Research Article

Effect of different starting materials on the synthesis of $Ba_{0.8}Ca_{0.2}TiO_3$

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Abstract: Literature has reported the synthesis of barium calcium titanates by various synthesis methods such as solid state reaction, co-precipitation and polymer precursors. These compounds are usually obtained using calcium carbonate ($CaCO_3$), barium carbonate ($BaCO_3$) and titanium oxide as starting materials. This study investigated the effect of different starting reagents on the synthesis of $Ba_{0.8}Ca_{0.2}TiO_3$ (BCT) by complex polymerization method (CPM). Two sets of starting precursors were used: titanium citrate, $CaCO_3$ and $BaCO_3$, and titanium citrate and $Ba_{1-x}Ca_xCO_3$ solid solution precursor. Samples were crystallized at a temperature range from 400 ℃ to 700 ℃ for different time. The obtained powders were characterized by X-ray diffraction (XRD), thermogravimetry (TG) and differential thermal analysis (DTA), and Raman and infrared spectroscopy. The infrared spectroscopy indicated that the chelation processes of Ba, Ca, Ti and CA ions are very similar. The results showed that the use of $CaCO_3$ and $BaCO_3$ or $Ba_{1-x}Ca_xCO_3$ solid solution as precursors does not affect the final properties of BCT powders obtained by CPM.

Keywords: ceramic; synthesis; $Ba_{0.8}Ca_{0.2}TiO_3$ (BCT); complex polymerization method (CPM)

1   Introduction

Ceramic materials based on $BaTiO_3$ (BT) exhibit tetragonal phase with ferroelectric, piezoelectric and thermoelectric properties at room temperature [1,2]. However, BT presents an endothermic transition at 129.6 ℃ that corresponds to the tetragonal to cubic phase transition at the Curie temperature [3,4]. With the aim of increasing the Curie point, modifiers of the barium titanate network can be added. A metal that has been studied as BT modifier is calcium, which forms barium calcium titanate $Ba_{1-x}Ca_xTiO_3$ (BCT) [5]. BCT, with similar behavior to BT, is a ferroelectric material at room temperature and increases the stability of the tetragonal phase [6–8].

It can be found in the literature a variety of chemical routes used to obtain BT ceramics, such as Pechini precursor route [9,10], hydrothermal [11–13], sol–crystal method [14], carbonate–oxalate (COBCT), gel–carbonate (GCBCT) and gel-to-crystallite conversion (GHBCT) [15] and low-temperature direct synthesis (LTDS) [16]. Tiwari *et al.* [17–19] synthesized BCT via solid state reaction using

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$Ba_{0.9}Ca_{0.1}CO_3$ solid solution and titanium oxide (TiO_2) as starting materials. $Ba_{0.9}Ca_{0.1}CO_3$ was obtained by co-precipitation of barium and calcium chlorides using ammonium carbonate. The authors observed higher calcium stoichiometric homogeneity in powders synthesized from mixed carbonate than in preparations using barium ($BaCO_3$) and calcium carbonates ($CaCO_3$).

This study investigated the effect of using different starting materials on the synthesis of barium calcium titanate by complex polymerization method (CPM) in order to evaluate possible differences in the stability of the polymer resins and the formation of additional phases in calcined BCT powders. Two sets of starting precursors were used: titanium citrate, $CaCO_3$ and $BaCO_3$, and titanium citrate and $Ba_{1-x}Ca_xCO_3$ solid solution precursor.

2 Experimental

BCT powders were prepared by complex polymerization method (CPM). The reagents used were titanium isopropoxide(IV) ($[Ti[OCH(CH_3)_2]_4$, Aldrich, 97%), calcium carbonate ($CaCO_3$, Aldrich, 99%), barium carbonate ($BaCO_3$, Mallinckrodt, 99%), calcium chloride dehydrate ($CaCl_2 \cdot 2H_2O$, Merck, 99.5%), barium chloride dehydrate ($BaCl_2 \cdot 2H_2O$, Mallinckrodt, 99.9%), ammonium carbonate (NH_4CO_3, Mallinckrodt), citric acid ($H_3C_6H_5O_7$, Merck, 99.5%), ethylene glycol ($HOCH_2CH_2OH$, J.T. Baker, 99%) and ammonium hydroxide (NH_4OH, Merck, 99%).

Titanium citrate (TC) aqueous solution precursor was prepared using titanium isopropoxide(IV) (Ti) and citric acid (CA) in a molar ratio of Ti:CA = 1:4. For the synthesis of BCT resins, Ba^{2+} and Ca^{2+} cations were added to the titanium citrate solution. In the first set, the cation sources were $CaCO_3$ and $BaCO_3$, and for the second set, the cation source was $Ba_{1-x}Ca_xCO_3$ which was obtained by co-precipitation of barium and calcium chlorides by ammonium carbonate as shown elsewhere [20]. After the addition of cations, pH was adjusted to 7–8 with ammonium hydroxide, and ethylene glycol was added to the solution which was remained at a temperature of about 80 ℃ under stirring to promote the polyesterification reaction and the evaporation of excess water.

For the production of BCT ceramic powders, polymeric resins obtained were submitted to thermal treatment at 300 ℃ for 4 h at a heating rate of 10 ℃/min to promote the pyrolysis of organic compounds. After this treatment, the obtained material was separated and then calcined in a temperature range of 400–700 ℃ at a heating rate of 5 ℃/min, for different time from 1 h to 8 h.

Precursor solutions and calcined powders were both characterized. Characterizations were performed by X-ray diffraction (XRD) using a Rigaku diffractometer (Model D/max-2500/PC) with Cu Kα radiation in order to analyze the crystalline phases in the samples. Infrared spectroscopy was conducted using Bruker Equinox/55 spectrophotometer in the 400–4000 cm^{-1} region at room temperature. Thermogravimetry (TG) and differential thermal analysis (DTA) were conducted using a TA Instruments machine under oxygen flow (100 cm^3/min) and subjected to heating rate of 5 ℃/min from room temperature to 900 ℃ in order to estimate the temperature range in which phase changes occurred. Raman spectroscopy was conducted using Bruker RFS100 spectrophotometer, with Nd-YAG laser (1064 nm) as excitation source (power of 23 mW with 100 scans and resolution of 4 cm^{-1}).

3 Results and discussion

Analyses performed by infrared spectroscopy indicate the formation of complexes of metal ions (Ba, Ca and Ti) with citric acid (CA), even before the addition of ethylene glycol. Figure 1 shows the infrared spectra of titanium citrate (TC) and precursor solutions before polymerization by ethylene glycol. The results indicate similar spectra for solutions using different starting reagents. It could be seen that the spectra of BCT solutions (Ba–Ca–Ti–CA) do not exhibit non-ionized carboxylic groups in the region near 1720 cm^{-1}. This occurs because at pH ≈ 8, all carboxyl groups present are ionized [21]. In the infrared spectrum of barium calcium titanate, two bands are observed, both with asymmetric and symmetric stretchings. These are attributed to the presence of a metal–CA complex in the BCT with the production of various carboxylic groups [22,23]. In all complexes, frequencies of asymmetric and symmetric carbonyl stretchings are located at 1565–1665 cm^{-1} and 1145–1389 cm^{-1}, respectively. The difference between asymmetric (v_{as}) and symmetrical (v_s) stretchings ($\Delta(v_{as}-v_s)$) of the COO^- carbonyl group varies within the range of 176–220 cm^{-1}, suggesting that the carboxylic groups
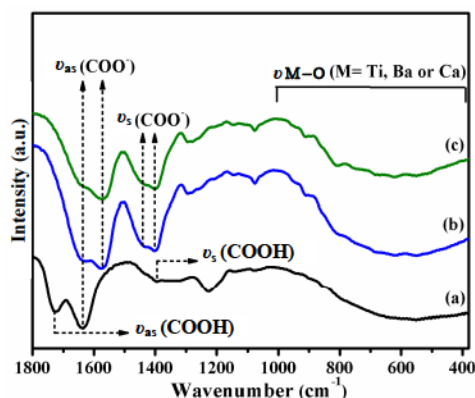
Fig. 1 Absorption spectra in the infrared region of precursor solutions: (a) TC, (b) $CaCO_3$ and $BaCO_3$, and (c) $Ba_{0.8}Ca_{0.2}CO_3$.

Fig. 2 (a) TG and (b) DTA of pre-pyrolyzed BCT powders with the starting reagents: (i) $CaCO_3$ and $BaCO_3$, (ii) $Ba_{0.8}Ca_{0.2}CO_3$.

show complexes with unidentate coordination [22,23]. If the carboxylic groups are involved in a chelation bridge of the complex with CA, $\Delta(v_{as}-v_s) \approx 170$ cm^{-1} would be expected. Characteristic peaks of free CA are observed in the region below 1000 cm^{-1}, which disappear after CA chelation, giving rise to a broad band attributed to the M–O stretching, where M = Ti, Ba or Ca [24]. This analysis suggests that both starting materials could be used to obtain the precursor solution of $Ba_{0.8}Ca_{0.2}TiO_3$ polymer resins [21,25].

TG/DTA analyses shown in Fig. 2 are performed on the resins after heat treatment at 300 ℃ for 4 h. The obtained curves for both starting materials show similar behavior. TG analysis (Fig. 2(a)) indicates four stages. The first stage (25–120 ℃) shows mass loss attributed to the removal of water and excess ethylene glycol. From 120 ℃ to 480 ℃, the highest mass loss is observed, which is attributed to the decomposition of the polymer chain and removal of CO_2 and H_2O. The third stage occurs from 480 ℃ to 558 ℃ and corresponds to the formation of an intermediate phase called barium oxycarbonate (($Ba_{0.8}Ca_{0.2}$)$_2$Ti$_2$O$_5$·CO_3) [26]. From 558 ℃ to 675 ℃, there are decomposition of this phase with mass loss of approximately 3% and subsequently the formation of crystalline $Ba_{0.8}Ca_{0.2}TiO_3$. No mass loss is observed above 675 ℃ [26,27].

DTA curves (Fig. 2(b)) show the presence of an exothermic peak around 450 ℃, which is attributed to the rupture of the polymer chain. A small weight loss from 500 ℃ is observed in the TG/DTA curves, suggesting the beginning of the crystallization process. However, the presence of two low-intensity exothermic peaks at 520 ℃ and 650 ℃, respectively, indicates the
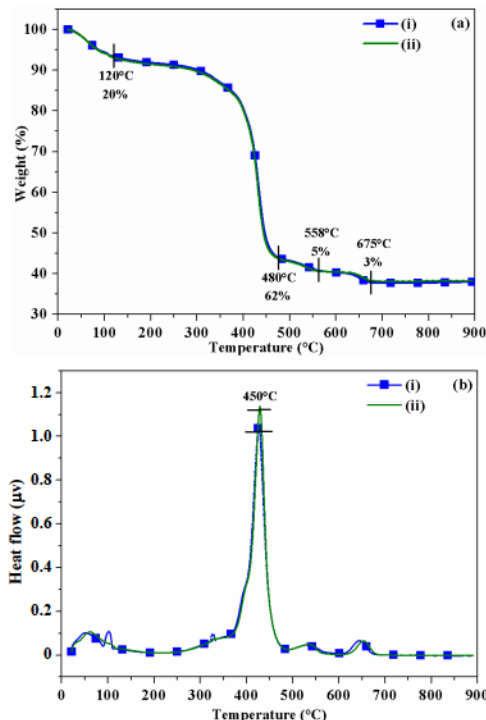
formation and decomposition of intermediate phases, such as barium calcium carbonate [28].

The thermal evolution of the $Ba_{0.8}Ca_{0.2}TiO_3$ phase is investigated by XRD and Raman spectroscopy in the samples calcined at different temperatures (400–700 ℃) and time (1–8 h). Figure 3 illustrates the XRD patterns of the samples treated at 700 ℃ for 4 h using both starting materials. Tetragonal perovskite-type $BaTiO_3$ (ICSD No. 95436) is present in all samples. No secondary phase peaks are found.

Figure 4 presents a time–temperature–transformation (TTT) phase diagram constructed from
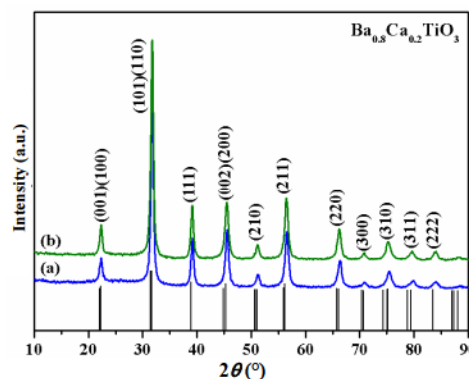

Fig. 3 X-ray diffractograms of BCT powders calcined at 700 ℃ for 4 h prepared using: (a) $CaCO_3$ and $BaCO_3$, (b) $Ba_{0.8}Ca_{0.2}CO_3$.
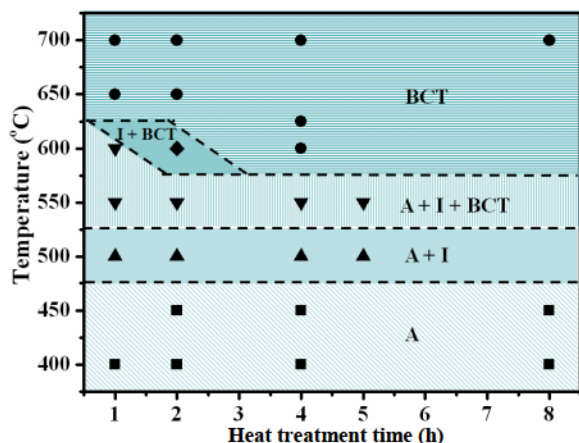
Fig. 4 Time–temperature–transformation (TTT) diagram and evolution of the BCT crystalline phase obtained from different starting materials (A = disordered, I = $(Ba_{0.8}Ca_{0.2})_2Ti_2O_5 \cdot CO_3$ and BCT = $Ba_{0.8}Ca_{0.2}TiO_3$).

Fig. 5 Raman spectra obtained for BCT powders calcined at 700 ℃ for 4 h using: (a) $CaCO_3$ and $BaCO_3$, (b) $Ba_{0.8}Ca_{0.2}CO_3$.

XRD results of BCT samples obtained with different starting materials (since the results are similar, only one figure is presented for simplicity). The diagram shows that within 8 h treatment at 400 ℃, all samples remain disordered. At 500 ℃, the formation of the intermediate phase $(Ba_{0.8}Ca_{0.2})_2Ti_2O_5 \cdot CO_3$ could be observed. Around 600 ℃ and after 2 h of thermal treatment, the intermediate layer is decomposed and the BCT phase is obtained. These results show that $Ba_{0.8}Ca_{0.2}TiO_3$ prepared with both starting reagents shows a similarity in the evolution of the formation of the crystalline phase with respect to the increasing temperature.

Figure 5 illustrates the Raman spectra of powders calcined at 700 ℃ for both starting materials. The Raman active modes for $BaTiO_3$ with tetragonal structure ($P4mm$) are $4E$ (TO + LO) + $3A_1$ (TO + LO) + $1B_1$ (TO + LO). The peak intensity at about 303 cm^{-1} is given by the overlap of modes E (3TO) + E (2LO) + B$_1$. This vibrational mode is characteristic of a tetragonal structure; therefore, an increase in the symmetry of the network tends to disappear in this peak. The band at 640 cm^{-1} is attributed to the hexagonal phase of $BaTiO_3$. However, Cho [29] reported that this hexagonal phase is the result of particles with defects on plane (111). These defects can generate satellite peaks that correspond to the hexagonal phase in the Raman effect. The spectra for the powders show the appearance of three characteristic bands of the tetragonal structure at 724 cm^{-1}, 523 cm^{-1} and 263 cm^{-1}. It can be seen that the use of different starting materials for the synthesis of BCT does not result in changes in the Raman spectra.
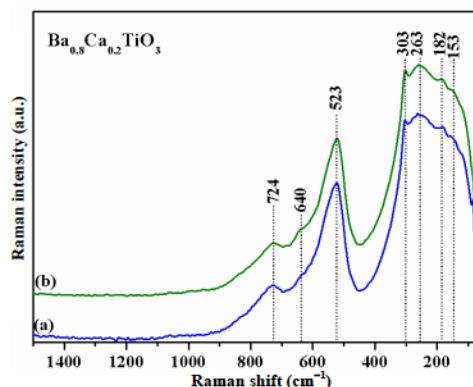
By means of field emission scanning electron microscopy (FE-SEM) analysis performed for both materials, it is verified that the materials synthesized from titanium citrate, $CaCO_3$ and $BaCO_3$ (Fig. 6(a)) and from titanium citrate and $Ba_{1-x}Ca_xCO_3$ solid solution (Fig. 6(b)) are composed of several agglomerated particles without the presence of well-defined morphology.

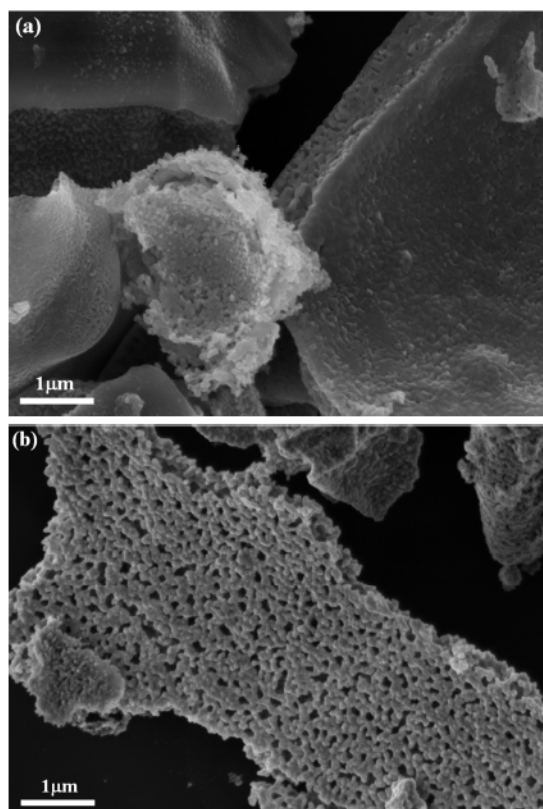**Fig. 6** FE-SEM images of the powders synthesized with different starting reagents: (a) $CaCO_3$ and $BaCO_3$, (b) $Ba_{1-x}Ca_xCO_3$.

According to the literature, due to the large amount of organic material, the polymeric precursor method needs to eliminate it for the synthesis of pure oxides, but may result in the formation of agglomerates especially after sintering [30]. It should also be taken into account the high reactivity of the particles along with the organic material, which facilitates the emergence of highly agglomerated morphologies [31].

Thus, powders submitted to 700 ℃ for 4 h for sintering result in the formation of agglomerated regions. There are no significant differences in their morphologies, which are possible to observe for both starting reagents.

4 Conclusions

$Ba_{0.8}Ca_{0.2}TiO_3$ (BCT) obtained using different starting reagents showed a similar chelation of Ba–Ca–Ti–CA ions for both sets and few differences were observed during thermal evolution study. BCT powders showed no structural differences as obtained from $CaCO_3$ and $BaCO_3$ or $Ba_{0.8}Ca_{0.2}CO_3$. This preliminary study showed that the synthesis of $Ba_{0.8}Ca_{0.2}TiO_3$ obtained by complex polymerization method was effective for all starting materials. Synthesis with individual carbonates ($CaCO_3$ and $BaCO_3$) involved fewer steps since only one synthesis was necessary to obtain BCT, thereby showing advantages in comparison to the synthesis using $Ba_{0.8}Ca_{0.2}CO_3$ solid solution as precursor.

Acknowledgements

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