Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 39 (2013) 9677–9681

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Phase evolution and dynamics of cerium-doped mullite whiskers synthesized by sol–gel process

Xiang Wang, Jin-hong Li*, Ling-xin Tong, Wu-wei Feng

National Laboratory of Mineral Materials, China University of Geosciences, 100083 Beijing, China

Received 16 April 2013; received in revised form 25 April 2013; accepted 23 May 2013
Available online 31 May 2013

Abstract

The effects of CeO_2 doping of aluminosilicate on mullite formation and the morphology of mullite whiskers are evaluated herein. CeO_2-doped mullite precursors were generated by a sol–gel process. The introduction of CeO_2 into the aluminosilicate precursor ($3Al_2O_3 \cdot 2SiO_2$) not only lowered the mullite formation temperature, but also promoted the crystallization of mullite grains. The mullitization activation energies calculated based on non-isothermal differential scanning calorimetry (DSC) were 473 and 722 kJ mol^{-1} for the 2 mol% CeO_2-doped and undoped samples, respectively.

Keywords: B. Whiskers; D. Mullite; D. CeO_2; Activity energy

1. Introduction

Mullite is a non-stoichiometric compound with good mechanical strength, excellent thermal shock and high creep resistance, low thermal conductivity, and high temperature stability, features that have been exploited in a variety of applications and prompted intensive investigations over the last few decades [1,2].

The mullite grain exhibits a strong tendency towards anisotropic growth due to the anisotropic mullite structure. Mullite whiskers may be used to reinforce mullite ceramics, thus, techniques for fabrication of these whiskers are highly desired [3]. Thus far, sol–gel, co-precipitation, and spray pyrolysis have been utilized to synthesize mullite whiskers. Okada and Otsuka [4] synthesized mullite whiskers by firing a mixture of xerogel, silica gel, and aluminum fluoride in an airtight crucible at 900–1600 °C. Mullite whiskers grown from erbia-doped aluminum hydroxide-silica gel have been studied by Souza et al. [5] by firing 3 mol% erbia-doped pellets isostatically pressed at 1600 °C for 1–8 h. A high surface concentration of mullite whiskers was obtained, according to their report, with a maximum whisker length of 50 μm, and a maximum aspect ratio of 23. Investigation of the nucleation and growth of mullite whiskers from lanthanum-doped aluminosilicate melts by Regiani et al. [6] demonstrated that the mullitization temperature decreased from 1350 °C to 1240 °C in response to the rare earth dopant.

However, the growth of mullite whiskers doped with rare earth oxide has been reported in several studies, with a consistently positive effect on the mullitization behavior, the phase evolution, and morphology of mullite whiskers after doping has been analyzed in only a few studies. Mechnich and co-workers [7] demonstrated the efficacy of the dopant CeO_2 for lowering the reaction temperature in a study of CeO_2-doped reaction-bonded mullite. It was postulated that the formation of transient, low-viscosity Ce–Al–Si–O liquids accelerated Si oxidation and mullite formation. The present study aims to further illuminate the phase evolution and morphology of mullite whiskers formed from the CeO_2-doped aluminosilicate precursor via the sol–gel process.

2. Materials and methods

CeO_2-doped mullite whiskers were prepared according to the synthesis scheme illustrated in Fig. 1. Aluminum nitrate

---

*Corresponding author. Tel.: +86 010 82323201; fax: +86 010 82322974.
E-mail address: jinhong@cugb.edu.cn (J.-h. Li).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.05.093

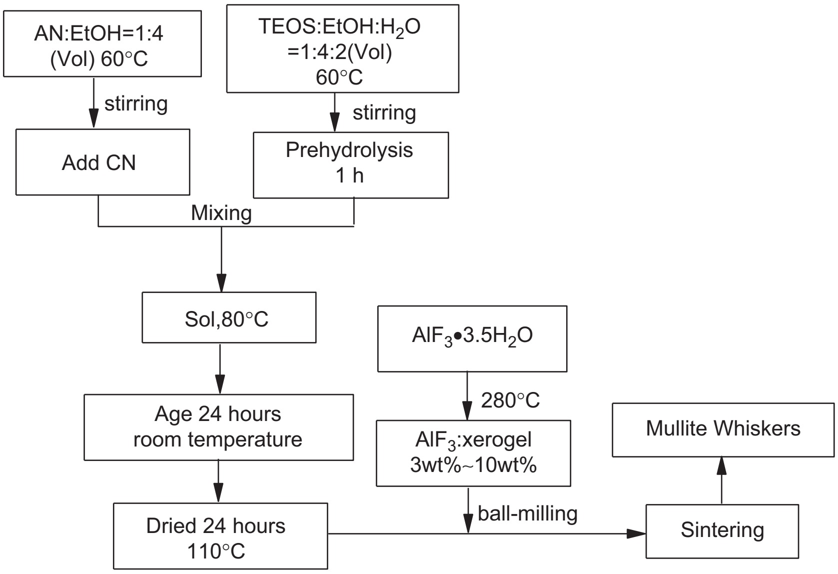

Fig. 1. Schematic of the preparation procedure of CeO_2 doped mullite whiskers.

(AN, AR grade, Xilong Chemical Co., Ltd., China), cerous nitrate (CN, AR grade, Tianjin Fu Chen Chemical Reagents Factory, China), and tetraethyl orthosilicate (TEOS, AR grade, Xilong Chemical Co., Ltd., China) were used as the starting materials for the aluminosilicate precursors ($3Al_2O_3 \cdot 2SiO_2$). The as-prepared samples were denoted according to the content of Ce^{3+} to Al^{3+} dopant as 0 mol% CeO_2, 1 mol% CeO_2, 2 mol% CeO_2, 3 mol% CeO_2, and 5 mol% CeO_2.

The aluminosilicate precursor was ground with fluoride via ball milling, using corundum vials and balls. The pellets (20 mm in diameter and 10 mm in thickness) were dry-pressed uniaxially at 20 MPa. The green pellets were sintered in air, for 3 h, at temperatures from 900 °C to 1100 °C, at a heating rate of 5 °C/min, using an electrically heated muffle furnace. Phase characterization was performed via X-ray diffraction (XRD) (D'Max-Ra12 kW, Ouyatu, Japan) using Cu-Kα radiation and a scanning rate of 8.0° (2θ) min^{-1}. Mullitization kinetics were studied between 0 and 1200 °C in air using non-isothermal differential scanning calorimetry (DSC) coupled with a Simultaneous Thermal Analyzer (SDT Q600). The morphology of the whiskers was investigated by means of scanning electron microscopy (SEM, S-4800, Hitachi, Japan).

3. Results and discussion

3.1. Phase evolution

Figs. 2–4 show the XRD patterns of the samples doped with 0–5 mol% CeO_2 and calcined at various temperatures. The precursor was amorphous at 900 °C, but after heating to 1000 °C, an almost single phase of mullite was obtained, as shown in Fig. 2. In addition, the increased peak intensities observed in the case of the 2 mol% CeO_2-doped sample were indicative of enhanced mullitization behavior. In contrast, the peak intensities of the 1 mol% CeO_2-doped sample were almost the same as that of the undoped sample. However, at dopant concentrations exceeding 2 mol%, the degree of crystallinity was lessened and an impurity phase corresponding to CeO_2 was evident.

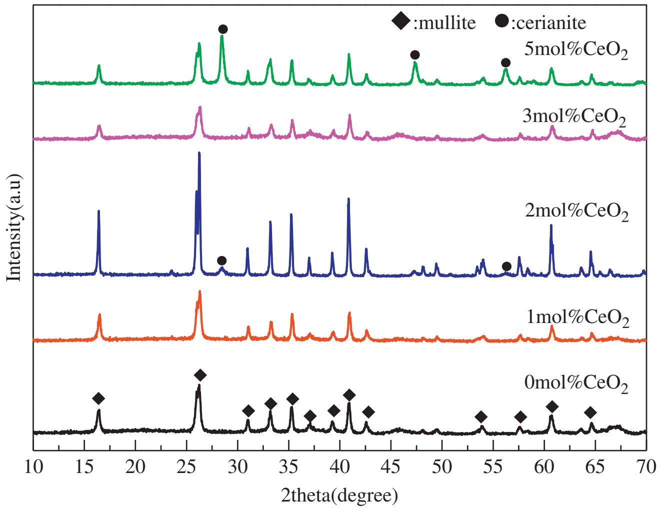

Fig. 2. XRD patterns of the 1000 °C calcined samples doped with different content of CeO_2.

The XRD patterns of the precursors calcined at 1100 °C are shown in Fig. 3. The diffraction peaks of the 0–2 mol% CeO_2-doped sample and of the precursor were similar when calcined at 1000 °C, with the exception that CeO_2 is a minor phase in the 1 mol% CeO_2 and 2 mol% CeO_2-doped samples. However, the peaks corresponding to CeO_2 are distinctly enhanced in the 3 mol% CeO_2 and 5 mol% CeO_2-doped samples. It is believed that excessive doping with CeO_2 inhibits the mullitization behavior, which is sensitive to the dopant content and temperature.

In Fig. 4, the relatively strong overlapping diffraction peaks ascribed to the (120) and (210) crystalline planes in the region

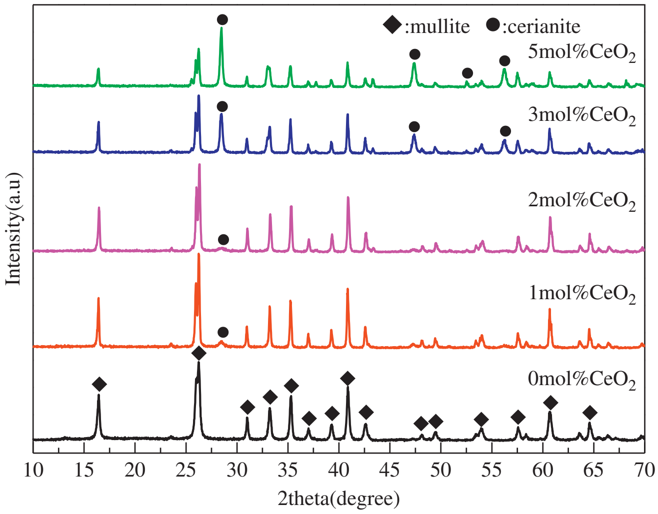

Fig. 3. XRD patterns of the 1100 °C calcined samples doped with different content of CeO_2.

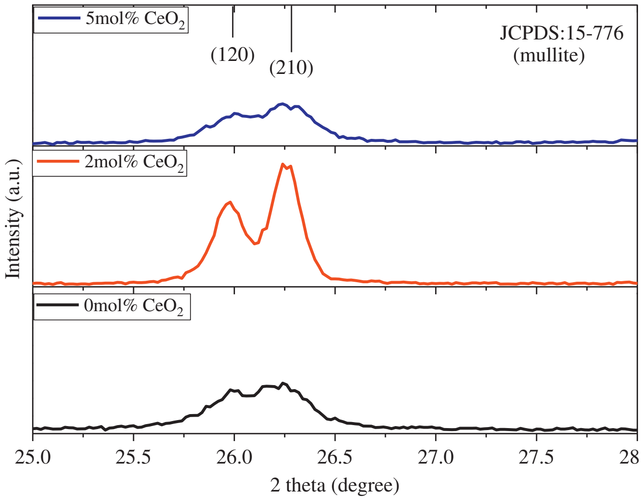

Fig. 4. Splitting of peaks (120) and (210) in XRD of 1000 °C calcined samples doped with different content of CeO_2.

$2\theta = 26°$ are utilized to illustrate the effect of 2 mol% CeO_2 doping on mullitization of the precursor. The intensity of this peak is enhanced in the case of the 2 mol% CeO_2-doped sample compared to the undoped and 5 mol% CeO_2-doped samples, indicative of enhanced mullitization by CeO_2 doping at this concentration. Thus, in conjunction with the results presented in Figs. 2 and 3, these results indicate that the optimum concentration of CeO_2 to promote mullite formation is ca. 2 mol%.

3.2. Activation energy

The activation energy of mullitization determined by isothermal or non-isothermal methods has been reported in various studies, the value of which was affected by the particle size, particle distribution, packing state, etc. [8,9]. Non-isothermal measurements provide a simpler means of analyzing the data than isothermal measurements. The Kissinger equation [10] given below was used to calculate the activation energy from the obtained data.

$$\ln\left(\frac{\varphi}{T_p^2}\right) = -\frac{E_a}{RT_p} + C \qquad (1)$$

In this equation, T_p represents the maximum temperature of the exothermic peak (crystallization temperature), φ is the heating rate, E_a is the activation energy, and R is the universal gas constant [11,12].

The mullitization kinetics were studied via DSC analysis performed at different heating rates between 5 and 20 °C/min. DSC scans of the 0 mol%, 2 mol%, and 5 mol% CeO_2 samples acquired at a heating rate of 20 °C/min are shown in Fig. 5. The three endothermic peaks are assigned to dehydration of the residual water and decomposition of hydroxides in the dried xerogel. All of the three samples exhibited a sharp exothermic peak around 1000 °C, attributed to mullite formation. Based on the chemical homogeneity of the precursor and the resultant crystallization behavior, the chemical homogeneity is on the atomic level scale and mullitization is controlled by the nucleation-growth [13]. The exothermic peak is observed to shift toward lower temperature with increased CeO_2 doping. This behavior indicates that the activation energy for mullitization decreases due to the addition of CeO_2. Furthermore, all of the samples exhibit a second exothermic peak above 1100 °C. These peaks were assigned to crystallization of the excess CeO_2 [14–17].

The activation energies for mullite formation were calculated from an Arrhenius plot of $\ln(\varphi/T_p^2)$ versus $1/T_p$ (Fig. 6). An E_a of 722 kJ mol^{-1} was derived for the 0 mol% CeO_2 sample and an E_a of 473 kJ mol^{-1} was obtained for the 2 mol % CeO_2-doped sample. Notably, the E_a value of the 2 mol% CeO_2-doped sample is much smaller than that of the undoped sample.

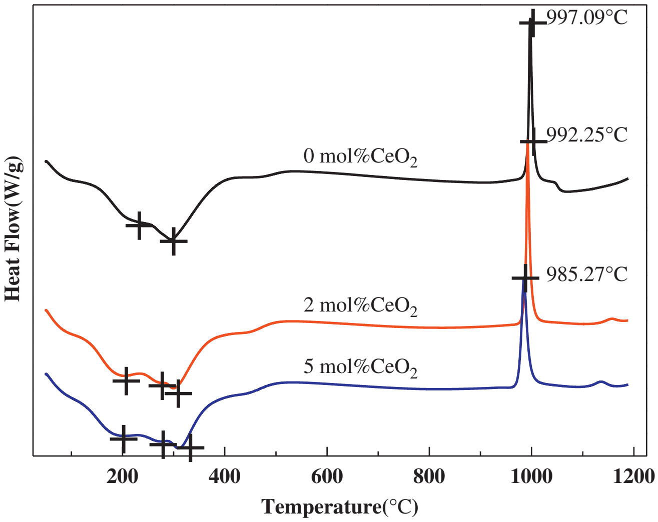

Fig. 5. DSC curves of the aluminosilicate $(3Al_2O_3 \cdot 2SiO_2)$ precursor doped with different content of CeO_2.

3.3. Morphology

SEM images of the untreated surface of the undoped and 2 mol% CeO_2-doped samples calcined at various temperatures are shown in Fig. 7. Fig. 7(a) shows that calcination of the undoped sample at 1000 °C was ineffective for producing mullite whiskers, whereas initiation of the formation of mullite whiskers was evident for the 2 mol% CeO_2-doped sample, as shown in Fig. 7(d).

Fig. 7(b) shows that the undoped sample calcined at 1100 °C was composed of small anisotropic mullite grains with a vermiform structure [18]. On the other hand, Fig. 7(e) demonstrates that 2 mol% CeO_2 doping promotes the growth of whiskers significantly to give a length of around 2 μm and an aspect ratio above 20. Several thick whiskers were observed among the predominantly thin whiskers found in the matrix (Fig. 7(c)). Increasing the sintering temperature to 1200 °C resulted in a significant increase in the number of thick whiskers, and fewer thin whiskers, which implies that the former grows at the expense of the latter. However, with increasing temperature, the 2 mol% CeO_2-doped sample (Fig. 7(f)) comprised smaller whiskers with lower aspect ratios, along with a small amount of glass phase, and open spaces between the whiskers, indicating that the higher temperature had a negative impact on the mullite whisker growth [19].

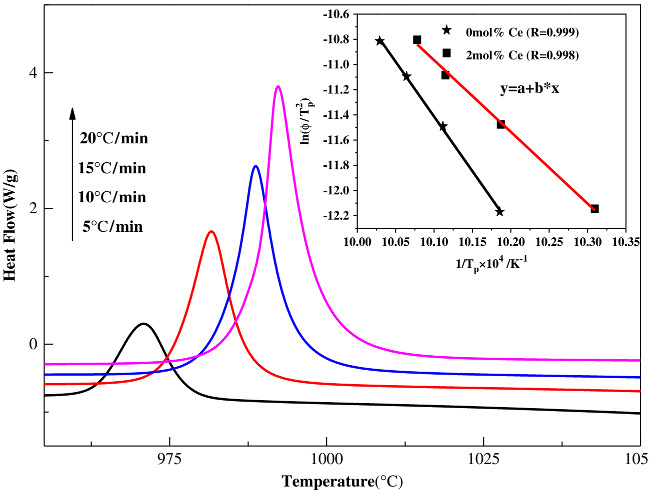

Fig. 6. DSC curves of the sample doped with 2 mol% CeO_2 under different heating rates. The inset shows the activation energy of mullitization plotted based on Eq. (1).

The effect of CeO_2 on the mullitization temperature and the morphology of the mullite whiskers can be explained by the dissolution-precipitation mechanism. Regiani et al. [6] suggested that rare earth elements in the aluminosilicate systems produce a small volume of glass. It is thought that a layer of liquid glass spreads over the mullite grains and percolates into the grain boundaries of the mullite ceramic body. The peculiarities of whisker formation in these systems are associated with the rare-earth aluminosilicate glass melt during liquid sintering. Similar behavior is observed in the samples doped with 2 mol% CeO_2 sintered at 1100 °C. We attribute this effect to the formation of a low-viscosity liquid glassy phase and an obstacle-free surface at this temperature. Eutectic temperatures support this discussion and provide evidence of a viscosity drop [20,21].

4. Conclusions

Mullite whiskers were obtained from an aluminosilicate ($3Al_2O_3 \cdot 2SiO_2$) precursor via the sol–gel process. Mullite phase formation was enhanced by 2 mol% doping with CeO_2 at temperatures below 1000 °C, whereas excessive CeO_2 doping inhibits mullitization at higher calcination temperatures. The mullitization behavior varied with the ceria content and calcination temperature. The morphology of the whiskers is strongly dependent on the presence of CeO_2 and the calcination temperature. The activation energy of mullitization for the 2 mol% CeO_2-doped sample, determined by non-isothermal

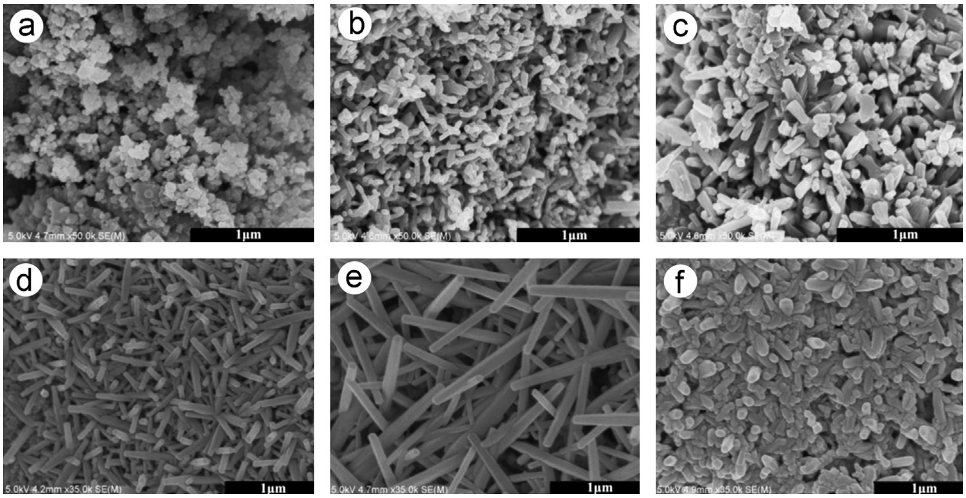

Fig. 7. SEM images of the untreated surface of the undoped and the 2 mol% CeO_2 doped samples sintered at different temperatures: (a) no dopant samples calcined at 1000 °C for 3 h, (b) no dopant samples calcined at 1100 °C for 3 h, (c) no dopant samples calcined at 1200 °C for 3 h, (d) 2 mol% CeO_2 doped samples calcined at 1000 °C for 3 h, (e) 2 mol% CeO_2 dopant samples calcined at 1100 °C for 3 h and (f) 2 mol% CeO_2 dopant samples calcined at 1200 °C for 3 h.

differential thermal analysis, was 473 kJ mol^{-1}, which was much smaller than the E_a of the undoped sample ($E_a = 722$ kJ mol^{-1}). The 2 mol% CeO_2-doped samples exhibited a high degree of anisotropic growth in comparison to the undoped sample at the same calcination temperature. This effect is attributed to the formation of a low-viscosity liquid glassy phase and an obstacle-free surface in the CeO_2–Al_2O_3–SiO_2 system.

Acknowledgments

This project was supported by the program for New Century Excellent Talents in University (NCET-08–828), the Fundamental Research Funds for the Central Universities (Grant no. 2011YXL003), and Research Fund of the National Laboratory of Mineral Materials (No. A08002).

References

[1] I.A. Aksay, D.M. Dabbs, M. Sarikaya, Mullite for structural, electronic, and optical applications, Journal of the American Ceramic Society 74 (1991) 2343–2358.

[2] L.B. Kong, H. Huang, T.S. Zhang, J. Ma, F. Boey, R.F. Zhang, et al., Growth of mullite whiskers in mechanochemically activated oxides doped with WO_3, Journal of the European Ceramic Society 23 (2003) 2257–2264.

[3] J. Roy, N. Bandyopadhyay, S. Das, S. Maitra, Role of V_2O_5 on the formation of chemical mullite from aluminosilicate precursor, Ceramics International 36 (2010) 1603–1608.

[4] K. Okada, Y. Hoshi, N. Otsuka, Formation reaction of mullite from SiO_2–Al_2O_3 xerogels, Journal of Materials Science Letters 5 (1986) 1316–1318.

[5] M.F. de Souza, J. Yamamoto, I. Regiani, C.O. Paiva-Santos, D.P.F. de Souza, Mullite whiskers grown from erbia-doped aluminum hydroxide-silica gel, Journal of the American Ceramic Society 83 (2000) 63–64.

[6] I. Regiani, W.L.E. Magalhaes, D.P.F. de Souza, C.O. Paiva-Santos, M.F. de Souza, Nucleation and growth of mullite whiskers from lanthanum-doped aluminosilicate melts, Journal of the American Ceramic Society 85 (2002) 232–238.

[7] P. Mechnich, M. Schmucker, H. Schneider, Reaction sequence and microstructral development of CeO_2-doped reaction-bonded mullite, Journal of the American Ceramic Society 82 (1999) 2517–2522.

[8] E. Tkalcec, S. Kurajica, J. Schmauch, Crystallization of amorphous Al_2O_3–SiO_2 precursors doped with nickel, Journal of Non-Crystalline Solids 353 (2007) 2837–2844.

[9] E. Tkalcec, R. Nass, J. Schmauch, H. Schmidt, S. Kurajica, A. Bezjak, et al., Crystallization kinetics of mullite from single-phase gel determined by isothermal differential scanning calorimetry, Journal of Non-Crystalline Solids 223 (1998) 57–72.

[10] K. Okada, Activation energy of mullitization from various starting materials, Journal of the European Ceramic Society 28 (2008) 377–382.

[11] H.B. Tan, Y.P. Ding, J.F. Yang, Mullite fibers preparation by aqueous sol-gel process and activation energy of mullitization, Journal of Alloys and Compounds 492 (2010) 396–401.

[12] T. Takei, Y. Kameshima, A. Yasumori, K. Okada, Crystallization kinetics of mullite from Al_2O_3–SiO_2 glasses under non-isothermal conditions, Journal of the European Ceramic Society 21 (2001) 2487–2493.

[13] S. Prusty, D.K. Mishra, B.K. Mohapatra, S.K. Singh, Effect of MgO in the microstructure formation of zirconia mullite composites from sillimanite and zircon, Ceramics International 38 (2012) 2363–2368.

[14] H.B. Tan, Y.P. Ding, H.H. Zhang, J.F. Yang, G.J. Qiao, Activation energy for mullitization of gel fibers obtained from aluminum isopropoxide, Bulletin of Materials Science 35 (2012) 833–837.

[15] W.Y. Cong, S.M. Li, Y.J. Wang, L. Tao, X.Y. Liu, W.M. Zheng, Photoluminescence study of Ce-doped silica films, Journal of Luminescence 132 (2012) 161–163.

[16] L.B. Kong, T.S. Zhang, J. Ma, F. Boey, Some main group oxides on mullite phase formation and microstructure evolution, Journal of Alloys and Compounds 359 (2003) 292–299.

[17] W. Wang, D. Weng, X.D. Wu, Structure evolution and thermal stability of La_2O_3-doped mullite fibers via sol-gel method, Journal of Rare Earths 30 (2012) 175–180.

[18] J.H. She, T. Ohji, P. Mechnich, M. Schmucker, H. Schneider, Mullitization and densification of Y_2O_3-doped reaction-bonded mullite ceramics with different compositions, Materials Chemistry and Physics 76 (2002) 88–91.

[19] J.E. Lee, J.W. Kim, Y.G. Jung, C.Y. Jo, U. Palk, Effects of precursor pH and sintering temperature on synthesizing and morphology of sol–gel processed mullite, Ceramics International 28 (2002) 935–940.

[20] S. Stanislav, E. Tkalcec, V. Mandic, J. Schmauch, Mullite crystallization kinetics of lanthanum doped sol–gel derived precursors, Journal of the European Ceramic Society 31 (2011) 377–383.

[21] F. Soleimani, M. Rezvani, The effects of CeO_2 addition on crystallization behavior and pore size in microporous calcium titanium phosphate glass ceramics, Materials Research Bulletin 47 (2012) 1362–1367.