J Electroceram (2008) 21:805–809
DOI 10.1007/s10832-007-9301-5

Glycothermal synthesis of α-Al_2O_3 in 1,4-Butadional organic solvent

K. X. Song · S. Y. Wu · X. M. Chen · N. Qin

Abstract α-Al_2O_3 powders with different grain sizes and morphologies have been synthesized in the system of Al - 1, 4-butadional by glycothermal treatment. The effects of reaction temperature, and reaction time on synthesis of α-Al_2O_3 powders have been investigated. After the glycothermal treatment, the morphologies of α-Al_2O_3 powders are mainly hexagonal platelets, hexagonal prism, and icohedron. The crystal habits of α-Al_2O_3 powders have been also discussed.

Keywords α-Al_2O_3 · Glycothermal synthesis · 1,4-butadional · Growth habits

1 Introduction

Alumina is an important raw-material in ceramic material industries, which is widely used as insulator material, microelectronic substrate, structural material, and catalyst supports [1–3]. At present, the major methods of alumina production are the Bayer process and thermal decomposition. However, in these methods, well-dispersed α-alumina powders are hardly obtained because calcination of powders obtained by these methods is needed in order to yield α-Al_2O_3 powders at temperatures above 1100°C, where the powders agglomerate seriously. At the same time, the range of size distribution of the powders is as large as from several to several hundreds of nano-meters [4].

Recently, hydrothermal methods, is acknowledged as a promising way to obtain high quality electroceramic powders. If reaction conditions such as pH of solution, solute concentration, reaction temperature, reaction time, solute concentration, types of solvent are exactly arranged, ceramic powders with desired shape and size can be produced. So far, the thermodynamic phase equilibria for α-Al_2O_3 have been established in water [5, 6]. But the experiments are usually performed at high pressures with mixtures of solvent (water, alkaline solution, or HCl solution) and aluminum hydroxide in close pressure vessels, which need endure the pressure above 20 MPa at temperature above about 415°C. So, the supercritical temperature and high pressure make the research difficult [7–9]. In the studies by Inoue and Cho, gibbsite was suspended in 1,4-butanediol and set in an autoclave, and the mixture was heated to 300°C under the autogenous pressure (about 4 MPa) to yield α-Al_2O_3 [10, 11].

In the present paper, α-Al_2O_3 with various morphological forms and different particle size distribution is prepared in the 1,4-butanediol. The synthesis conditions are investigated together with the grain growth habits.

2 Experimental

The process to prepare α-Al_2O_3 by glycothermal treatment in 1,4-butanediol solutions is schematically illustrated in Fig. 1. All chemicals were reagent grade, and 1,4-butanediol(AR) should be subject to vacuumized distillation. Aluminum hydroxide precursors were precipitated from 2 M/l $Al(NO_3)_3$•9 H_2O(CP) solutions by slowly adding KOH(CP) with the rapid magnetic force stirring, and the pH of solutions was adjusted to 10.5. The precipitated precursors were washed by repeated cycles of

---

K. X. Song · S. Y. Wu · X. M. Chen (✉) · N. Qin
Department of Materials Science & Engineering,
Zhejiang University,
Hangzhou 310027, China
e-mail: xmchen@cmsce.zju.edu.cn

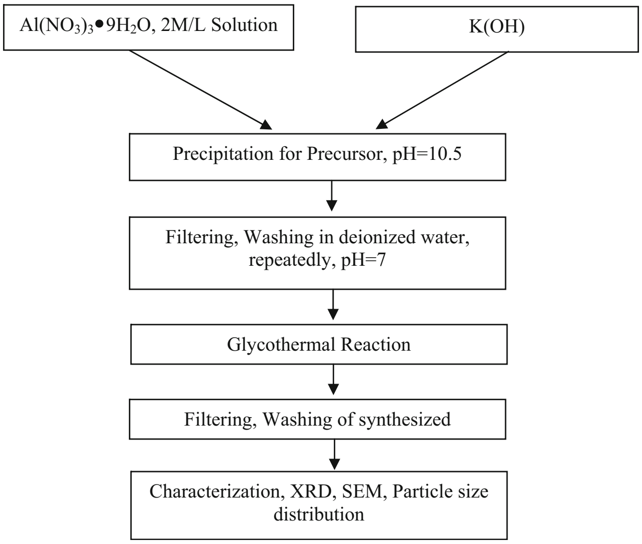


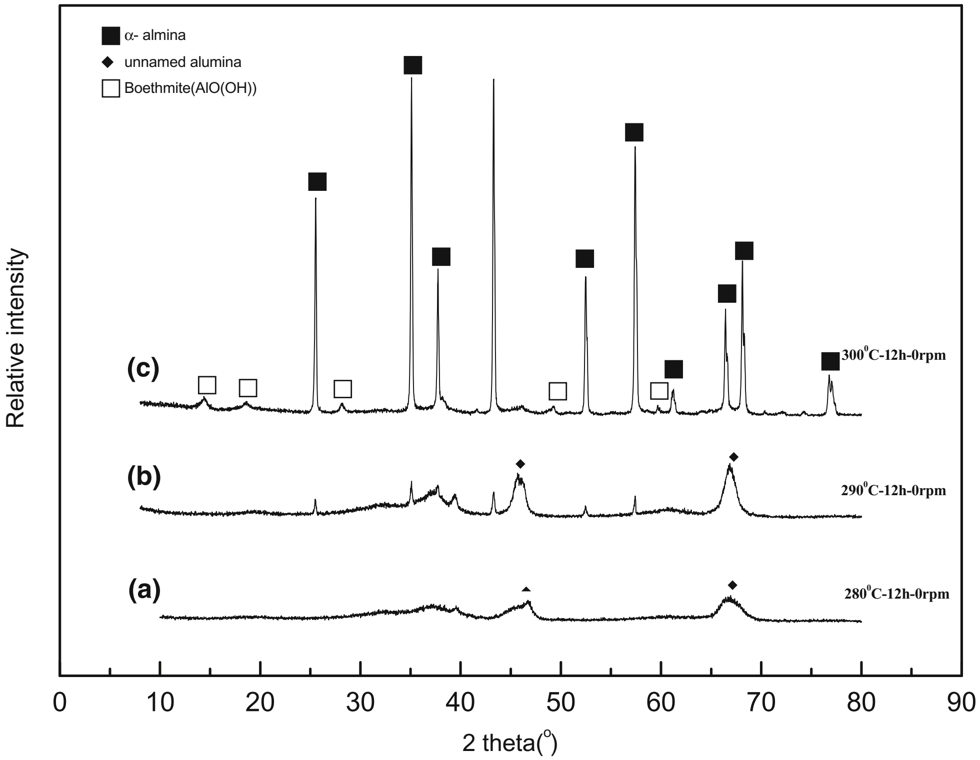
Fig. 1 Schematic pattern of procedure of glycothermal treatment

filtration in deionized water until pH=7. The wet precursors were redispersed in 200 ml 1,4-butanediol for 12 h under vigorous stirring. The resulted suspension was placed into a 350 ml stainless pressure vessel equipped with a magnctically stirred head. Before the vessel was heated the desired temperature at a rate of 2°C /min, the atmosphere inside the vessel was vacuumized, then filled with nitrogen to 4 MPa. After glycothermal treatment, the vessel was cooled to about 60°C. The residual pressure of the vessel was relieved via a pressure release valve. The solid-reaction products were filtrated, then dispersed in the ethanol, and the cycles were repeated many times. Whereafter, the obtained powders were dried at 80°C in the desiccator for 2 days. The dried powders were grinded in the agate, then the phase composition was evaluated using X-ray diffraction. The morphology of the synthesized particles was observed using scanning electron microscopy.

3 Results and discussion

As shown in Fig. 2, the reaction temperature is a significant parameter for α-Al_2O_3 formation. The products synthesized at the temperature of 280 and 290°C are calcined at the temperature of 500°C for 30 min in order to eliminate the boethmite, as we know aluminum oxide transfers to γ-Al_2O_3 at 500–600°C, and to α-Al_2O_3 until 1000–1200°C. XRD pattern in Fig. 2(a) shows some unknown phase after the reaction at 280°C. When the temperature increases to 290°C, α-Al_2O_3 grains begin to form [Fig. 2(b)], which illuminates that the transformation from boehimite to α-Al_2O_3 occurs at the temperature of 290°C. The processes of reaction from the precursor to α-Al_2O_3 are almost completed with a little remaining boehmite (AlO(OH)) at 300°C [Fig. 2(c)]. The nearly monodispersed α-Al_2O_3 grains with morphology of hexag-

Fig. 2 X-ray diffraction patterns of the α-Al_2O_3 powders synthesized as a function of reaction temperature by glycothermal treatment in 1,4-butadinol: (**a**) 280°C reaction time=12 hour, stirring speed=0 rpm; (**b**) 290°C reaction time=12 hour, stirring speed=0 rpm; (**c**) 300°C, reaction time=12 hour, stirring speed=0 rpm



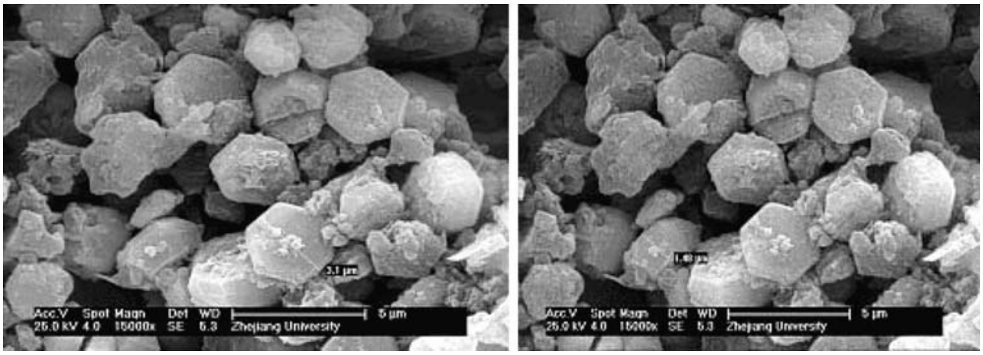


Fig. 3 SEM photomicrographs of the α-Al_2O_3 powers synthesized by glycothermal treatment in 1,4-butadinol at 300°C,reaction time=12 hour, stirring speed=0 rmp

onal platy and icosahedron are obtained with the intact crystal form and uniform particle size distribution (Fig. 3). According to Innoue [10], the precursor firstly reacted with 1,4-butanediol to get the ethylene glycol derivatives of boehmite with a unique honeycomb-like texture, and this boehmite phase was believed to be the intermediate phase for the formation of α-Al_2O_3. The authors further consider that the process of reaction from the precursor to α-Al_2O_3 is firstly to get the ethylene glycol derivatives of boehmite, and then the ethylene glycol derivatives of boehmite directly transform to α-Al_2O_3 at 290°C.

The reaction time plays an important role in the phase transformations from the precursor to α-Al_2O_3 and influences growth habits and morphology of α-Al_2O_3. Fig. 4 shows the XRD patterns of the products, after reaction by glycothermal method, α-Al_2O_3 is observed as the major phase combined with minor amount of boethmite (AlO(OH)). With increasing reaction time, contents of boethmite (AlO(OH)) decreases. When the reaction time reach 18 h, boethmite(AlO(OH)) almost disappears. As shown in Fig. 5, the grain morphologies and grain sizes vary significantly with reaction time. For a reaction time of 6 h, the α-Al_2O_3 grains take on the morphologies of hexagonal platelets and icosahedron. The transverse axis of the icosahedron grains is ~7 μm, the ordinate axis is ~5 μm, and the aspect ratio of transverse axis and to ordinate axis is 0.71. With increasing the reaction time to 12 h, the morphologies of α-Al_2O_3 grains become hexagonal platelets and hexagonal prism, and both the transverse and ordinate axises are ~7 μm for the hexagonal prism. For a prolonged reaction time of 18 h, the excessively growth icosahedron α-Al_2O_3 grains are ob-

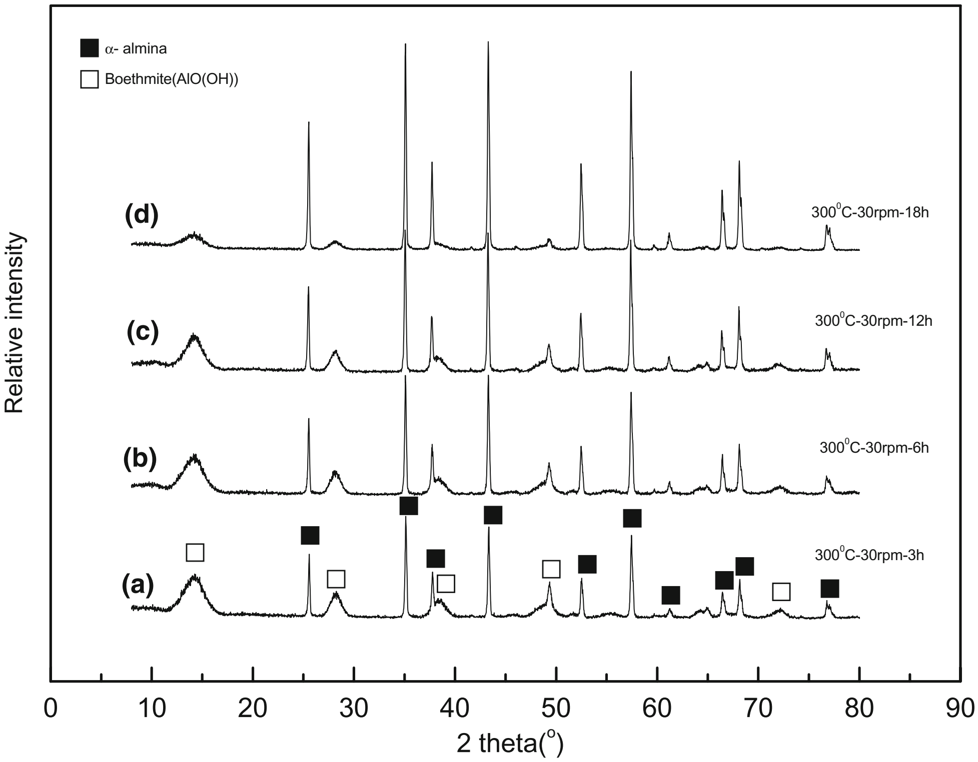


Fig. 4 X-ray diffraction patterns of theα-Al_2O_3 powders synthesized by glycothermal treatment in 1,4-butadinol (300°C, 30 rpm) as s function of reaction time: (**a**) 3 h, (**b**) 6 h, (**c**) 12 h, (**d**) 18 h

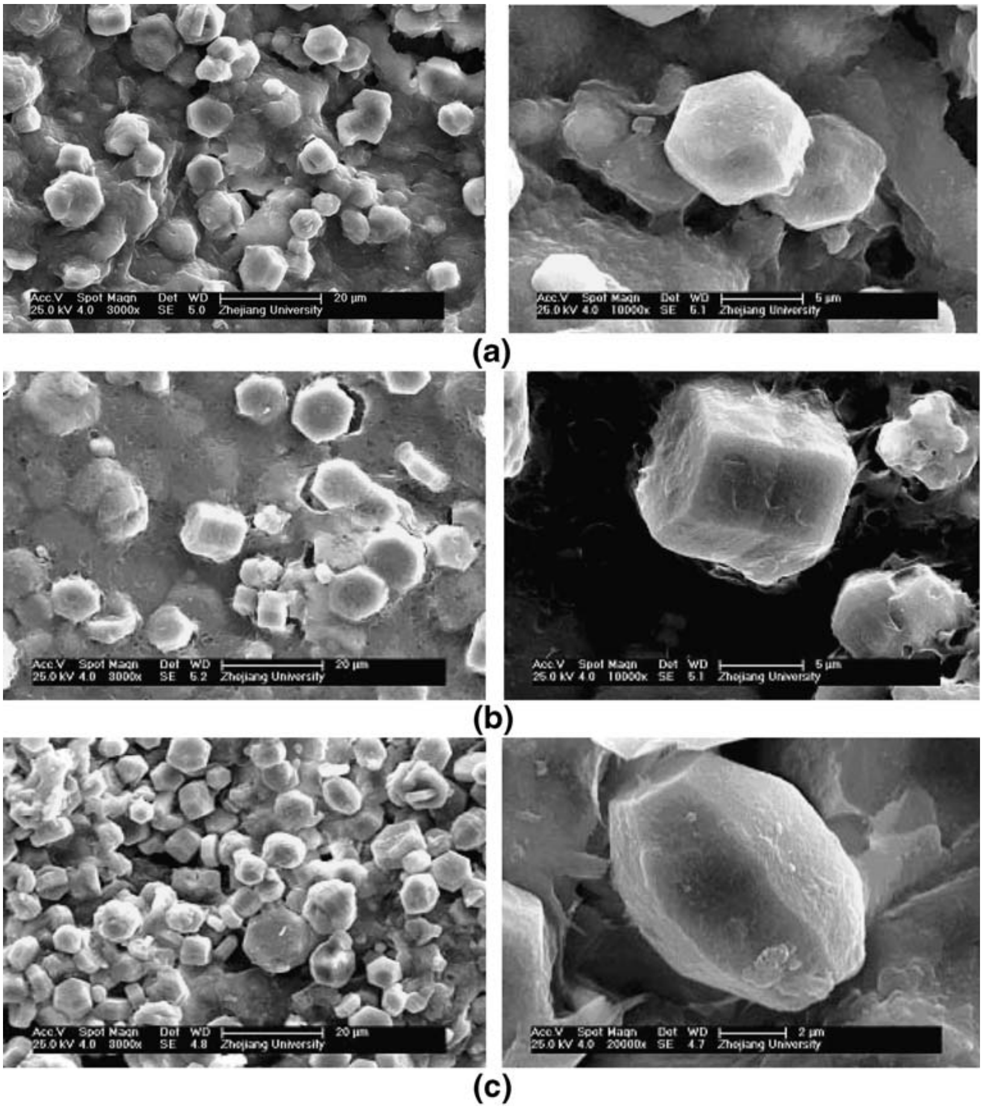


Fig. 5 SEM micrographs of the powders synthesized by glycothermal treatment in 1,4-butadinol (300°C, 30 rpm) as a function of reaction time: (**a**) 6 h, (**b**) 12 h, (**c**) 18 h

served together with hexagonal platelet and prism grains. In this case, the transverse axis for the icosahedron grain is ~7 μm, and its ordinate axis is ~8.21 μm.

As shown in Figs. 3 and 5, the morphologies of α-Al_2O_3 grains synthesized in the 1,4-butanediol show hexagonal platelets, hexagonal prism, and icosahedron, which are common shapes of corundum in the nature. The equilibrium shapes are depicted in Fig. 6. The formation of a specific grain shape is a complex process requiring a fundamental understanding of the interaction between solid-state chemistry, interfacial reactions and kinetics, and solution (or vapor) chemistry [11]. Classcial theories to control grain morphology are based primarily upon the packing of the crystallographic unit cell to control grain shapes. On the basis of these theories, some qualitative observations are investigated regarding the formation of particle with different shape in the system of Al- 1, 4-butanedinol.

In the present work, hexagonal platelets are the most common shape observed by SEM photomicrographs, and they are consistent with the unit cell and space group of α-Al_2O_3, which belongs to the trigonal crystal system, in the space group of $D_6^{3d} - R\bar{3}c$. The crystal lattice constants are a_0=47.7 nm, and c_0=130.4 nm. The corundum structure is an approximate h.c.p. array of O atoms in which Al^{3+} ions occupy two thirds of the octahedral holes, and the coordination number of O is 4. The $[AlO_6]$ octahedrons may constitute a layer by sharing edge, which is perpendicular to threefold axis, at the direction parallel to threefold axis, the hexagonal platelet (prism) is formed by the interval arrangement between two kinds of octahedrons: $[AlO_6]$ octahedrons which are stacked by sharing-facet and octahedrons which are surrounded by O^{2-}, and three fold axis is formed by linkage of $[AlO_6]$ octahedrons along *c*-axis [12]. The predominance of the {0001} basal plane of the grain shown in Fig. 6 indicates that growth of {0001} is inhibited in this crystallographic direction relative to the rate of growth in other predominant direction such as $\{11\bar{2}3\}$. It is reported that, in the different solvent, {0001}

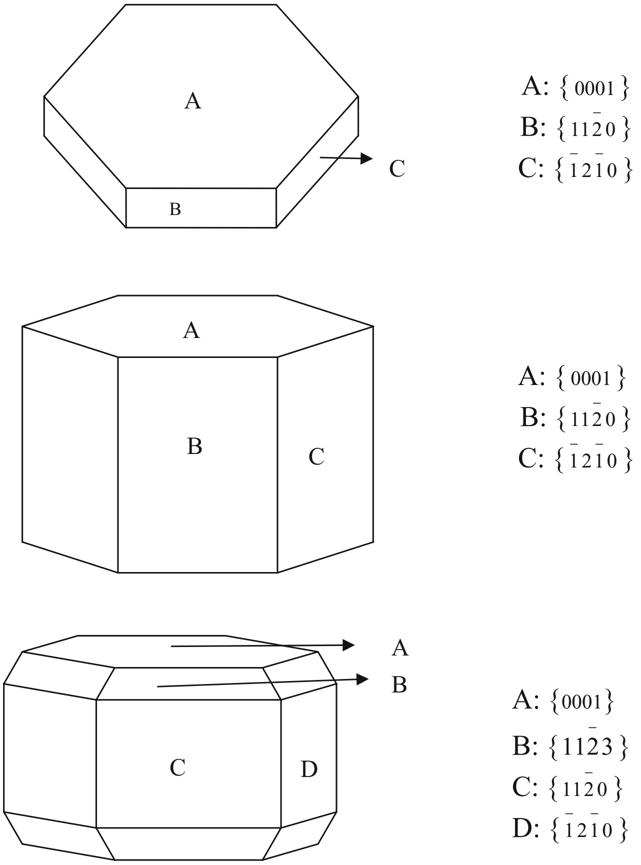


Fig. 6 The schematic patterns of growth shape of α-Al_2O_3 with facet indexes

of the facets is showed up as feature of shape. According to Bravais rules, PBC theories, and Pauling cryatal chemistry rules, with a view to the relation between the stacking direction of crystal growth unit and crystal morphologies, the more faster the crystal facet grows, the more quickly this crystal facet disappears. In other words, the more slowly the crystal facet grows, the easier this crystal facet shows up. The orders of growth rate of α-Al_2O_3 facets are $\{0001\} < \{11\bar{2}3\} = \{11\overline{23}\} < \{11\bar{2}0\}$. The growth rate of the facet {0001} grows the slowest, so that the facet {0001} is the feature shape of α-Al_2O_3 to show up. The crystal particles grow in layer by linkage of $[AlO_6]$ octahedrons along *c*-axis, based on the facet of {0001}. So, with the increase of time, crystal particles grow larger along the *c*-axis.

4 Conclusion

α-Al_2O_3 powders with different size and morphologies have been synthesized by glycothermal method. When temperature increases from 290 to 300°C, α-Al_2O_3 grains begin to form at 290°C, and the phase transformation from the precursor to α-Al_2O_3 has completed at 300°C. During the process of reaction, boethmite is considered as an intermediate phase for the formation of α-Al_2O_3, and then directly forms α-Al_2O_3 at 290°C. With prolonging time, the transformation from boethmite to α-Al_2O_3 takes place completely. The facet {0001} is the feature shape of α-Al_2O_3 to show up. The orders of growth rate of α-Al_2O_3 various facets are $\{0001\} < \{11\bar{2}3\} = \{11\overline{23}\} < \{11\bar{2}0\}$. When the reaction time prolongs, the α-Al_2O_3 crystal grains grow in layer by linkage of $[AlO_6]$ octahedrons along *c*-axis, based on the facet {0001}.

Acknowledgements The present work was partially supported by the National Science Foundation of China (Grant no. 50332030), and Chinese National Key Project for Fundamental Researches (Grant no. 2002CB613302). The authors would like to thank Professor Richard E. Riman, Department of Ceramic and Materials Engineering, Rutgers University, USA, for his valuable advices.

References

1. C.P. Dogan, J.A. Hawk, Wear **225–229**, 1050 (1999)
2. J. Molla, R. Moreno, A. Ibrra, J. Appl. Phys., **80**(2), 1028 (1996)
3. N.M. Alford, S.J. Penn, J. Appl. Phys., **80**(10), 5895 (1996)
4. T. Takamori, L.D. David, Am. Ceram. Soc. Bull., **65**(9), 282 (1986)
5. R.A. Laudise, A.A. Ballman, J. Am. Chem. Soc., **80**, 2655 (1958)
6. G.C. Kennedy, Am. J. Sci., **257**, 563 (1959)
7. D.F. Weirauch, R. Kung, J. Cryst. Growth, **19**,139 (1972)
8. A.W. Laubergayer, R.S. Weitz, J. Am. Chem. Soc., **65**, 247 (1943)
9. W.J. Li, E.W. Shi, Z.W. Yin, J. Cryst. Growth, **208**, 546 (2000)
10. M. Inoue, H. Tanino, Y. Kondo, J. Am. Ceram. Soc., **72**(2), 352 (1989)
11. S.B. Cho, S. Venigalla, J.H. Adair, J. Am. Ceram. Soc., **79**(1), 88 (1996)
12. M. Inoue, Y. Kondo, T. Inui, Inorg. Chem., **27**(2),215 (1988)