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Synthesis of high aspect ratio platelike $Ba_{1-x}Ca_xTiO_3$ particles by topochemical microcrystal conversion method

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Abstract

A-site complex perovskite $Ba_{1-x}Ca_xTiO_3$ ($x \leq 0.25$) platelike particles with high aspect ratio (edge length to thickness) of 8–10 and micron sizes (6–8 μm) were synthesized via a topochemical microcrystal conversion reaction between the platelet $Bi_4Ti_3O_{12}$ and the powdered $BaCO_3$–$CaCO_3$ mixture at 950 °C in KCl flux. The morphology and A-site elemental composition of the resulting particles has been studied with reference to the effect of the concentration and molar ratio of the Ca^{2+} and Ba^{2+} in molten salt. The A-site elemental composition of the resultant particles was correspond linearly to the molar ratio of the Ca^{2+} and Ba^{2+} in molten salt. The morphology and size distribution of the synthetic $Ba_{1-x}Ca_xTiO_3$ particles was inherited from that of the precursor phase $Bi_4Ti_3O_{12}$. The designed synthesis routine has potential to synthesize other A-site complex perovskite platelike particles with high aspect ratio and micron sizes, which serving as a suitable template and seeded crystals can be employed to produce highly textured ceramics via TGG/RTGG method and single crystals by SPC technique.

Keywords: A. Powders: chemical preparation; B. Platelets; B. Grain size; D. Perovskites; $Ba_{1-x}Ca_xTiO_3$

1. Introduction

High aspect ratio platelet-shaped perovskite particles play a vital role in thin film, highly textured ceramics via templated grain growth (TGG), reactive templated grain growth (RTGG) and single crystals by seeded polycrystal conversion (SPC), where anisotropic perovskite particles serve as ideal substrates and templates to seed oriented grain growth in oriented film and polycrystalline matrix to form highly textured ceramics and single crystals for achieving optimum properties [1–8].

Anisotropic perovskite particles with high aspect ratio are difficult to synthesize directly using conventional methods for the high crystal symmetry. In the past decade, the most successful approaches for producing anisotropic perovskite particles rely on topochemical microcrystal conversion (TMC) of layered perovskite structures compounds, which consist of two-dimensional perovskite slabs interleaved with cations or cationic structural units, such as Aurivillius phases (structural formula $Bi_2O_2^{2+}[A_{n-1}B_nO_{3n+1}]^{2-}$). TMC technique is essentially the soft chemistry methods which offer potentially powerful tools for controlling thermodynamically inaccessible structural and morphological features at the kinetic level [9,10]. Recently, employing Aurivillius phase compounds with $n \geq 4$ as a precursor phase, many perovskite compounds with highly controlled morphologies were produced using multistep TMC process, such as platelet $BaTiO_3$, $SrTiO_3$, $CaTiO_3$, and $PbTiO_3$ were produced from Aurivillius phase compounds ($n \geq 4$) $BaBi_4Ti_4O_{15}$, $SrBi_4Ti_4O_{15}$, $CaBi_4Ti_4O_{15}$ and $PbBi_4Ti_4O_{15}$, respectively [11–14]. These synthetic perovskite platelike particles have the A-site chemistries dominated by only one kind of alkaline earth metals Sr, Ca, Pb, and Ba, the chemical composition inhomogeneity of the target textured ceramics would arouse for the difference of the composition between the template microcrystals and matrix materials using these particles as templates and seeded crystals in TGG/RTGG and SPC [3]. Therefore, the perovskite particles with the target A-site elemental composition and controlled morphology are used as ideal templates and suitable seeds crystals for

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RTGG/TGG and SPC technique [3,4,6]. So far, there are no reported methods for growing perovskite particles with both morphology and A-site elemental composition controlled simultaneously by the TMC method, in which using one kinds of Aurivillius compounds as a proper precursor is the key to success in the TMC technique.

In this paper, A-site complex perovskite $Ba_{1-x}Ca_xTiO_3$ platelike particles with high aspect ratios and micron sizes were synthesized successfully via the TMC reaction method, in which the Aurivillius phase compound (n=3) $Bi_4Ti_3O_{12}$ was employed as precursor. The morphology and A-site elemental composition of the synthetic particles has been studied with reference to the effect of the concentration and molar ratio of the Ca^{2+} to Ba^{2+} in molten salt.

2. Materials and methods

Platelike $Ba_{1-x}Ca_xTiO_3$ particles were prepared by topochemical microcrystal conversion method. Firstly, high aspect ratio platelike $Bi_4Ti_3O_{12}$ microcrystals used as a precursor were obtained by the reaction of Bi_2O_3 and TiO_2 in KCl–NaCl molten salts (formula (1)). Then the A-site complex perovskite $Ba_{1-x}Ca_xTiO_3$ particles with controlled morphologies and composition of the A-site element were obtained by the one-step topochemical microcrystal conversion reactions used $Bi_4Ti_3O_{12}$ as precursor and $CaCO_3$–$BaCO_3$ as complementary compounds (formula (2)):

$$2Bi_2O_3 + 3TiO_2 \rightarrow Bi_4Ti_3O_{12} \quad (1)$$

$$3xCaCO_3 + 3(1-x)\,BaCO_3 + Bi_4Ti_3O_{12} \rightarrow 3Ba_{1-x}Ca_xTiO_3 + 2Bi_2O_3 + 3CO_2 \quad (2)$$

All the reagents used in this experiment were of analytical grade and from Sinopharm Chemical Reagent Co. Ltd.

Platelike precursor $Bi_4Ti_3O_{12}$ microcrystals were synthesized by reacting Bi_2O_3 and TiO_2 in KCl–NaCl molten salts. Stoichiometric amounts of Bi_2O_3 and TiO_2 with an equal weight of KCl–NaCl (1:1 M ratio) flux were mixed in analytical purity ethanol by ball milling for 12 h. After evaporating the ethanol, dried mixed powders were heated in a covered Al_2O_3 crucible at 900 °C for 2 h. Platelike $Bi_4Ti_3O_{12}$ microcrystals were recovered by dissolving the KCl–NaCl flux with heated deionized water at 80 °C.

The platelike $Ba_{1-x}Ca_xTiO_3$ particles were synthesized by topochemical microcrystal conversion reaction between platelike precursor $Bi_4Ti_3O_{12}$ and powdered $BaCO_3$–$CaCO_3$ mixture in an equal weight of KCl molten salts. Both carbonates $BaCO_3$ and $CaCO_3$ (the designed molar ratio of Ca to Ba is 1:9, 2:8, 3:7, both carbonates are 30% excess) were firstly mixed with KCl by ball milling in analytical purity ethanol for 24 h, after which $Bi_4Ti_3O_{12}$ was added by magnetic stirring to avoid destroying the platelike shape of $Bi_4Ti_3O_{12}$. After evaporating the ethanol, the dried precursor mixture was heated in a covered Al_2O_3 crucible at 950 °C for 4 h. The salt flux was removed by washing with deionized water, byproduct Bi_2O_3 was removed by soaking in 30% HCl for 1–3 h. The $Ba_{1-x}Ca_xTiO_3$ particles were then dispersed by ultrasonicating and rinsed 3 times with DI water.

The phase purity and structure of $Ba_{1-x}Ca_xTiO_3$ particles, prepared as described above, were analyzed by X-ray diffraction (D/Max2550VB+/PC, Rigaku, Tokyo, Japan). The morphologies of $Ba_{1-x}Ca_xTiO_3$ particles were observed using FESEM (JSM-6701F, Japan Electron Co., Tokyo, Japan) with energy-dispersive spectroscopy (EDS: Oxford Instruments, UK) for determining elemental composition. In each sample with given molar ratio of Ca to Ba, more than five single product particles were measured by EDS and the final result was the average of the measured particles.

3. Results and discussion

3.1. Selection and preparation of precursor phase for synthesizing high aspect ratio platelike $Ba_{1-x}Ca_xTiO_3$ particles via the TMC process

The entire process of the topochemical microcrystal conversion from layered precursor $Bi_4Ti_3O_{12}$ to perovskite $Ba_{1-x}Ca_xTiO_3$ is illustrated in Fig. 1. The key to succeed in producing A-site elemental composition and morphology of the synthetic particles controlled simultaneously by the TMC method is the selecting and synthesizing a suitable precursor, which should has a pseudo-perovskite structure and can be transformed to $Ba_{1-x}Ca_xTiO_3$ easily. Because the morphology of synthetic perovskite particles is inherited from the precursor phase, the suitable precursor used in the TMC method must have layered morphology and high aspect ratio. According to the literature, the layered bismuth compounds which typically undergo strongly anisotropic growth and thus show high aspect ratio are reasonable candidates, these compounds were first studied by Aurivillius, Aurivillius phase compounds with a general structure formula of $Bi_2O_2^{2+}$ $[A_{n-1}B_nO_{3n+1}]^{2-}$ are intergrowths of perovskite and bismuth oxide and have a covalent network of $Bi_2O_2^{2+}$ between the two-dimensional pseudo-perovskite blocks, where B is a small transition metal cation and A is a larger s-, d-, or f-block cation, n is an integer between 1 and 5. Generally, the A-site of the Aurivillius phase compounds with $n \geq 4$ was occupied completely by one kinds of cation, the another kinds of cation have no chance to enter A-site to form A-site complex perovskite via the TMC method. Therefore, the Aurivillius phase compounds with $n \geq 4$ were not a suitable precursor for producing A-site complex perovskite $Ba_{1-x}Ca_xTiO_3$ platelike microcrystals via TMC reaction method.

$Bi_4Ti_3O_{12}$ with $n=3$ is one member of the Aurivillius phase compounds, the A-site cation of $Bi_4Ti_3O_{12}$ was vacant and occupied partially by the Bi^{3+} cation, it is the vacancy of A-site cation in $Bi_4Ti_3O_{12}$ crystal lattice that offers a possibility for other one or more kinds of cation enter to form A-site complex perovskite phase. The crystal structure of $Bi_4Ti_3O_{12}$ consists of three perovskite-like layers between the two $Bi_2O_2^{2+}$ oxide layers. The $Bi_2O_2^{2+}$ oxide interlayers can easily

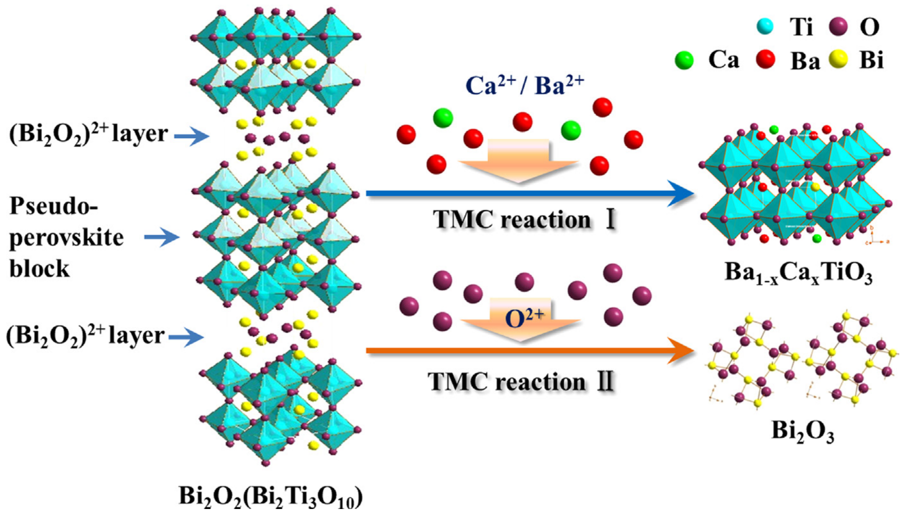

Fig. 1. Schematic illustration of crystal structure conversion from Aurivillius phase $Bi_4Ti_3O_{12}$ to perovskite phase $Ba_{1-x}Ca_xTiO_3$ by the TMC reaction.

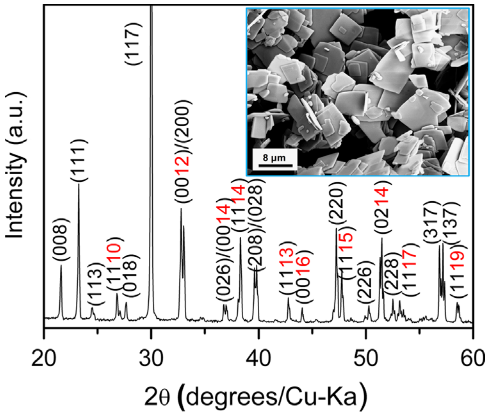

Fig. 2. XRD pattern and surface SEM image of the precursor $Bi_4Ti_3O_{12}$ microcrystals.

be removed during a high-temperature treatment, the A-site Bi^{3+} ions can be replaced by other one or more elements through TMC techniques. Moreover, $Bi_4Ti_3O_{12}$ with phase pure and desired morphology was obtained by controlling the heating rate and soaking time via the molten salt synthesis technique. Therefore, using $Bi_4Ti_3O_{12}$ as a precursor phase, there is a potential for synthesizing perovskite compounds with morphology and chemical composition of the A-site element was controlled simultaneously by the only one-step TMC process.

As shown in Fig. 1, by employing the Aurivillius phase $Bi_4Ti_3O_{12}$ as a precursor to synthesize the perovskite phase $Ba_{1-x}Ca_xTiO_3$ with morphology and chemical composition of the A-site element was controlled simultaneously by the one-step TMC reaction, in which process there should exist two kinds of TMC reactions occurred separately within the crystal of the precursor $Bi_4Ti_3O_{12}$. One is the ion-exchange reaction, the Ba^{2+} and Ca^{2+} with a designed molar ratio diffused simultaneously into the TiO_6 octahedral layers in $Bi_4Ti_3O_{12}$ to replace the A-site $Bi^{3+}$and filled completely the A site of the perovskite-like layers, this reaction results in the formation of A-site complex perovskite $Ba_{1-x}Ca_xTiO_3$ microcrystals with a preserved platelike shape of the precursor $Bi_4Ti_3O_{12}$ crystals and target chemical composition of A site elements [15]. Another reaction is the topochemical condensation reaction, implying the $(Bi_2O_2)^{2+}$ interlayers and the A-site Bi^{3+} ions of the precursor $Bi_4Ti_3O_{12}$ crystal reacted with ambient O^{2+} and decompounded from $Bi_4Ti_3O_{12}$ crystal lattice in the form of Bi_2O_3 powders, finally, a three-dimensional perovskite microcrystal was formed [9,10]. Because this topochemical microcrystal conversion reaction is a sequence of low-temperature reactions which modified the crystal structure of the precursor $Bi_4Ti_3O_{12}$ without extensive rearrangement of the structural framework. Therefore, the layered shape of Aurivillius precursor phase $Bi_4Ti_3O_{12}$ was preserved while the chemical composition has transformed to A-site complex perovskite phase.

Fig. 2 shows the XRD pattern and surface SEM image of the precursor $Bi_4Ti_3O_{12}$ microcrystals prepared by molten salt synthesis technique. The XRD pattern shows that the $Bi_4Ti_3O_{12}$ microcrystals were phase pure. Surface SEM image shows that the $Bi_4Ti_3O_{12}$ microcrystals have a microstructure of regular square platelike morphology with a size of about 8–10 μm and a thickness of 0.5 μm. The aspect ratio is high enough for $Bi_4Ti_3O_{12}$ to be a suitable precursor for the one-step TMC reaction.

3.2. *Synthesis of high aspect ratio platelike $Ba_{1-x}Ca_xTiO_3$ particles by TMC reaction method*

Fig. 3(a)–(c) shows the surface SEM image of the resulting particles synthesized by the TMC reaction using $Bi_4Ti_3O_{12}$ as a precursor and carbonates $CaCO_3$ and $BaCO_3$ with different molar ratios as started materials in KCl molten salt at 950 °C for 4 h. The synthetic particles with different contents of Ca and Ba all exhibit platelike shape, indicating that the platelike shape of the precursor $Bi_4Ti_3O_{12}$ was preserved during this TMC reaction process. The average size of the resulting particles is about 6–8 μm and the thickness is less than 0.5 μm. The moderate size, platelike morphology and high

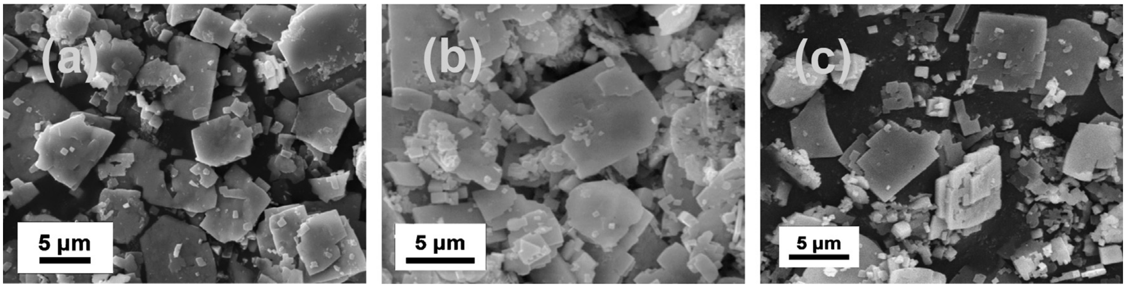

Fig. 3. Surface SEM images of the product particles synthesized by the designed TMC reaction used different molar ratio carbonates of $CaCO_3$ and $BaCO_3$. The molar ratio of $CaCO_3/BaCO_3$ is (a) 1:9, (b) 2:8, (c) 3:7.

aspect ratio (edge length to thickness) of 8–10 of the synthesized particles are all the desired characters for a suitable template and seeded crystal to produce highly textured ceramics by TGG/RTGG method [3].

The effect of the molar ratio of Ca^{2+} to Ba^{2+} in the KCl molten salt on the phase structure of the resultant particles was investigated. Fig. 4 shows the XRD patterns of the product particles synthesized by the TMC reaction in different molar ratio carbonates of $CaCO_3$ and $BaCO_3$. For all the samples, the strong intensities and sharp diffraction peaks shown in Fig. 4 (a)–(c) indicated that all the particles with different contents of Ca and Ba elements have good crystallinity. The major peaks were indexed definitively according to perovskite-structured crystal, indicating the TMC reaction from Aurivillius precursor phase $Bi_4Ti_3O_{12}$ to perovskite is complete. The phase structure of the synthetic particles changed gradually with increasing of the molar ratio of Ca^{2+} to Ba^{2+} from 10 mol% to 30 mol% in molten salt shown in Fig. 4(a)–(c). The major phase of all synthetic particles produced with the designed molar ratio of Ca^{2+} to Ba^{2+} from 10 mol%, 20 mol% to 30 mol% are indexed similarly by the $BaTiO_3$. Considering that the another A-site element Ca existing in molten salts have the same chance to diffuse into the precursor $Bi_4Ti_3O_{12}$ and finally incorporate into the resulting particles, the major phase of the synthetic microcrystal should be A-site complex $BaTiO_3$ base solid solution $Ba_{1-x}Ca_xTiO_3$. With the relative molar concentration of Ca^{2+} ions increased in molten salt the major phase of the product particles has transformed from tetragonal to cubic crystal structure, which maybe stems from the fact that the more Ca^{2+} ions with smaller ionic radius than that of Ba^{2+} has already incorporated into the resulting microcrystals [16]. According to the phase equilibrium diagram for the system $BaTiO_3$–$CaTiO_3$, the maximum solid solubility of Ca in $BaTiO_3$ is 25 mol%, when the designed molar ratio of Ca^{2+} to Ba^{2+} in molten salts was smaller than the maximum solid solubility of Ca in $BaTiO_3$, the single solid solution phase $Ba_{1-x}Ca_xTiO_3$ was formed [16]. When the given molar ratio of Ca^{2+} to Ba^{2+} in molten salts was larger slightly beyond the max solid solution of 25–30 mol%, the resulting particles were still the solid solution phase $Ba_{1-x}Ca_xTiO_3$, means the law of the maximum solid solution worked in forming $Ba_{1-x}Ca_xTiO_3$ particles using different molar ratio of Ca^{2+} to Ba^{2+} in molten salts by the TMC process. Larger (00l) diffraction peaks of the synthetic microcrystals with different contents of Ca and Ba elements such as (001) and (002) were observed, indicating that these particles have the largest developed plane in (00l) planes, which is consistent with the morphology of platelike and high aspect ratio of the synthetic microcrystals showed in SEM image.

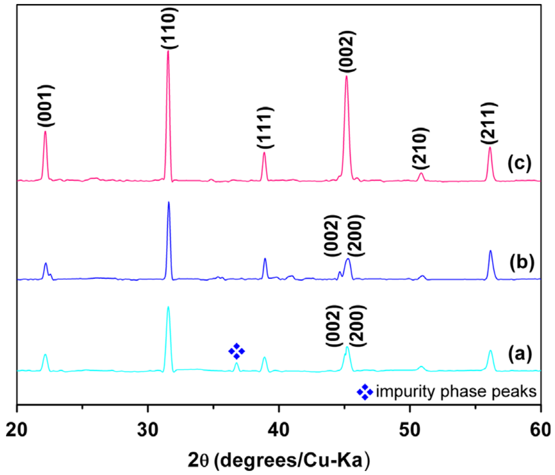

Fig. 4. XRD patterns of the product particles synthesized by the designed TMC reaction used different molar ratio carbonates of $CaCO_3$ and $BaCO_3$. The molar ratio of $CaCO_3/BaCO_3$ is (a) 1:9, (b) 2:8, (c) 3:7.

To evaluate the element types and chemical composition of the A-site element in the resultant particles, the EDS analysis was made.

Table 1 summarizes the average results of chemical composition of the resultant particles synthesized with different molar ratio of Ca^{2+} to Ba^{2+} in molten salt by TMC method. It is showed that for all the measured microcrystals the atomic ratio of the Ba:Ca:Ti:O and Ca:Ti:O approximate closely to the perovskite-structured chemical formula ABO_3, implying the A-site complex perovskite microcrystals were synthesized by this designed TMC reaction. The same result about phase structure was also confirmed previously by the XRD analyzed. The remnant Bi in the final products was observed means it cannot be replaced completely in once TMC reaction and by a short reaction time [12–14]. However, it shows no influence on the resulting phase structure according to the XRD, implying that the remnant Bi totally incorporated into $Ba_{1-x}Ca_xTiO_3$ crystals lattice.

Fig. 5 summarizes the statistical EDS results of Ca and Ba element content in synthetic microcrystals versus the molar

Table 1
Atomic composition of platelike $Ba_{1-x}Ca_xTiO_3$ particles synthesized by TMC method.

Element	**Ba**	**Ca**	**Ti**	**O**	**Bi**	
a[a]						
Composition (atomic %)	15.32	1.68	17.52	63.99	1.49	$Ba_{0.9}Ca_{0.1}TiO_3$
Mean ratio	0.901	0.099	1	3.652	\	
b[a]						
Composition (atomic %)	15.62	4.22	20.21	57.71	2.24	$Ba_{0.8}Ca_{0.2}TiO_3$
Mean ratio	0.787	0.213	1	2.856	\	
c[a]						
Composition (atomic %)	14.97	4.91	20.08	57.92	2.13	$Ba_{0.75}Ca_{0.25}TiO_3$
Mean ratio	0.753	0.247	1	2.884	\	

[a] All elements composition measured by EDS was normalized and the results were the average of the measured particles.

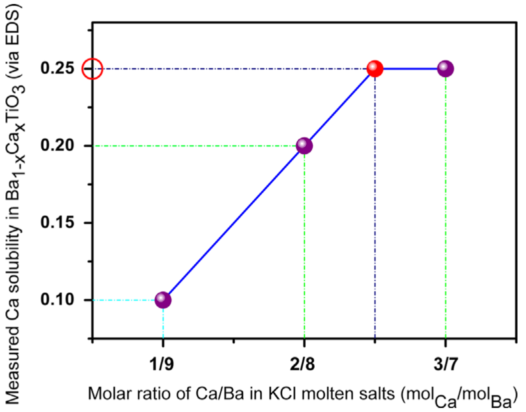

Fig. 5. Statistical result of the elemental composition of Ca and Ba in product particles as a function of the molar ratio of $CaCO_3$ to $BaCO_3$ in the KCl molten salt via EDS.

ratio of Ca^{2+} to Ba^{2+} in molten salt. It shows that both the elements Ca and Ba were detected simultaneously in every single microcrystals, the stoichiometric composition of Ca and Ba elements in synthetic microcrystals are consistent with which in molten salt when the molar ratio of Ca^{2+} to Ba^{2+} in molten salt is smaller than 25 mol%, while the molar ratio of Ca^{2+} to Ba^{2+} in molten salt is slightly larger than 25 mol% reached to 30 mol%, the Ca content in synthetic microcrystals is still 25 mol%. Suggesting the solid solution phase $Ba_{1-x}Ca_xTiO_3$ with $x > 0.25$ could not be formed, in spite of the designed molar ratio of Ca^{2+} to Ba^{2+} in molten salts was larger beyond the max solid solution of 25 mol% up to 30 mol%. The A-site elemental composition of the synthetic particles measured by EDS is consistent with the phase structure transformation showed by the XRD result.

4. Conclusions

A-site complex perovskite $Ba_{1-x}Ca_xTiO_3$ ($x \leq 0.25$) platelike particles with high aspect ratio and micron sizes were synthesized via a designed topochemical microcrystal conversion reaction between the platelet $Bi_4Ti_3O_{12}$ and the powdered $BaCO_3$–$CaCO_3$ mixture at 950 °C in KCl flux. It is concluded that the A-site elemental composition of the product particles was correspond linearly to the molar ratio of the Ca^{2+} and Ba^{2+} in molten salt when the molar ratio of Ca^{2+} to Ba^{2+} in molten salt is smaller than 25 mol%, while the molar ratio of Ca^{2+} to Ba^{2+} in molten salt is slightly larger than 25 mol% reached to 30 mol%, the Ca content in synthetic microcrystals reached the max solid solution which is 25 mol%. The morphology and size distribution of the synthetic $Ba_{1-x}Ca_xTiO_3$ particles was inherited from the precursor phase $Bi_4Ti_3O_{12}$. The average size of the resulting particles is about 6–8 μm and the thickness is less than 0.5 μm, the aspect ratio (edge length to thickness) of 8–10 is high. A-site complex perovskite $Ba_{1-x}Ca_xTiO_3$ microcrystals with high aspect ratio and micron sizes can serve as a suitable template and seeded crystal, which can be employed to produce highly textured ceramics by TGG/RTGG method and single crystal via SPC technique. The designed synthesis routine has potential to synthesize other A-site complex perovskite platelike particles with high aspect ratios and micron sizes, such as platelike $(Ba,Sr)TiO_3$, $(Sr,Pb)TiO_3$, $(Ba,Sr,Ca)TiO_3$.

Acknowledgments

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