell volume due to the incorporation of smaller Ti⁴⁺ ions. The lattice parameter of BT remains constant indicating there is no diffusion of Zr⁴⁺ ion into BT lattices. The lattice parameter of BTZ ($a_0 = 4.0832(37)$) decreases to ($a_0 = 4.0811(19)$) with the increase in reaction time from 2 hours to for 16 hours at 1200°C. This confirms the diffusion of titanium from BT in to BZ. It indicates that the initial solid solution was higher in Zr⁴⁺ 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.

To understand the sintering behavior, linear shrinkage of powder compact was measured up to 1450°C at different heating rates as described by J. Jean *et al* [17]. Fig. 6 shows shrinkage behavior of compact powder at different constant heating rates. The shrinkage seems to start from around 1150°C onwards. The onset sintering temperature is around 1300°C and materials can be sintered within 1400°C, which is lower than solid state synthesized power sintering temperature [9]. As expected the shrinkage curve shifted to higher temperature with increase in heating rate. The activation energy for the densification has been calculated from the equation as

$$\text{Ln} \left[T \frac{d\left(\frac{\Delta L}{L_0}\right)}{dT} \right] = \text{Ln} \left[\frac{1}{n} K_0 a^{\frac{1}{n}} \right] - \frac{1}{n} \text{Ln}(a) - \frac{Q}{nRT} \quad (6)$$

where $\frac{\Delta L}{L_0}$ is the fractional shrinkage over time, T is the temperature, n is the experimental exponent, K_0 is the pre-exponential term, a is the heating rate, Q is the apparent activation energy of sintering and R is the gas constant. The value of n can be determined from Fig. 7

by replotting the data in Fig. 6 as $\text{Ln} \frac{d\left(\frac{\Delta L}{L_0}\right)}{dT}$ versus $\text{Ln}(a)$ at different temperatures. No

significant change in slope ($-\frac{1}{n}$) is observed when the temperature is increased from 1150°C

to 1350°C. These slopes have a range of $\frac{1}{1.8} - \frac{1}{2.2}$ and a mean value of $\frac{1}{2}$. With the

knowledge of the value 'n', the value of Q of the rate-limiting step during constant-rate

heating is determined by replotting the data used in Fig. 6 as $\text{Ln} \frac{d\left(\frac{\Delta L}{L_0}\right)}{dT}$ versus $\frac{1}{T}$ at

different heating rates (Fig. 8). The activation energy at different heating rates is determined

from the slopes ($\frac{-Q}{2R}$) of these straight lines. The mean activation energy was calculated to be 550 KJ mol⁻¹. Here again, the rate may be limited by the diffusion of Ba and/or O movement, as the activation energy is similar to that found for the BTZ phase formation.

4. Conclusion

BaTi_{0.6}Zr_{0.4}O₃ perovskites has been synthesized from the mixture of barium oxalate hydrate, titanium dioxide and zirconium oxy-hydroxide. Studies on phase formation mechanism show that, the BT and BZ phases are formed separately in the system. Then, BaTi_{0.6}Zr_{0.4}O₃ was formed by the reaction between BT and BZ. Formation of intermediate phases likes Ba₂ZrO₄, Ba₂TiO₄ or BaTi₃O₇, etc., has not been detected. BT formation activation energy, 134 KJ mol⁻¹, was lower than BZ formation energy, 167.5 KJ mol⁻¹. That may be due to the difference in their ionic radius. BT–BZ solid solution was formed mainly by the diffusion of titanium from BT into the BZ lattice, where the latter phase acts as diminishing core. Activation energy for BTZ solid solution formation was 503.6 KJ mol⁻¹, which may be due to the diffusion of Ba and/or O ions through solid solution interface. The mean activation energy for sintering of compact powder was evaluated to be 550 KJ mol⁻¹.

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