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Crystallization and infrared radiation properties of iron ion doped cordierite glass-ceramics

Shu-Ming Wang[a,*], Feng-Hua Kuang[a], Qing-Zhi Yan[a], Chang-Chun Ge[a], Long-Hao Qi[b]

[a] School of Materials Science and Engineering, University of Science & Technology Beijing, HaiDian District, Xue Yuan Road 30#, Beijing 100083, China
[b] State Key Laboratory of New Ceramic and Fine Processing Tsinghua University, Beijing 100084, China

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ABSTRACT

Heterogeneous ion solution is an important method to improve the wanted property of polycrystalline materials. In this paper, for the purpose of infrared radiation property modification, different contents Fe_2O_3 were doped in $MgO–Al_2O_3–SiO_2$ system glasses. The effects of Fe_2O_3 doping on nucleation mechanism, crystallization behaviors and especially infrared radiation properties of this cordierite-crystalline based glass-ceramics were systematically investigated by means of differential thermal analysis (DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The results show that, the doping of iron ion can promote the phase separation of this magnesium aluminosilicate glass, and therefore change the crystallization mechanism of this glass from surface crystallization to bulk crystallization. The iron ion incorporates into the crystal structure of cordierite by mean of substituting Mg^{2+} in M site. The substitution of Fe^{3+} to Mg^{2+} can form the vacant site of Mg^{2+} cations. For the effects of lattice distortion, impurity and vacancy defects which caused by the incorporation of iron ion, the infrared radiation performance of cordierite based glass-ceramics can be improved effectively.

1. Introduction

As the global energy shortage aggravates increasingly, utilizing the existing resources rationally and effectively has gained more and more attention. Presently, infrared heating and drying technology is being used more and more in industry for the advantages of energy conservation and pollution reduction [1,2]. As a consequence, there is an increasing demand for high infrared emissivity materials. $MgO–Al_2O_3–SiO_2$ system glass-ceramics with the main phase of cordierite crystalline have many beneficial properties, such as elevated thermal and chemical stabilities, low dielectric constant (~5.0 at 1 MHz) and coefficient of thermal expansion ($\sim 2 \times 10^{-6}/^{\circ}C$), and good infrared radiation performance [3–5], all of which are promising for the use of this material for infrared heating and drying applications.

In recent years, much research has been focused on improving the infrared emissivity of the cordierite based glass-ceramics [6,7], and heterogeneous ion solution is an important method to improve the wanted property of polycrystalline materials [8–11]. Magnesium cordierite ($Mg_2Al_4Si_5O_{18}$) has three polymorphic forms [12,13]: α-cordierite (space group P6/mmc), which is a hexagonal high-temperature form. β-cordierite (space group Cccm), which is an orthorhombic low-temperature form, and a metastable form referred as μ-cordierite, which is a solid solution with β-quartz structure. The structural unit of cordierite is composed by Al–O/T_1-tetrahedron and Mg–O/M-octahedron connected vertically by Si–O six-membered rings T_2-tetrahedron: $M_2(T_11)_2(T_26)_2(T_23)_2(T_21)_2(T_16)O_{18}$, where M-position is Mg^{2+}, T_11- and T_26-positon were occupied by Al^{3+}, T_16-, T_21- and T_23-position were occupied by Si^{4+} [14]. The incorporation of transition metal ions into this framework has been discussed for a long time [15,16], and the response of the properties to the incorporation of transition metal cations is of interest. There is much research about the effects of the transition metal ions doping on coefficient of thermal expansion [17], crystal structure and lattice dynamics [18,19], but there is few research carried out about the effects of transition metal ions incorporation on the infrared radiation property of this material.

In this work, the iron ion substituted cordierite ($[Mg/Fe]_2Al_4Si_5O_{18}$) glass-ceramic was synthesized by the method of crystal growth from a homogenous Fe_2O_3 doped glass. The effects of iron ions doping on the crystallization behaviors and infrared radiation property of this magnesium aluminosilicate glass were examined, and influence mechanism of iron ion incorporation on the infrared radiation property of this modified material were analyzed.

* Corresponding author. Tel.: +86 10 62332472; fax: +86 10 62334951.
E-mail address: wangshuming03@mails.tsinghua.edu.cn (S.-M. Wang).

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Table 1
Chemical composition of the glass-ceramics studied (wt.%).

Sample no.	1	2	3	4	5
MgO	13.3	12.6	12.3	12.0	11.7
Al_2O_3	33.5	31.7	31.1	30.4	29.7
SiO_2	49.2	46.7	45.6	44.6	43.6
TiO_2	3.0	3.0	3.0	3.0	3.0
Fe_2O_3	–	2.0	4.0	6.0	8.0
Clearing agent	1.0	1.0	1.0	1.0	1.0

2. Experimental procedures

2.1. Samples preparation

The starting materials were analytical grade reagents (99.5%, Yatai Fine Chemical Co., Beijing, China) SiO_2, Al_2O_3, MgO, TiO_2 and Fe_2O_3. The molar ratio of SiO_2, Al_2O_3 and MgO was 5:2:2, which is the stoichiometric comparison of magnesium cordierite [20]. 0, 2.0, 4.0, 6.0, 8.0 wt.% Fe_2O_3 were added respectively. 3.0 wt.% TiO_2 was added as the nucleating agent and a small quantity of NH_4NO_3 and Sb_2O_3 was added as fluxes and clearing agent [21]. The detailed compositions of these parent glass samples were given in Table 1.

Powder mixtures of reagent grade chemicals were mixed by ball-milling for 36 h and thereafter melted in a platinum crucible in an electrically heated furnace at 1600–1650 °C for 3 h. The melts were poured onto a 300 °C preheated stainless steel plate, then transferred to an annealing furnace and held at 650 °C for 1 h. Thus the primary glass sample was obtained.

2.2. Characterization techniques

The resulting glass was crushed and ground though an agate mortar, and sieved through a 200 mesh (0.074 mm) to produce glass powder suitable for DTA, which was performed using a DuPont 2100 Thermal Analyzer. The weight of the glass powder was 50 mg and the reference material was α-Al_2O_3 powder. The samples were heated in air from ambient temperature to 1200 °C at a rate of 10 °C/min.

The type of crystalline phases of the heat-treated glass samples were identified from XRD patterns, obtained using an X-ray diffractometer (Model D/max-RB, Rigaku, 40 kV and 20 mA, αmonochromatic Cu *K*α radiation), at a scanning speed of 4° min^{-1}.

SEM, EDS analysis was carried out using a JSM-6301F. The specimens were prepared by standard metallographic techniques followed by chemical etching in an HF solution (vol. 5%) for 1.5 min. Etched glass-ceramic samples were coated with a thin layer of gold.

Coefficient of thermal expansion was tested by a SETRAM-TMA 92 thermal analyzer, at a heating rate of 10 °C/min, size of each sample was 8 mm × 8 mm × 8 mm.

The infrared radiation characteristics were examined using an infrared radiation tester (Model IRE-2, China). The surfaces of the bulk testing samples were polished. The size of each sample was 60 mm × 60 mm × 3 mm. Measurements were carried out at 70 °C; the accuracy of temperature control was ±0.1 °C.

3. Results and discussion

3.1. Crystallization behavior of Fe_2O_3-doped cordierite glass-ceramics

The typical DTA traces which depict the thermal behaviors of glass samples including the glass transition temperature (T_g) and the peak temperature (T_P, corresponding to the temperature of crystallization) are shown in Fig. 1. The curves exhibited two distinct exothermic peaks, which indicate the formation of μ-cordierite and α-cordierite crystalline phases respectively (Fig. 2, for the reason of solid solution, the diffraction peaks present a shifting to some extent) [22]. No crystalline of Fe_2O_3 or other phases were detected after the heat-treatments of heating at temperature of T_P for 2 h. The exothermic peak of Fe_2O_3 doped sample is sharper than the non-doped one, and with the increasing of Fe_2O_3 content the peak temperature (T_P) shifted to lower trend [23,24].

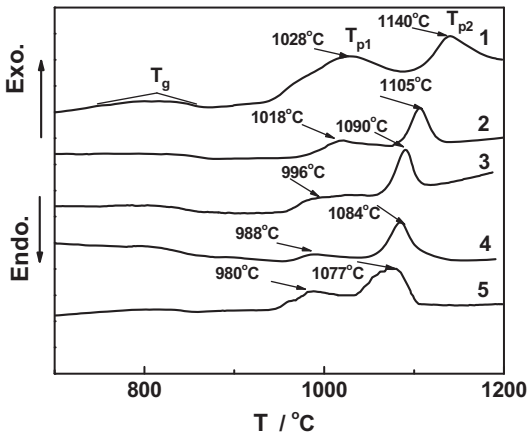

Fig. 1. The DTA curves of glass samples at the heating rate of 10 °C min^{-1}.

Samples after different heat-treatment were analyzed by SEM. Droplets sized 10–20 nm which are distributed homogeneously among the glass matrix was found in Fe_2O_3 doped glass samples after 800 °C/1.5 h heat-treatment (Fig. 3, B–E), and EDS analysis conducted on the droplets and glass matrix exhibits that Ti element and Fe element are concentrated in the small amorphous droplet (Fig. 3, F–G).

Based on the above experiment results, crystallization behaviors of the doped glasses have been studied. It can be concluded that phase separation generated in the initial stage of nucleation of the Fe_2O_3 doped glasses, small amorphous droplets (Ti, Fe-rich phase) distributed homogeneously among the glass matrix (Al, Si-rich phase). The interfaces of the two phases provide the core of heterogeneous nucleation for the consequent precipitation of cordierite crystalline [25], and thereby reducing crystallization activation energy and promote crystallization of this system glasses (in Fig. 1, the exothermic peak of Fe_2O_3 doped samples are sharper than non-doped one) [26]. The SEM results also showed that, by Fe_2O_3-

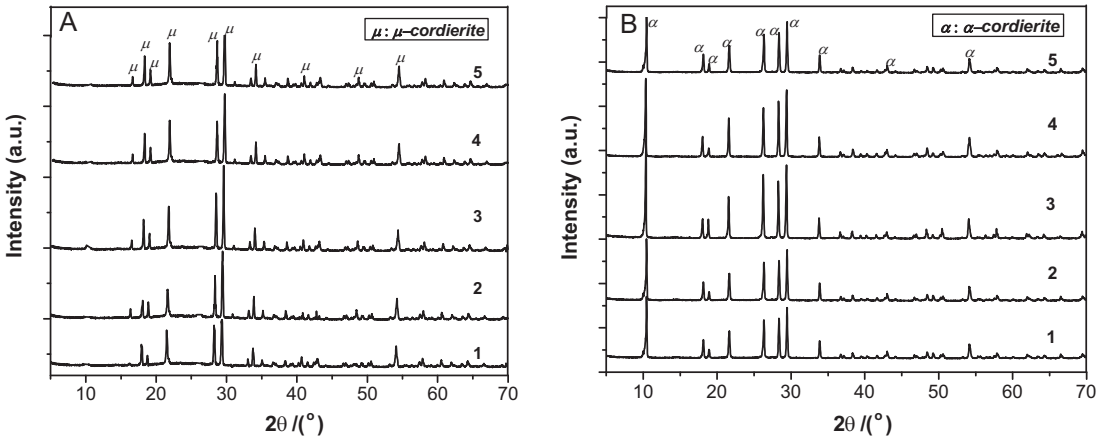

Fig. 2. XRD patterns of the glass samples heat treated at T_{P1} for 2 h (A) and T_{P2} for 2 h (B).

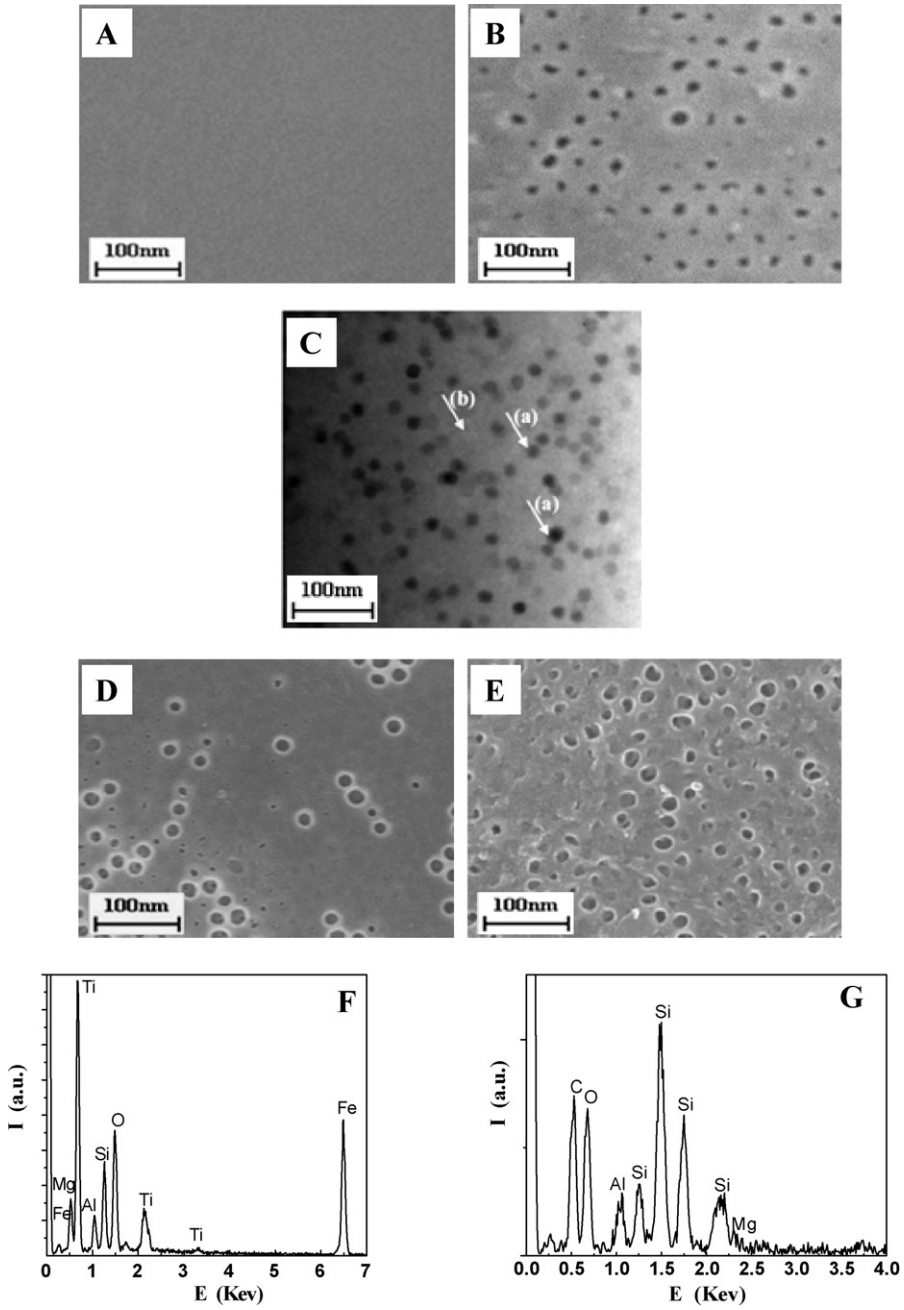

Fig. 3. SEM micrographs of samples (1–5, A–E) after the heat-treatment of 800 °C/1.5 h and EDS spectra of typical 4% Fe_2O_3-doped samples ((F) (a) part shown in C, (G) (b) part shown in C).

doping, the crystallization mechanism of Fe_2O_3-doped cordierite glass-ceramics is mainly changed from the surface crystallization to bulk crystallization, which microstructure changed from sheet shape crystal (Fig. 4a), to columnar shape crystal (Fig. 4b), and to granular equiaxed grains, sized 200–400 nm, distributed homogeneously among the glass matrix (Fig. 4c) [27].

3.2. *Influence of Fe_2O_3-doping on infrared radiation property*

The measurement results of normal direction infrared radiance and coefficient of thermal expansion of the glass-ceramic samples are shown in Table 2. As can be seen from the results, the doping of Fe_2O_3 can improve the infrared radiation performance of this material, the whole-band normal direction radiance increased from 0.82 to 0.91. At the same time, the coefficient of thermal expansion increases with the increases of the amount of doping, and a sharp increase occurs when the doping amount exceeds 4%, this is not benefit to the actual applications of this material.

As we know, the structural unit of cordierite is composed by Al–O/T_1-tetrahedron, Mg–O/M-octahedron and Si–O/T_2-tetrahedron, and different as Al–O/T_1-tetrahedron and Si–O/T_2-tetrahedron which were tightly fastened, the Mg–O/M-octahedron is much looser. Meantime, the radius of Fe^{3+} (0.64 Å) is close to that of Mg^{2+} (0.66 Å). Circumstantial evidence indicates that the limited cooperation of Fe^{3+} into the tetrahedral framework of cordierites, it will preferentially occupy the M-site. Many studies have proved that the occupied position of iron ions in cordierite crystal structure is not contested, which will substitute the Mg^{2+} and occupy the

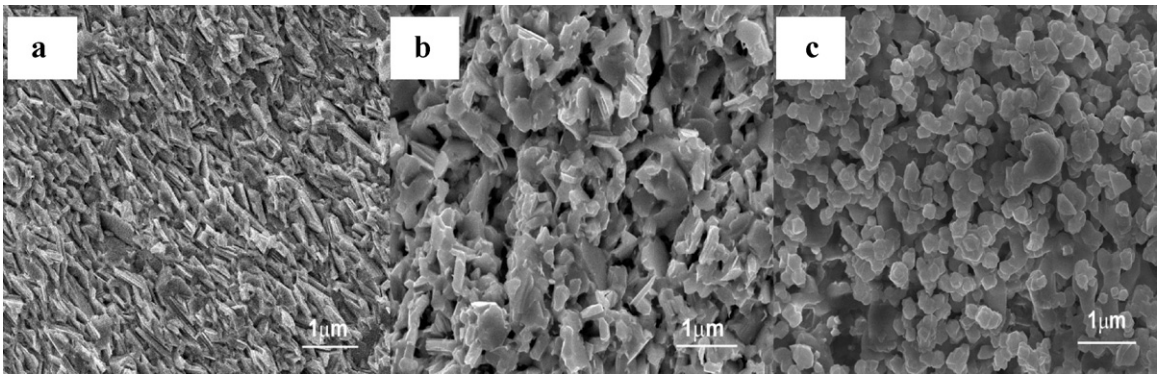

Fig. 4. SEM images of different amount of Fe_2O_3-doped glass-ceramic samples (nucleation at 880 °C for 2 h, and crystallization at 1100 °C for 2 h). (a) non-doped, (b) 2% Fe_2O_3-doped, (c) 4% Fe_2O_3-doped.

Table 2
Comparison of infrared radiance and coefficient of thermal expansion of doped and non-doping samples.

Sample no.	1	2	3	4	5
Whole-band infrared radiance	0.81	0.85	0.90	0.91	0.91
Coefficient of thermal expansion ($\times 10^{-7}$/°C)	20.0	22.0	24.0	46.0	48.0

M-site of cordierite crystal structure, forming isomorphous substitution solution [14,16,28,29]. In order to maintain the balance of valence state, the substitution of Fe^{3+} to Mg^{2+} can form the vacant site of Mg^{2+} cations. The vacancy defect-reaction equation can be written as:

$$2Fe_2O_3 \xrightarrow{Mg_2Al_3[AlSi_5]O_{18}} 4Fe^{\bullet}_{Mg} + 2V^{//}_{Mg} + 9Al_{Al} + 3Al_{Al} + 15Si + 54O_O \quad (1)$$

where $Fe^{\bullet}_{Mg}$ is the Fe^{3+} occupies the lattice position of Mg^{2+}, with a positive charge; $V^{//}_{Mg}$ is the Mg^{2+} vacancy, with two negative charges; O_O is the in situ oxygen.

The defect chemical formula of Fe^{3+} substituted Mg^{2+} in the cordierite crystal structure is as follows:

$$Mg_{2-(3X/2)}Fe_XAl_3V^{//}_{Mg}[AlSi_5]O_{18} \quad (2)$$

The formation of Mg^{2+} cations vacancies is bound to cause lattice distortion, and the introduction of Fe^{3+} will lead to the formation of impurity energy levels in the local area, which increasing the transition possibility of electrons from the full to the conduction band [30–32]. In conclusion, the presence of vacancies can change the activity of lattice vibrations, and the introduction of impurities increases transition possibility of electrons and phonon, all of which are favorable for the improvement of the infrared radiation performance of this material in the corresponding band.

4. Conclusions

The influence of iron ion doping on crystallization behavior and infrared radiation property of cordierite glass-ceramics was systematically studied, and the mechanism of their effects was analyzed, main conclusions are drawn as: (a) Fe_2O_3-doping can promote the phase separation of cordierite glass-ceramics, as a result, the crystallization of cordierite can be promoted, and the crystallization mechanism changed from surface crystallization to bulk crystallization. (b) The iron ion incorporates into the crystal structure of cordierite by mean of substituting Mg^{2+} in M site. The substitution of Fe^{3+} to Mg^{2+} can form the vacant site of Mg^{2+} cations which will affect the infrared radiation property of this system glass-ceramics significantly. (c) The doping of iron ions can effectively modify the infrared radiation performance of cordierite glass-ceramics, and improve the near infrared waveband and the middle and far infrared waveband radiation performance. Its mechanisms are mainly three aspects: Impurity effect; vacancy defect effect; lattice distortion effect.

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References

[1] C. Huang, L. Han, Z. Yang, X. Liu, Energy Convers. Mange. 49 (2008) 3433–3438.
[2] F. Tanaka, P. Verboven, N. Scheerlinck, K. Morita, K. Iwasaki, B. Nicolai, J. Food Eng. 79 (2007) 445–452.
[3] G. Chen, X. Liu, J. Alloys Compd. 431 (2007) 282–286.
[4] P. Amista, M. Cesari, A. Montenero, G. Gnappi, L. Lan, J. Non-Cryst. Solids 192–193 (1995) 529–533.
[5] Z. Acimovic, L. Pavlovic, L. Trumbulovic, L. Andric, M. Stamatovic, Mater. Lett. 57 (2003) 2651–2656.
[6] G. Feng, S. Zhou, J. Bao, X. Wang, S. Xu, J. Qiu, J. Alloys Compd. 457 (2008) 506–509.
[7] S. Wang, K. Liang, J. Non-Cryst. Solids 354 (2008) 1522–1525.
[8] S.A.M. Abdel-Hameed, A.M. Fathi, J. Alloys Compd. 498 (2010) 71–76.
[9] H. Pan, Y. Chen, C. Wang, J.X. Ma, C.P. Chen, Q.D. Wang, Electrochim. Acta 44 (1999) 2263–2269.
[10] Y. Zhao, M. Gao, Y. Liu, L. Huang, H. Pan, J. Alloys Compd. 496 (2010) 454–461.
[11] M. Gao, H. Miao, Y. Zhao, Y. Liu, H. Pan, J. Alloys Compd. 484 (2009) 249–255.
[12] E. Salje, Phys. Chem. Miner. 14 (1987) 455–460.
[13] V.K. Marghussian, O. Balazadegan, B. Eftekhari-yekta, J. Alloys Compd. 484 (2009) 902–906.
[14] B. Winkler, M.J. Harris, R.S. Eccleston, K. Knorr, B. Hennion, Phys. Chem. Miner. 25 (1997) 79–82.
[15] J.H. Wallace, H.R. Wenk, Am. Miner. 65 (1980) 96–111.
[16] C.A. Geiger, H. Voigtländer, Contrib. Miner. Petrol 138 (2000) 46–50.
[17] H. Ikawa, J. Am. Ceram. Soc. 69 (1986) 492–498.
[18] S. Sundar, A.M. Umarji, J. Am. Ceram. Soc. 76 (1993) 1873–1876.
[19] Y.F. Chen, J. Eur, Solid State Inorg. Chem. 32 (1995) 1065–1076.
[20] P. Hing, V. Sinha, P.B. Ling, J. Mater. Process. Technol. 63 (1997) 604–609.
[21] H. Shao, K. Liang, F. Zhou, G. Wang, F. Peng, J. Non-Cryst. Solids 337 (2004) 157–160.
[22] M. He, M. Wu, S. Zhang, X. Zhou, T. Zhang, S. Chen, J. Alloys Compd. 506 (2010) 757–760.
[23] J. Banjuraizah, B. Mohamad, Z.A. Ahmad, J. Alloys Compd. (2010), doi:10.1016/j.jallcom.2010.10.077.
[24] S.F Wang, Y.R. Wang, Y.F. Hsu, C.C. Chiang, J. Alloys Compd. 498 (2010) 211–216.
[25] P.W. McMillan, Glass-Ceramics, 2nd ed., Academic Press, London, New York, San Francisco, 1979.
[26] S.M. Wang, F.H. Kuang, J. Li, Phase Trans. 83 (2010) 397–403.

[27] M.B. Volf, Chemical Approach to Glass, Elsevier, Amsterdam, 1984.
[28] R.H. Pratt, Phys. Chem. 70 (2004) 595–603.
[29] F. Liu, E. Ma, D. Chen, Y. Wang, Y. Yu, P. Huang, J. Alloys Compd. 467 (2009) 317–321.
[30] S.M. Wang, Environ. Sci. Technol. 44 (2010) 4816–4820.
[31] T. Akazawa, H. Matsubara, J. Takahashi, K. Kodaira, J. Ceram. Soc. Jpn. 1 (1993) 991–995.
[32] V.K. Tikhomirov, C. Görller-Walrand, K. Driesen, J. Alloys Compd. 451 (2008) 542–544.