



Combustion synthesis and bulk thermal expansion studies of Ba and Sr thorates

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Abstract

Nanocrystalline BaThO₃ and SrThO₃ powders have been prepared at a relatively low calcination temperature by a gel combustion technique using citric acid as a fuel and the nitrate as an oxidizer. These powders resulted in highly dense (sintered density > 90% of th.d.) pellets on sintering at 1923 K. The orthorhombic lattice parameters of BaThO₃ were found to be as $a = 0.635(1)$, $b = 0.6387(9)$ and $c = 0.8995(9)$ nm whereas SrThO₃ was monoclinic with $a = 0.6319(4)$, $b = 0.3240(1)$, $c = 0.4928(3)$ nm and $\beta = 117.38(5)^\circ$. It was observed that the average linear thermal expansion coefficients, $\bar{\alpha}$, for BaThO₃, SrThO₃ and ThO₂ are 11.09×10^{-6} , 10.49×10^{-6} and $9.10 \times 10^{-6} \text{ K}^{-1}$, respectively, which are about 21.9% and 15.3%, respectively, higher than that of pure ThO₂ between room temperature and 1123 K. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Thorium has attracted a considerable attention in the recent past as it is expected to play an important role in the third stage of the Indian nuclear power generation program [1]. Since Th itself is not a fissile material by thermal neutrons, it is proposed to use about 4–6% of fissile uranium and plutonium dioxides in a ThO₂ matrix. A large number of fission products are formed during the fission of uranium. It is desired to study the chemical state of these fission products. The probability of formation of oxides of fission products is much higher in the case of thorium based fuels as compared to that of uranium based because, unlike UO₂, the ThO₂ lattice cannot accommodate oxygen at interstitials due to its fixed oxidation state. The existence of various compounds formed by the interaction of oxides of some of these fission products with ThO₂ is not well documented. Recently, the Gibbs energy of formation of BaThO₃ was

measured by Bharadwaj et al. [2] in the temperature range 1275–1410°C using an automatic recording transpiration apparatus. They also investigated the thermal stability of BaThO₃ by the Knudsen effusion method [3]. In addition, it is also important to study their various thermophysical properties e.g., thermal expansion, thermal conductivity, etc. This study will be useful in predicting the mechanical integrity of the fuel pins.

BaThO₃ and SrThO₃ are reported [4,5] to be prepared by a conventional solid state route. Nakamura et al. [4] prepared BaThO₃ by repeated grinding and calcination of BaCO₃ and ThO₂ at about 1673 K. This type of solid state synthesis has several disadvantages like high calcination temperature, longer synthesis time and contamination from the grinding media. Recently, the combustion synthesis has been used successfully for the preparation of ultra-fine powders of a variety of oxide ceramics [6–8]. The utilization of exothermicity of a redox reaction between a fuel (e.g., citric acid, urea etc.) and an oxidizer (i.e., nitrates) is well known in such type of processes [9–11]. The powders obtained by this process are usually ultra-fine (crystallite size < 100 nm) with high surface area which is responsible for better sinterability [12]. The calcination temperature in a combustion synthesis is much lower than that in solid state synthesis.

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Since it is better to use pellets with high bulk density in dilatometric experiments, this route assumes further significance.

In this paper, we report on the synthesis of nanocrystalline powders of BaThO_3 and SrThO_3 by a gel combustion route. The effect of solution parameters, the sinterability of these powders and their bulk thermal expansion behavior were also investigated.

2. Experimental

2.1. Chemicals used

A.R. grade $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ (citric acid), $\text{Ba}(\text{NO}_3)_2$, SrCO_3 , HNO_3 and NH_4OH were used. $\text{Sr}(\text{NO}_3)_2$ was prepared by reacting SrCO_3 with a small volume of dilute HNO_3 . Nuclear grade thorium nitrate was obtained from Indian Rare Earths, Mumbai, India.

2.2. Gel and powder preparation

The aqueous solution of $\text{M}(\text{NO}_3)_2$ (where $\text{M} = \text{Ba}$ or Sr) and $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ were mixed in an equimolar ratio. The citric acid was added in these metal nitrate solutions so as to maintain the total metal ions to citric acid molar ratio at 1:1.5. The pH of citrate–nitrate solutions was adjusted at 5 by using dilute NH_4OH . The thermal dehydration of these pH adjusted citrate–nitrate solutions on a hot plate resulted in transparent viscous gels. Any phase separation or precipitation was not observed during the gel formation under these conditions. As soon as the gel was formed, temperature of the hot plate was raised to about 473 K. The gels then burnt over the surface with a low flame with evolution of large amounts of gases, yielding the blackish ashes termed here as precursors. These precursors were calcined at different temperatures to find out the lowest temperature for the formation of the desired phase.

2.3. Characterization methods

The XRD patterns were recorded for phase identification using monochromatic $\text{Cu-K}\alpha$ radiation on a Philips X-ray diffractometer, Model PW 1729. Since both the products (BaThO_3 and SrThO_3) are considerably hygroscopic, the XRD patterns were recorded immediately after the preparation. The powders were compacted using an uniaxial hydraulic press in the form of 12 mm diameter cylindrical pellets at a pressure of about 175 MPa and sintered at 1923 K for 90 min in static air. The sintered densities were determined by the Archimedes principle. The unit cell parameters were determined using a least-squares refinement program.

The bulk thermal expansion measurements were carried out from ambient temperature to 1123 K in air at

a heating rate of 5 K min^{-1} , using a fused quartz push rod dilatometer, Model LKB 3185. The samples were used in the form of sintered cylindrical pellets with diameter and height of about 12 and 10 mm, respectively.

3. Results and discussion

The gel formation by thermal dehydration of the citrate–nitrate solution without any precipitation or phase separation was found to be highly sensitive to the amount of citric acid used for gelation and pH of the solution. The total metal ions-to-citric acid molar ratio was fixed as 1:1 and 1:1.5 and the effect of pH on the gel formation was observed from the citrate–nitrate solution after evaporation of the excess solvent. The experimental observations can be summarized as follows: When a solution containing $\text{Th}(\text{NO}_3)_4$, $\text{M}(\text{NO}_3)_2$ ($\text{M} = \text{Ba}$ or Sr) and citric acid (i.e., solution without adjusting pH) was heated on a hot plate, immediately a white precipitate of thorium citrate was formed irrespective of the metal ion-to-citric acid molar ratio. This observation is in agreement with the literature [13]. At total metal ions-to-citric acid molar ratio as 1:1, a white precipitate was observed during gel formation irrespective of pH. Hence, these conditions were also not suitable for the gel formation. However, with total metal ions-to-citric acid molar ratio as 1:1.5, no precipitate was observed during the gel formation at $\text{pH} \approx 5$ –10.

These experimental observations indicate the importance of solution parameters in preventing the precipitation or phase separation during gel formation. The transparency of the gels is an indication of compositional homogeneity. A similar kind of effect of solution parameters was also observed in the synthesis of BaTiO_3 [14] and LiCoO_2 [15].

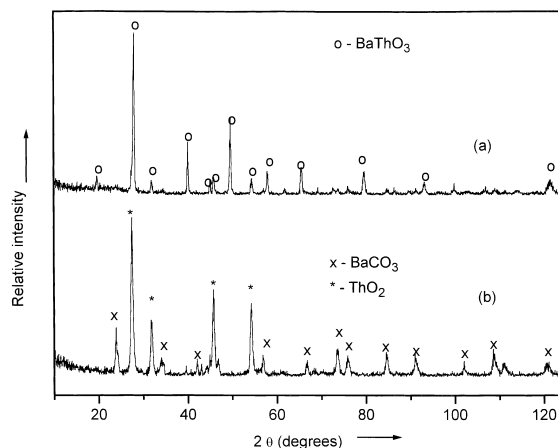


Fig. 1. XRD pattern of BaThO_3 precursor calcined at: (a) 1000°C for 90 min; (b) 900°C for 90 min.

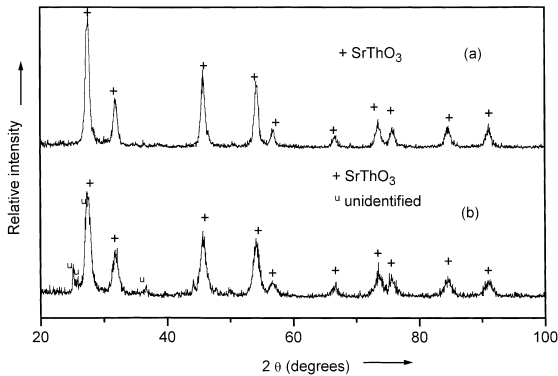


Fig. 2. XRD pattern of SrThO₃ precursor calcined at: (a) 900°C for 90 min; (b) 800°C for 90 min.

The XRD patterns of the calcined precursors of BaThO₃ and SrThO₃ are shown in Figs. 1 and 2, respectively. The prominent peaks of BaCO₃ were observed in the XRD pattern of the BaThO₃ precursor calcined at 1173 K for 90 min, which subsequently reacted, with ThO₂ at 1273 K for 90 min to give single-phase BaThO₃. Tsay and Fang [14] also observed BaCO₃ as an intermediate during calcination of the BaTiO₃ precursor. XRD patterns of the final product were refined to get the lattice parameters. BaThO₃ is reported in JCPDS data [16] to have a cubic unit cell with the dimension 0.449 nm. However, Nakamura [4] indexed its XRD pattern based on an orthorhombic unit cell with the lattice parameters 0.6345, 0.6376 and 0.8992 nm. We made attempts to refine the observed XRD data of BaThO₃ on both cubic and orthorhombic unit cells. The refinement of the cubic unit cell was not satisfactory whereas that of the orthorhombic lattice yielded the lattice parameters, 0.635(1), 0.6387(9) and 0.8995(9) nm which are in a close agreement with that reported by Nakamura [4].

The XRD pattern of the SrThO₃ precursor calcined at 1073 K for 90 min showed SrThO₃ peaks along with some unidentified peaks. However, all the peaks in the XRD pattern of the product obtained by calcining the precursor at 1173 K for 90 min matched well with that of SrThO₃. According to JCPDS data [17] the XRD pattern of SrThO₃ is fitted based on a pseudo-monoclinic unit cell with $a = b = c = 0.884$ nm and $\beta = 90^\circ$. This kind of unit cell is, though, difficult to comprehend but still we attempted to refine our observed d -spacings on a similar pseudo-monoclinic cell. It was found that a similar cell could not be used to index the observed XRD data. Hence, indexing of the observed data was done afresh which resulted in a very satisfactory fitting (Table 1) on a monoclinic unit cell with the following lattice parameters: $a = 0.6319(4)$, $b = 0.3240(1)$, $c = 0.4928(3)$ and $\beta = 117.38(5)^\circ$. Such a monoclinic unit cell for SrThO₃ is not difficult to rationalize as the tol-

erance factor of SrThO₃ is smaller than that of BaThO₃ which itself is orthorhombic. According to Nakamura [4] the orthorhombic unit cell of BaThO₃ was shown to consist of four monoclinic perovskite units. The cell volume of SrThO₃ is 0.0896 nm³, which is little less than the one-fourth of the orthorhombic unit cell volume of 0.36475 nm³ for BaThO₃. This slight difference in the unit cell volume per molecule could be due to the difference between ionic sizes of Ba²⁺ and Sr²⁺.

The crystallite size of the BaThO₃ and SrThO₃ samples was calculated from X-ray line broadening of the peaks $d_{200} = 0.3178$ nm and $d_{010} = 0.3243$ nm, respectively, using the Scherrer formula [18]. Silicon was used as a reference material for applying the correction due to instrumental broadening. The crystallite size was found to be about 35 and 25 nm for BaThO₃ and SrThO₃, respectively. Sintering at 1923 K for 90 min resulted in bulk densities of about 92% and 96% th.d. for BaThO₃ and SrThO₃, respectively.

A pure thoria pellet of about 10 mm diameter and 10 mm height with bulk density 96% th.d. was taken as a reference for dilatometric experiments. Its linear thermal expansion was measured up to 1123 K as a function of temperature. Its average linear thermal expansion coefficient, $\bar{\alpha}$, in this temperature range was found to be $9.10 \times 10^{-6} \text{ K}^{-1}$. The present data are in good agreement with those of literature [19]. Subsequently the thermal expansion behavior of BaThO₃ and SrThO₃ was investigated under similar conditions. The linear thermal expansion data for both the samples along with that of pure ThO₂ are represented in Fig. 3. The observed data (from 298 to 1123 K) could be fitted as per the following equations (T in K, $\Delta l = 0$ at 298 K).

ThO₂:

$$100 \cdot \Delta l / l_0 = 0.00063(T - 298) + 1.9053 \times 10^{-6}(T - 298)^2 - 3.9747 \times 10^{-9}(T - 298)^3 + 2.5070 \times 10^{-12}(T - 298)^4. \quad (1)$$

Table 1
Fitting of the XRD data of SrThO₃

| d_{obs} (nm) | d_{cal} (nm) | hkl |
|-----------------------|-----------------------|-------|
| 0.3243 | 0.3240 | 0 1 0 |
| 0.2870 | 0.2806 | 1 1 0 |
| 0.2188 | 0.2188 | 0 0 2 |
| 0.1982 | 0.1983 | 2 0 1 |
| 0.1692 | 0.1692 | 2 1 1 |
| 0.1619 | 0.1620 | 3 1 0 |
| 0.1463 | 0.1463 | 2 1 3 |
| 0.1403 | 0.1403 | 2 2 0 |
| 0.1287 | 0.1287 | 4 1 0 |
| 0.1255 | 0.1255 | 2 2 1 |
| 0.1149 | 0.1149 | 2 1 4 |
| 0.1080 | 0.1080 | 0 3 0 |

SrThO₃:

$$100 \cdot \Delta l/l_0 = 0.00066(T - 298) + 1.2810 \times 10^{-6}(T - 298)^2 - 1.1164 \times 10^{-9}(T - 298)^3 + 1.5808 \times 10^{-13}(T - 298)^4. \quad (2)$$

BaThO₃:

$$100 \cdot \Delta l/l_0 = 0.00071(T - 298) + 1.5877 \times 10^{-6}(T - 298)^2 - 2.4856 \times 10^{-9}(T - 298)^3 + 1.3884 \times 10^{-12}(T - 298)^4. \quad (3)$$

The coefficients of the average linear thermal expansion, $\bar{\alpha}$, of BaThO₃ and SrThO₃ are 11.09×10^{-6} and $10.49 \times 10^{-6} \text{ K}^{-1}$, respectively, between 298 and 1123 K. It can be seen that the $\bar{\alpha}$ values of BaThO₃ and SrThO₃ are about 21.9 and 15.3% higher than that of pure ThO₂ in the same temperature range. This observation can be rationalized taking into account the average linear thermal expansion coefficients of alkaline-earth oxides. There are no reports on thermal expansion studies of BaO and SrO by dilatometry probably due to their extreme sensitivity to moisture. However, Beals et al. [20] performed high temperature XRD studies on several MO oxides (M = Be, Mg, Ca and Sr). They reported the

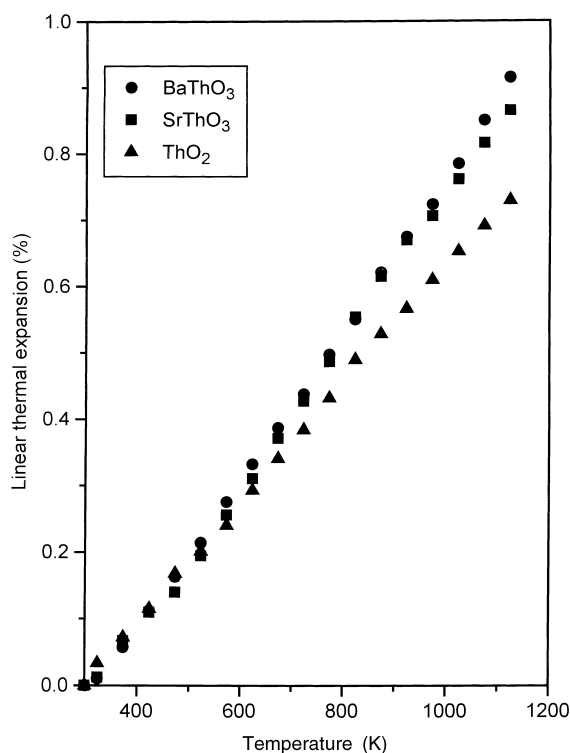


Fig. 3. Linear thermal expansion of BaThO₃, SrThO₃ and ThO₂ as a function of temperature.

average linear thermal expansion coefficient for SrO as $13.80 \times 10^{-6} \text{ K}^{-1}$ in the temperature range 298–1123 K. Another striking observation of their study is that the average linear thermal expansion coefficients increase on going from BeO to SrO. Though the thermal expansion data for BaO are not available but based on this trend, it is expected that the average linear thermal expansion coefficient of BaO must be higher than that of SrO. It appears from the present study that pseudo-binary compounds of ThO₂ with these alkaline-earth oxides have a thermal expansion behavior which is somewhat in-between that of pure ThO₂ and BaO or SrO. Both ThO₂ and BaO or SrO are cubic, though not isostructural, hence the observed difference of thermal expansion of MThO₃ (M = Ba²⁺, Sr²⁺) is not very surprising. In order to further ascertain this explanation, a few more MThO₃ (M = Mg²⁺, Ca²⁺) compounds are being prepared.

4. Conclusions

A simple chemical route for the preparation of nanocrystalline powders of BaThO₃ and SrThO₃ at a relatively low calcination temperature has been developed. The solution parameters like pH ≈ 5–10 of the citrate–nitrate solution and total metal ions-to-citric acid molar ratio 1:1.5 were found to be suitable for obtaining the gels without any precipitation or phase separation. This process seems to be promising for the synthesis of ThO₂ based multi-component oxide systems which otherwise need very high calcination temperatures for a prolonged duration. The bulk thermal expansion behavior of these two pseudo-binary oxides is considerably different from that of pure ThO₂. This difference should be considered while designing the fuel pin assembly even if the content of BaThO₃ and SrThO₃ is expected to be low.

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