

# Influence of reaction conditions on products of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ derived from hydrothermal process

S. Y. Wu · X. M. Chen · L. M. Chen

Received: 30 June 2005 / Accepted: 16 November 2005 / Published online: 20 November 2007  
© Springer Science + Business Media, LLC 2007

**Abstract**  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$  powders were prepared by a hydrothermal process, in which  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{BaCl}_2$ ,  $\text{Ba}(\text{OH})_2$  were used as Ba-precursors. The effect of Ba-precursor on the particle size, shape and structures was examined by XRD and SEM analyses. The influences of reaction time on reaction conversions for  $\text{Nb}_2\text{O}_5$  and particle size were discussed. The fill degree and the concentration of precursors affected the products morphology, and the particle size increased with increasing the fill degree.

**Keywords** Hydrothermal process · X-ray methods · Niobates · Microwave dielectric ceramics

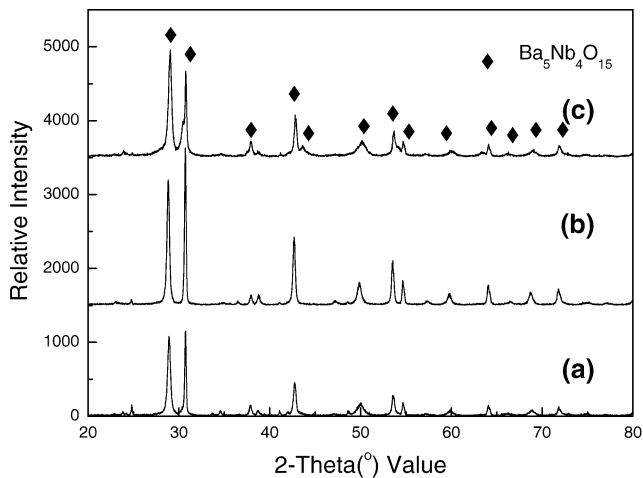
## 1 Introduction

Dielectric materials with dielectric constant greater than 20 and high quality factors ( $Qf > 2,000$  GHz) have attracted increasing interests in microwave applications. The hexagonal perovskite oxide  $\text{A}_5\text{B}_4\text{O}_{15}$  ( $\text{A} = \text{Ba}, \text{Sr}$ ;  $\text{B} = \text{Nb}, \text{Ta}$ ) system have been characterized at microwave frequencies. These materials combine a relatively high permittivity ( $39 < \epsilon_r < 46$ ) with a low dielectric loss ( $11583 \text{ GHz} < Qf < 31839 \text{ GHz}$ ) and small temperature coefficient of resonant frequency ( $-36 \text{ ppm}/^\circ\text{C} < \tau_f < 79 \text{ ppm}/^\circ\text{C}$ ) and they are expected as good candidates for microwave dielectric materials [1]. Among  $\text{A}_5\text{B}_4\text{O}_{15}$  ( $\text{A} = \text{Ba}, \text{Sr}$ ;  $\text{B} = \text{Nb}, \text{Ta}$ ) system,  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$  is the most attractive due to the low cost and good dielectric properties. The structure of  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$

has been well studied in the previous work [2–5]. It has the hexagonal structure in  $P3m1$  space group with one formula unit per cell ( $Z=1$ ). The compound has five-layer closet packing of oxygen and barium ions. The  $\text{Nb}^{5+}$  ions are positioned at the octahedral sites of five  $\text{AO}_3$  layers which altogether constitute the unit cell. Most of  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$  powders are prepared by the conventional solid reaction method in the previous reports [1–9]. Sreemoolanadhan et al. synthesized  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$  by blending stoichiometric amounts of  $\text{BaCO}_3$  and  $\text{Nb}_2\text{O}_5$  and heating at  $1250^\circ\text{C}$  for 4 h, while Srivastava et al. synthesized  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$  at  $1100^\circ\text{C}$  for 10 h and second phase was detected in the final product [8]. Chemically synthesized powders often possess fine, narrow particle size distributions and low aspect ratio particle morphologies, as well as good microstructural and chemical homogeneity. These properties tend to result in the improved sinterability as compared to conventional mixed oxide route powders. One particularly promising route is the hydrothermal process, in which the ceramic powders are synthesized from precursor chemicals in aqueous or part-aqueous solution at temperatures where the pressure is higher than the atmospheric pressure. This route has the advantage over some other chemical synthesis routes that relatively inexpensive salts (such as acetates or nitrates) can be used as metal ion precursors. Additionally, quite a number of compounds can be produced directly in the desired crystalline phase without requiring a calcinations step [10]. Zhao et al. has reported hydrothermal synthesis of  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$  ceramics with a Ba/Nb mole ratio 2/1 [11]. We have found a new hydrothermal approach and improved the Ba/Nb mole ratio to 3/2, the reaction conversion values for  $\text{Nb}_2\text{O}_5$  have been improved to 99% [12].

So far, there have been no report of influence of reaction conditions on hydrothermal synthesis of  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$  powders, such as Ba-precursors, fill degree, synthesis time and

S. Y. Wu · X. M. Chen (✉) · L. M. Chen  
Department of Materials Science and Engineering,  
Zhejiang University,  
Hangzhou 310027, People's Republic of China  
e-mail: xmchen@cmsce.zju.edu.cn



**Fig. 1** XRD spectra of  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$  synthesized from different Ba-precursors: (a)  $\text{BaCl}_2$ ; (b)  $\text{Ba}(\text{NO}_3)_2$ ; (c)  $\text{Ba}(\text{OH})_2$  at  $230^\circ\text{C}$  for 5 h

precursors concentration on the particle size and morphology of  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$  ceramics. In the present work, the above various effects on the synthesis of  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$  particles are examined.

## 2 Experiment procedures

Analysis grade barium salt and 4 N niobium oxide were adopted as the raw materials. Hydrothermal synthesis of  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$  powders was carried out in a  $200\text{ cm}^3$  stainless

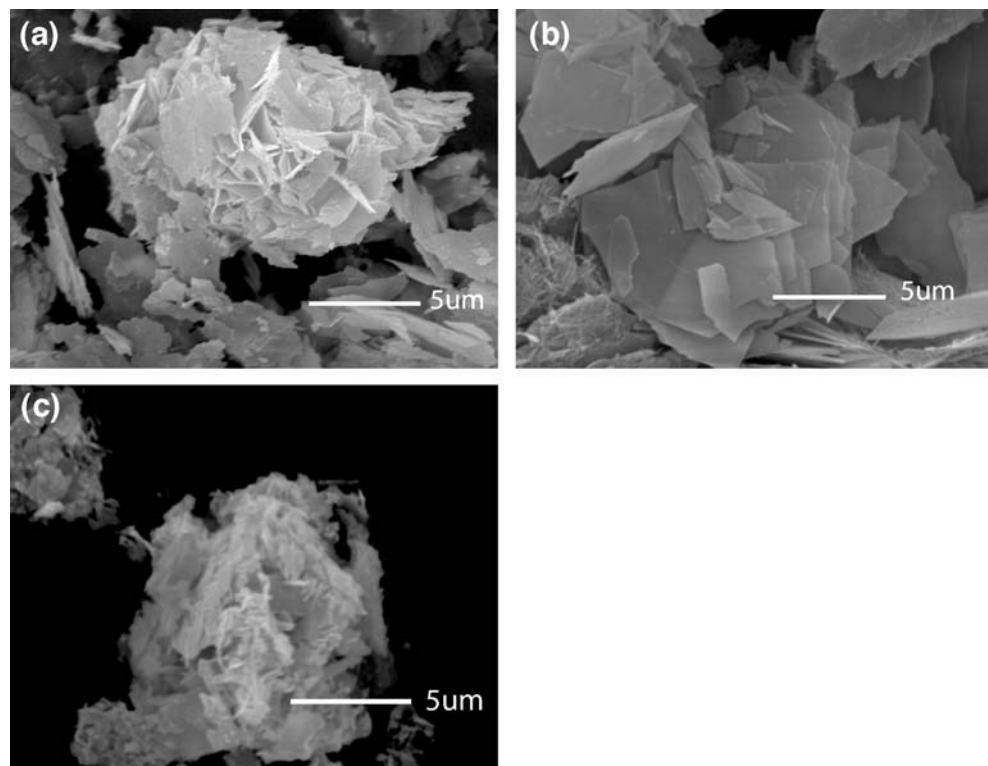
autoclave with a Teflon line under autogenous pressure. First, the niobium oxides were dissolved in hot hydrofluoric acid, and the mixture was heated at  $80^\circ\text{C}$  inside a ventilator to remove the residuary HF. Then, the niobium oxide solution was mixed to the barium salt which was dissolved in distilled water. After that, sodium hydroxide was vigorously added to the mother solutions until the pH value attained the desired value. Then, resultant suspension was transferred to the autoclave and heated at 200 to  $250^\circ\text{C}$  for 6 h, where the filling factor was 80 vol.%. After cooling, the product was filtered and washed with distilled water until the pH was between 7 and 8. Finally, the product was poached ultrasonically with distilled water and dried at  $80^\circ\text{C}$  in an oven.

The XRD analysis using  $\text{CuK}\alpha$  radiation (Rigaku D/MAX2550PC) was conducted to determine the crystal structure. The microstructures and morphology of the product powders were examined using a scanning electron microscope (XL-30-ESEM) with a field gun where an accelerating voltage of 20 kV was used.

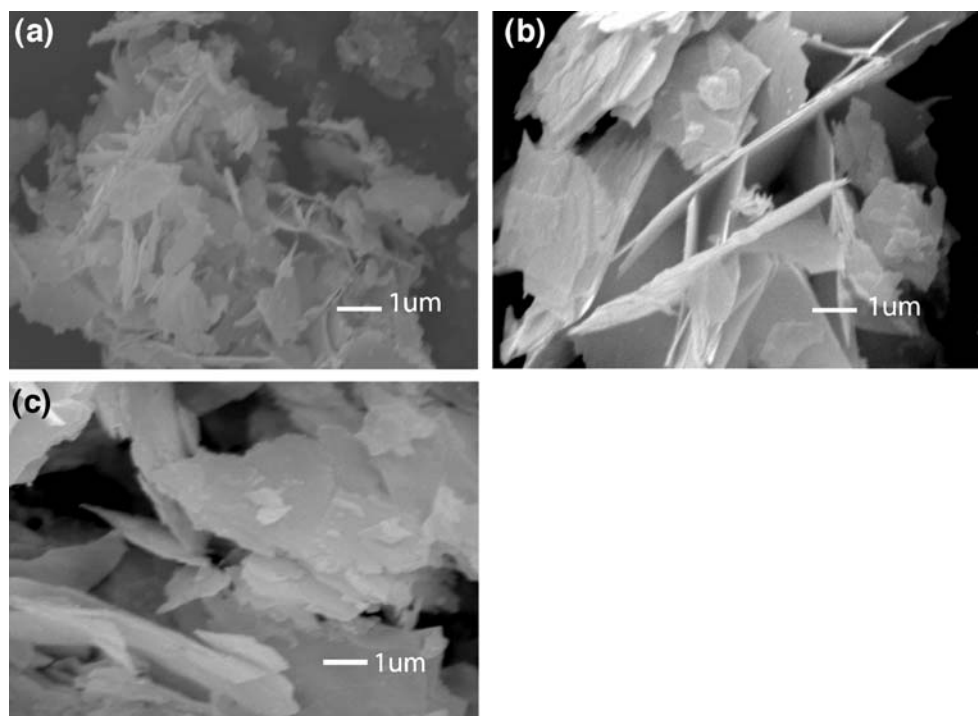
## 3 Results and discussion

$\text{Ba}_5\text{Nb}_4\text{O}_{15}$  fine particles were prepared by hydrothermal synthesis with an autoclave using various Ba precursors. The synthesis was performed at  $230^\circ\text{C}$ , for 6 h, with a pH value of 12. Figure 1 shows the XRD spectra of  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$

**Fig. 2** SEM micrographs of  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$  synthesized from different Ba-precursors: (a)  $\text{BaCl}_2$ ; (b)  $\text{Ba}(\text{NO}_3)_2$ ; (c)  $\text{Ba}(\text{OH})_2$  at  $230^\circ\text{C}$  for 5 h



**Fig. 3** SEM micrographs of  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$  synthesized at  $230^\circ\text{C}$  with  $\text{pH}=12$  and fill degree of 75% for (a) 2 h; (b) 4 h; (c) 6 h



ceramic converted from  $\text{Nb}_2\text{O}_5$  with  $\text{Ba}(\text{OH})_2$ ,  $\text{BaCl}_2$ ,  $\text{Ba}(\text{NO}_3)_2$ . Only  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$  is detected in the product, this indicates that  $\text{Nb}_2\text{O}_5$  has been consumed completely in all reactions.

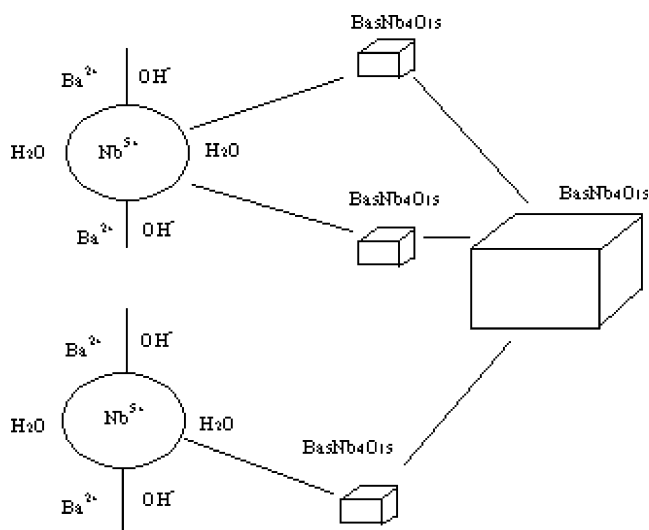
Figure 2 shows the SEM photographs of the products synthesized from different Ba-precursors. The products are all plate-like particles of  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ . The particle size of  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$  from  $\text{Ba}(\text{NO}_3)_2$  is the largest, while that of  $\text{Ba}(\text{OH})_2$  is the smallest. The particle size of the former is all most 100 times larger than the later. These results demonstrate that  $\text{Cl}^-$ ,  $\text{NO}_3^-$  anions can facilitate the formation of larger crystals of  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$  under hydrothermal conditions. This shows that the type of precursor has a strong influence on the size of  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ , suggesting that they have different reaction mechanisms. The  $\text{Ba}(\text{OH})_2$  has a better solubility in water than  $\text{BaCl}_2$  and  $\text{Ba}(\text{NO}_3)_2$ , when  $\text{Ba}^{2+}$  meet  $\text{Nb}^{5+}$  in the reaction species, a lot of  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$  crystal nucleus produced, so it has a small particle size. Some authors reported that the reaction rate is possibly dependent on the particle size [13], but we did not have enough proof to demonstrate it.

Figure 3 shows the morphology of  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$  prepared through  $\text{BaCl}_2$  as Ba-precursor at  $230^\circ\text{C}$ , with  $\text{pH}=12$  and the reaction time of 2, 4, and 6 h, respectively. SEM micrographs indicate no obvious difference in the morphology. The particle size becomes larger by extending the processing time from 2 h to 4 h, but there is no apparent difference between 4 h and 6 h.

When the reaction time is 2 h, the reaction conversion for  $\text{Nb}_2\text{O}_5$  is 99% and almost the same as that of 4 h. There are two crystal growth mechanisms in hydrothermal

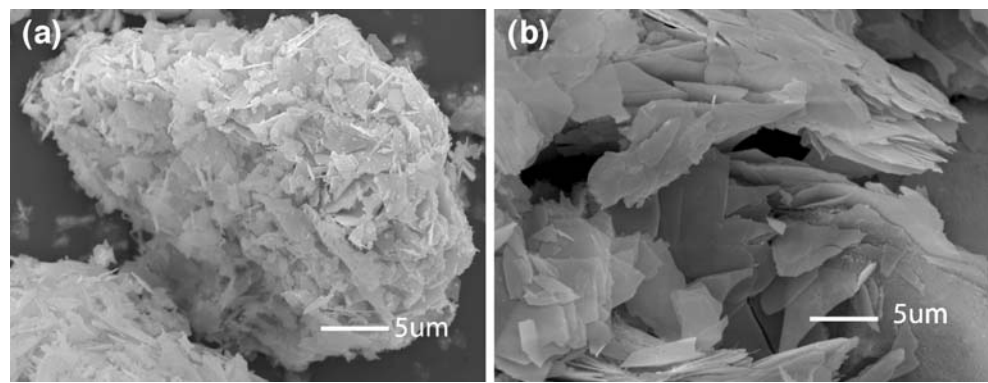
synthesis: (i) in-situ transformation and (ii) dissolution–precipitation transformation models. In the first model, the crystal size and reaction conversion increase with prolonging the reaction time. In the second mechanisms, as show in Fig. 4, the precursors react each other by homogeneous nucleation or heterogeneous nucleation, producing small crystals, then the small crystals congregate together, become a large crystal. Thus, the particle morphologies support a dissolution–precipitation mechanism in this reaction system.

One of the most noticeable advantages of hydrothermal crystallization is the use of the autogenous pressure in the



**Fig. 4** Schematic sketch of dissolution-precipitation

**Fig. 5** SEM micrographs of  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$  synthesized from  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  at  $230^\circ\text{C}$  for 6 h with  $\text{pH}=12$  and different fill degree: (a) 50%; (b) 75%

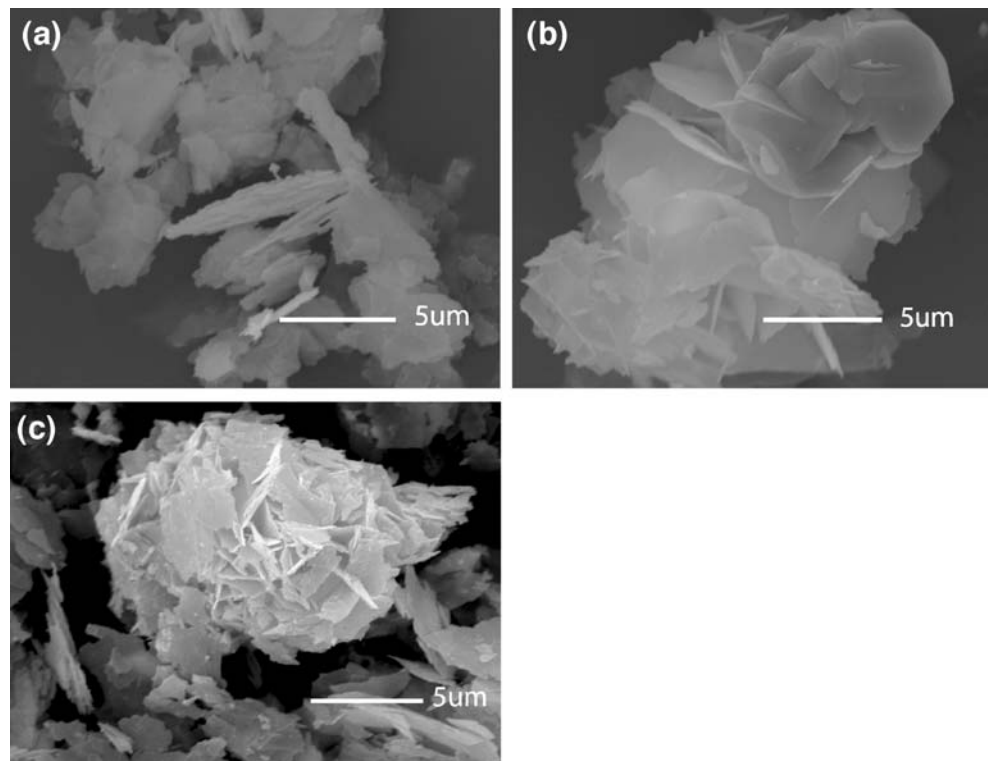


sealed reaction vessel to promote the nucleation and growth of the required product. A higher fill degree increases the pressure of the reaction system sharply, and facilitates the generation of larger size  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ . Figure 5 elucidates the effects of fill degrees on the morphology of the product. The ceramic particle size with 75% fill degree is far larger than that is 50%. This is because the transformation velocity of the material is speeded up with the increase of pressure and is propitious to the crystal growth.

SEM micrographs of the products with different precursor concentration are shown in Fig. 6. With increasing of the precursors concentration, the particle size increases first, then decreases. The size distribution of the particles that grow from solution generally depends on the rates of nuclei formation and crystallite growth. Crystal agglomeration can also contribute substantially to the overall particle growth process. The driving force of the reaction is provided by the

supersaturation. The supersaturation can be defined as the ratio between the product of the current concentration of the relevant aqueous species and the solubility product of  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ . The relative importance of nucleation and growth is determined by the supersaturation of the solution. In turn, supersaturation is very sensitive to the temperature, concentration, and mixing conditions [12]. It is well-known that a variation of supersaturation can induce a modification of crystal habit, because the growth rate of different surfaces can be differently influenced by concentration. When the precursors concentration is in a low range, increasing the concentration can increase the number of the reaction ions in the system, so the number of crystal nucleus increases during initial nucleation period. The probability of the ions action with the crystal nucleus is also increased, so the particle size is increased with increasing the precursors concentration in low concentra-

**Fig. 6** SEM spectra of  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$  synthesized at  $\text{pH}=12$   $230^\circ\text{C}$ , 6 h with different precursors concentration  
(a)  $\text{BaCl}_2$ :0.01 mol,  $\text{Nb}_2\text{O}_5$ :0.00337 mol  
(b)  $\text{BaCl}_2$ :0.02 mol,  $\text{Nb}_2\text{O}_5$ :0.00667 mol  
(c)  $\text{BaCl}_2$ :0.03 mol,  $\text{Nb}_2\text{O}_5$ :0.01 mol



**Table 1** Summary of effects of reaction conditions upon particle size.

Reaction condition	Particle size
Reaction time	Increases with increasing reaction time
Fill degree	Increases with increasing fill degree
Precursors concentration	Increases first then decreases with increasing precursors concentration

tion range. But when the precursors concentration reaches a certain value, there are too many crystal nucleus in initial nucleation period, and the raw material attribute to every nuclear is decreased, and subsequently the crystal size is decreased when the precursors in high concentration. Besides, high concentration of precursors increases the viscosity of solution and restrains the material transfer in the solution and also restricts the crystal growth. The effects of reaction conditions on the particle size are summarized in Table 1.

#### 4 Conclusions

Ba<sub>5</sub>Nb<sub>4</sub>O<sub>15</sub> fine particles were prepared by a hydrothermal approach using different Ba-precursors. The reaction could be completed in 2 h, and dissolution-precipitation might be the dominant mechanism through out the Ba<sub>5</sub>Nb<sub>4</sub>O<sub>15</sub> synthesis. The powders synthesized from Ba(NO<sub>3</sub>)<sub>2</sub> have the largest particle size, and that for Ba(OH)<sub>2</sub> is the smallest. With increasing pressure, the transformation velocity of the material is speeded up, which is propitious

to the crystal growth. The particle size is sensitive to the reaction conditions, and it increases with increasing the reaction time and the fill degree. With increasing the precursors concentration, the particle size increases first, and then decreases.

**Acknowledgements** The present work was partially supported by Chinese National Key Project for Fundamental Researches under grant No.2002CB613302, National Science Foundation of China under grant numbers 50332030 and 50025205.

#### References

1. I.N. Jawahar, P. Mohanan, M.T. Sebastian, *Mater. Lett.* **57**, 4043 (2003)
2. J. Shannon, L. Katz, *Acta Crystallogr.* **B26**, 102 (1970)
3. F. Galasso, L. Katz, *Acta Crystallogr.* **14**, 647 (1961)
4. R.S. Roth, J.L. Waring, *J. Res. Natl. Bur. Stand. A. Phy. Chem.* **65A**, 337 (1961)
5. C. Vineis, P.K. davies, T. Negas, S. Bell, *Mater. Res. Bull.* **31**, 431 (1996)
6. I. Maclaren, C.B. Ponton, *J. Mater. Sci.* **33**, 17 (1998)
7. H. Sreemoolanadhan, M.T. Sebastian, *Mater. Res. Bull.* **30**, 653 (1995)
8. A.M. Srivastava, J.F. Ackerman, W.W. Beers, *J. Solid State Chem.* **134**, 187 (1997)
9. T.A. Vanderah, T.R. Collins, W. Wong-Ng, R.S. Roth, L. Farber, *J. Alloys Compd.* **346**, 116 (2002)
10. I. Maclaren, S. Wannakukorale, C.B. Ponton, *J. Mater. Chem.* **9**, 2663 (1999)
11. H. Zhao, S.H. Feng, *J. Mater. Chem.* **10**, 965 (2000)
12. S.Y. Wu, X.M. Chen, H.Y. Yu, *J. Eur. Ceram. Soc.*, **26**, 1973 (2006)
13. A. Testino, M.T. Buscaglia, V. Buscaglia, M. Viviani, C. Bottino, P. Nanni, *Chem. Mater.* **10**, 1536 (2004)