Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 453–457

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Enhanced surface crystallization of glass by adding traditional oxide nucleating agents

Huali Liu, Yinghui Wang, Tao Wang, Ruijuan Yang, Shiquan Liu*

School of Materials Science and Engineering, Shandong Provincial Key Laboratory of Preparation and Measurement of Building Materials, University of Jinan, Jinan 250022, Shandong, China

Received 22 April 2013; received in revised form 10 June 2013; accepted 11 June 2013
Available online 15 June 2013

Abstract

In the preparation of glass–ceramics, bulk crystallization of glasses can be improved by adding nucleating agents. However, surface crystallization of glasses conventionally can only be enhanced by using small particles, whose surfaces provide nucleating sites. Herein, oxide nucleating agents such as TiO_2 and Cr_2O_3 which are normally used to improve bulk crystallization were introduced into a lithium–iron-phosphate (LIP) glass. Differential thermal analysis results suggest that tendency to bulk crystallization of the LIP glass increases to some extent after addition of the nucleating agents. However, no bulk crystallization really occurred in the thermally treated samples. Instead, surface crystallization of the glass is facilitated by the nucleating agents. The samples containing nucleating agents show thicker crystallized surface layers compared with the pure LIP glass. It is proved nucleation stage to be important to increase the surface crystallization, further confirming the enhancement effect of the nucleating agents on surface crystallization. The results enrich the understanding of surface crystallization of glass and provide useful information for the preparation of glass–ceramics via glass powder sintering process which is based on surface crystallization.

Keywords: Surface crystallization; Nucleating agent; Lithium–iron-phosphate glass; Nucleation

1. Introduction

Glass–ceramics are composites consisting of fine crystallites and residual glass phase [1]. They are resistant to thermal and mechanical shocks [2]. Glass–ceramics have found applications in a wide variety of fields, such as cooking wares [3], electronic sealants [4], electrodes for lithium-ion batteries [5], bio-implants [6] and immobilization of nuclear wastes [7].

Glass–ceramics are prepared via controlled crystallization of parent glasses. The controlled crystallization is realized via thermal treatment, which typically includes nucleation and crystal growth steps. The crystallization of glasses is classified into bulk and surface crystallizations [8]. In the case of bulk crystallization, formation of crystallites initiates from nucleating sites homogenously distributed inside bulky glass samples. The nucleating sites are generated by either nucleating agents already dissolved in glass melt or phase separation occurred during thermal treatments. Traditional nucleating agents are mostly precious metals (Au, Ag and Pt) and oxides (TiO_2, Cr_2O_3) [9], which promote glass crystallization by forming high density of nucleating sites within bulky glasses. However, no nucleating agent is needed for surface crystallization. In this case, particles of a parent glass are used as precursors to prepare glass–ceramics. Thus, particle surface acts as the nucleating sites. Crystallites grow inward from particle surface. The smaller the glass particle is, the easier surface crystallization proceeds [10]. Therefore, fine glass powder benefits surface crystallization. However, too small glass particles lead to fast crystallization, which significantly increases viscosity of the glass and consequently retards sintering and densification of the glass powder, resulting in a porous glass–ceramic with low strength [11]. In addition, long time, energy-consuming grinding process is needed to obtain small glass particles.

Crystallization of lithium–iron-phosphate (LIP) glasses has been demonstrated as a new route to prepare lithium–iron-

---

*Corresponding author. Tel./fax: +86 531 82769106.
E-mail address: liusq_ujn@hotmail.com (S. Liu).

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.2013.06.022

phosphate crystalline materials, which are promising as cathode materials in rechargeable lithium ion batteries [12,13]. For example, Komatsu et al. [13] prepared $LiFePO_4$ crystals via the crystallization of LIP glass by Nd:YAG laser irradiation. Garbarczyk et al. [14] obtained lithium–iron-phosphate glass–ceramics with orthorhombic triphylite ($LiFePO_4$) and monoclinic Nasicon-like $Li_3Fe_2(PO_4)_3$ as crystalline phases. Our previous research has pointed out that LIP glasses show typical features of surface crystallization [15,16]. In this work, TiO_2, Cr_2O_3 and their mixtures were used for the first time as nucleating agents in an LIP glass. Influence of the nucleating agents on crystallization behavior of the LIP glass has been investigated by DTA, XRD and SEM techniques. The results indicate that the traditional oxide nucleating agents enhance surface crystallization of the LIP glass. The study gives a new insight into effect of nucleating agents on surface crystallization of glass and may provide a simple way to improve efficiency with which sintered glass–ceramics are made.

2. Experimental section

Analytic grade reagents of Li_2CO_3, Fe_2O_3, $NH_4H_2PO_4$, TiO_2 and Cr_2O_3 were used as raw materials for preparing glass batches. Pure LIP glass has a composition of Li_2O 8%, Fe_2O_3 29%, P_2O_5 63% by weight. TiO_2 (anatase), Cr_2O_3 (eskolaite) or their mixture was added as nucleating agent. Weight percentages of the nucleating agents in the glass batches are listed in Table 1. The samples are accordingly encoded as Ti0Cr0, Cr5, Ti2Cr3, Ti3Cr2, Ti0 (the same as Ti0Cr0), Ti2, Ti5 and Ti8 based on types and amounts of the nucleating agents added.

After the batches were melted in sintered silica crucibles at 1200 °C for 1 h, the melts were cast in a steel mold and annealed at 350 °C for 1 h. The annealed glasses were cut into small blocks, ultrasonically cleaned in ethanol and air-dried. Under otherwise specified, the samples were first soaked at temperatures 50 °C above glass transition points (T_g) for 2 h (nucleation stage) and then kept at crystallization peak temperatures (T_c) for 2 h (crystal growth stage). The heating rate used in the heat-treatments was 5 °C/min.

DTA measurements were carried out on an HCT-1 thermal analyzer (Henven, China). Powder glass samples with a grain size in the range of 105 μm and 125 μm or millimeter-sized bulky samples were put in alumina crucibles and heated with a rate of 5 °C/min to 800 °C. The crystallized surface layers of thermally-treated samples were analyzed by XRD technique on a D8-advanced diffractometer (Bruke, Germany). For SEM measurements, the heat-treated samples were first polished and then etched in 1% HF for 10 s to perform microstructure analysis on a QUANTA FEG250 scanning electron microscope. Thickness of the crystallized surface layers was determined on a stereoscope (SMZ-140, Motic).

Table 1
The transition and crystallization peak temperatures of the glass samples.

Sample	Amount of nucleating agent (wt%)		T_g (°C)	T_C (°C)		
	TiO_2	Cr_2O_3		Powder	Bulk	ΔT_c
Ti0Cr0	0	0	394	563	661	98
Cr5	0	5	440	621	682	61
Ti2Cr3	2	3	431	619	665	46
Ti3Cr2	3	2	438	621	668	47
Ti5	5	0	416	609	691	82

3. Results and discussion

DTA curves (Fig. 1a) of the powder glass samples indicate that the glasses containing different types of nucleation agents have higher T_g and T_c values than the pure LIP glass. From the data listed in Table 1, it can be seen that both the T_g and T_c values of the samples containing Cr_2O_3 and the complex nucleating agents (Ti2Cr3, Ti3Cr2) do not differ significantly. However, among all the nucleating agent-containing samples, sample Ti5 has the lowest T_g and T_c values, indicative of its smallest viscosity.

Depicted in Fig. 1b are DTA curves of the bulky samples containing different types of nucleating agents. Compared with the DTA curves presented in Fig. 1a, it can be seen that the glass transition points almost do not change, whereas the crystallization peaks displace to higher temperatures and become blunt (decreased peak height and increased peak width). The observed displacements of the crystallization peaks suggest the dominant surface crystallization of the studied LIP glasses [14]. Differences between the T_c values of the powder and bulky samples (listed in Table 1 as ΔT_c) are dependent on the nucleation agents applied. Generally, the samples containing nucleating agents have smaller ΔT_c values than the pure LIP glass, indicating that tendency to bulk crystallization of the glasses increases due to the addition of the nucleation agents [17,18]. Based on relative magnitude of the ΔT_c values, the order that the nucleating agents increase the tendency to bulk crystallization of the LIP glass is Ti2Cr3≈Ti3Cr2 > Cr5 > Ti5.

The nucleating agents increase the tendency to bulk crystallization of the LIP glass by providing heterogeneous nucleating sites distributed among the glass matrix. These nucleating sites are formed by either precipitation of the nucleating agents or phase separation induced by the nucleating agents. The difference in the solubility of Cr_2O_3 and TiO_2 explains why sample Cr5 has a larger tendency to bulk crystallization than Ti5. We have confirmed that the glass containing 8 wt% of TiO_2 was still amorphous, however, if the content of Cr_2O_3 reached 8 wt%, the parent glass was already crystallized. Therefore, when the amounts of Cr_2O_3 and TiO_2 are the same, the former will have more significant effect on crystallization, because it is easy to precipitate from the glass matrix, to act as the nucleating sites.

Regarding the complex nucleating agents of Cr_2O_3 and TiO_2, the results show they are more effective in inducing bulk crystallization than either of the single nucleating agent. The possible reason is that Cr ions in the glass may exist in the form of trivalent and hexavalent states [9,19,20]. Cr^{6+} ions are of high field strength, which increases phase separation in the glass, thus benefiting the bulk crystallization of the glass.

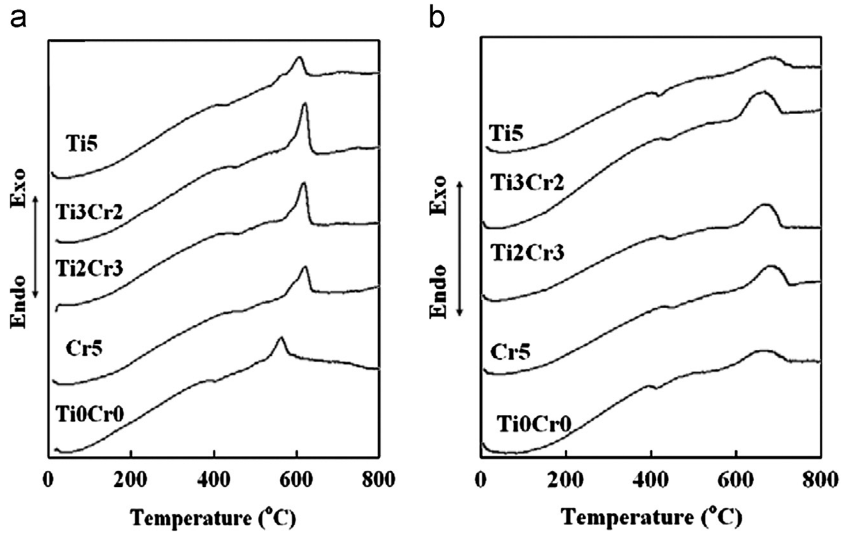

Fig. 1. DTA curves of the glasses: (a) powders and (b) bulk samples.

However, as indicated by the T_g values listed in Table 1, Cr_2O_3 increases the viscosity of glass most significantly, which on the other hand retards the phase separation and crystallization. This negative effect of Cr_2O_3 can be compensated by the addition of TiO_2, which was shown to decrease glass viscosity when its content is 2 wt% (see sample Ti2 in the latter discussion). Therefore, samples Ti2Cr3–Ti3Cr2 with mixed nucleating agents show the largest tendency to bulk crystallization.

After the thermal treatments, all samples exhibit surface crystallization characterized by inward growth of crystallized layers from sample surfaces as depicted in Fig. 2a. XRD measurements reveal that all samples have $LiFeP_2O_7$ as crystalline phase (Fig. 2b), indicating that the nucleating agents do not vary the crystalline phase in the heat-treated samples. However, the pure LIP glass shows the lowest crystallization upon the thermal treatment. In contrast, the samples with the complex nucleating agents (Ti2Cr3 and Ti3Cr2) show much more improved crystallization, which is indicated by the strongest crystallization peaks in their XRD patterns. SEM images of the crystallized surface layers of the samples are shown in Fig. 3. In sample Ti0Cr0, bar-like crystallites are about 10 μm in length and 500 nm in width. These crystals are distributed among a large area of residual glass matrix, suggesting that sample Ti0Cr0 has the lowest degree of crystallization among the studied LIP glasses. This result is consistent with the XRD results. In contrast, the crystallites in the samples with nucleating agents become much more widely distributed, indicating that the crystallization is improved by adding the nucleating agents. In addition, the morphology of the crystallites in all Cr_2O_3-containing samples turns to be spicate. However, the crystallites in sample Ti5 are exceptionally blocks sized about 1 μm and aligned.

The crystallized surface layers of samples Ti0Cr0, Cr5, Ti2Cr3, Ti3Cr2 and Ti5 are respectively 361.6, 1081.3, 2047.6, 1868.5 and 908.4 μm in thickness. These data show that the nucleating agents significantly accelerate surface crystallization of the LIP glass. In addition, the complex nucleating agents have the greatest enhancements of the surface crystallization. Further experiments proved that the thickness of the crystallized surface layers was reduced if the

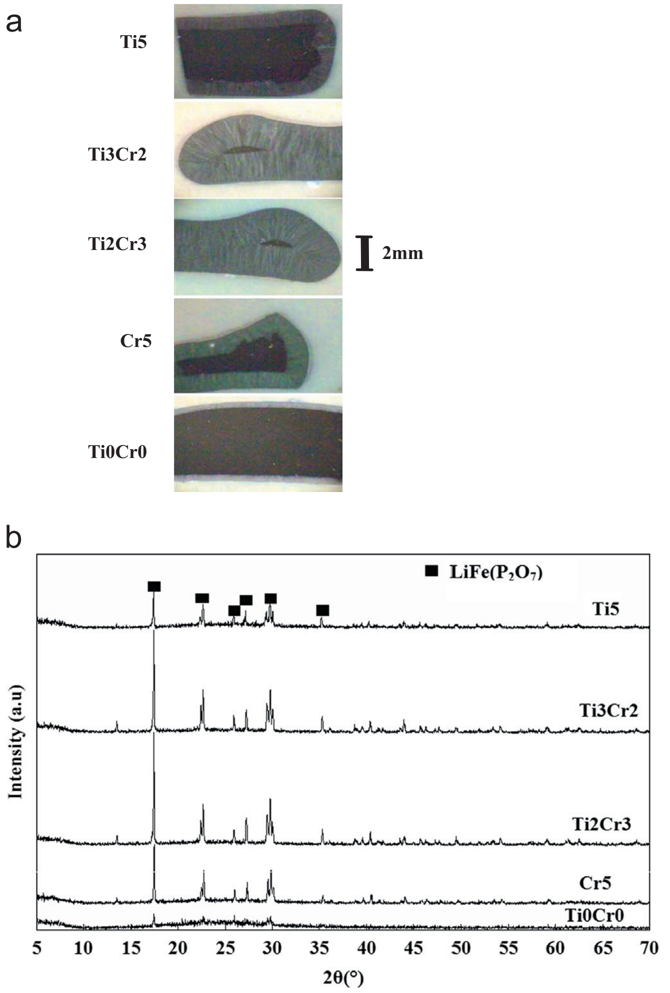

Fig.2. Cross-sections of the heat-treated samples (a) and the XRD patterns (b) of the crystallized surface layers.

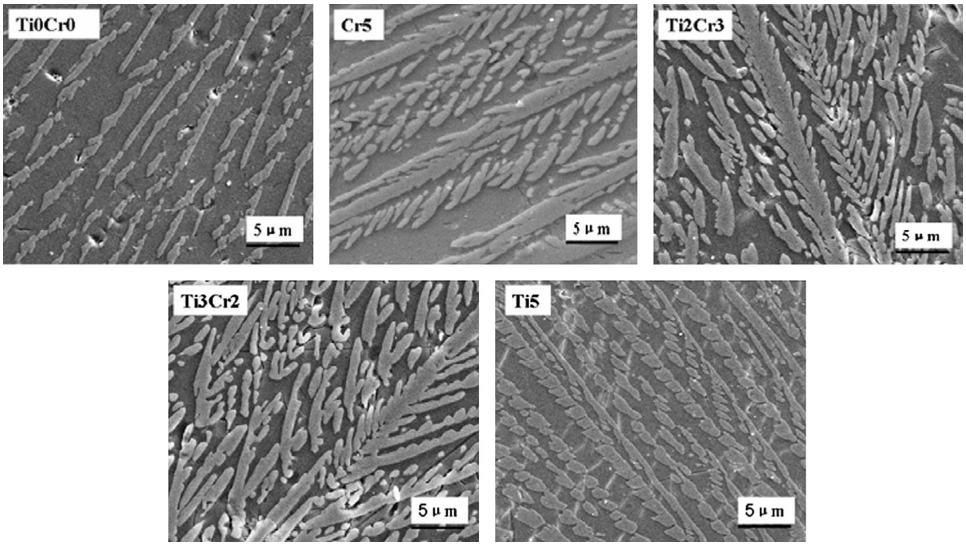

Fig. 3. SEM images of the crystallized surface layers of the heat-treated samples containing different types of nucleating agents.

time of the crystal growth stage was reduced. For example, when the crystal growth time was reduced to 1 h, the crystallized surface layers of samples Ti0Cr0, Cr5, Ti3Cr2 are 204.1, 785.7 and 1007.7 μm in thickness, respectively. When the nucleation stage was further omitted, the crystallized surface layers did not decrease at the same scale for all samples. For sample Ti0Cr0, the crystallized surface layer was slightly reduced from 204.1 to 194.1 μm, however, it was greatly reduced from 785.7 to 524.3 μm for sample Cr5. The above comparisons suggest the nucleation stage in the thermal treatments is also important for improving surface crystallization as in the case of bulk crystallization.

To further verify the importance of the nucleation stage, another series of samples (Ti*x*) with different amounts of TiO_2 were prepared. DTA analysis indicated that the crystallization peak temperatures for sample Ti0, Ti2, Ti5 and Ti8 were 563, 609, 609 and 623 °C, respectively. To avoid the influence of the crystal growth stage, heat-treatments of the Ti*x* samples were purposely carried out under same conditions (450 °C, 2 h; 600 °C, 2 h), in which the temperature (600 °C) set for crystal growth was higher than the crystallization temperature of sample Ti0, whereas it was lower than the crystallization peak temperatures of sample T2, Ti5 and Ti8.

Fig. 4 shows that Ti*x* samples exhibit surface crystallization. However, thickness of the surface crystallization layer decreases with increasing the content of TiO_2. The data are 1650, 950, 640 and 360 μm for samples Ti0 (the same as Ti0Cr0), Ti2, Ti5 and Ti8, respectively. XRD patterns of the crystallized surface layers of Ti*x* samples presented in Fig. 5 indicate that Ti*x* samples have $LiFeP_2O_7$ as crystalline phase. However, samples Ti2, Ti5, Ti8 depict much stronger crystallization peaks than sample Ti0. In addition, the circled band in the XRD pattern of sample Ti0 suggests that there exists significant residual amorphous phase inside its crystallized surface layer. This band decreases with increasing TiO_2. The decrease in the residual glassy phase is also identified by SEM observations. A large region of amorphous area in sample Ti0 can be observed, and the size of crystals is not uniform (Fig. 5). With increasing TiO_2, the region of amorphous area reduces, and the crystallites become widely distributed. The results show that more crystallites are formed when increasing the content of TiO_2 nucleating agent. As a result, connection or aggregation of the crystallites is visualized. Both the SEM and XRD results have proved that the content of crystallites in the crystallized surface layers increases with the content of TiO_2. Since the crystallized surface layers decrease in the thickness with TiO_2, the increased crystallites in the crystallized surface layer can only be as a result of more nuclei formed by the increasing addition of the nucleating agent.

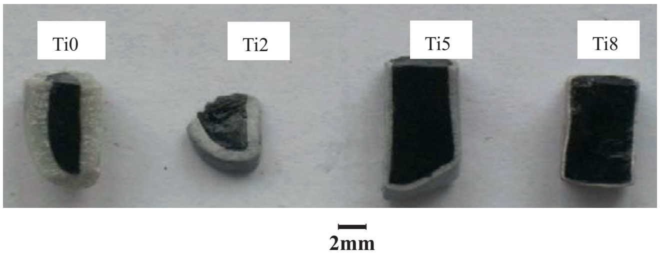

Fig.4. Digital photos showing the thickness of the crystallized surface layers of the heat-treated samples containing different amounts of TiO_2.

The reason why Ti0 has the thickest surface crystallization layer is due to the fact that the temperature set for the crystal growth process for sample Ti0 is higher than its crystallization temperature. In contrast, this temperature for other samples is lower than their crystallization temperatures. Therefore, Ti0 has the fast crystal growth rate. However, Ti0 is more amorphous because it has fewer nuclei than the other samples. The low density of nuclei of Ti0 may also contribute to its fast crystal growth, as otherwise more nuclei would initiate more crystallization, which increases glass viscosity and retards the crystal growth.

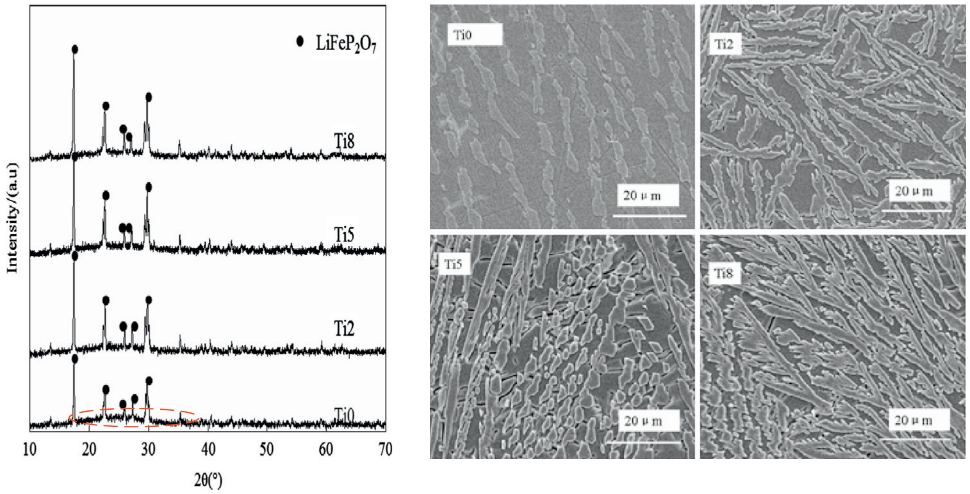

Fig. 5. XRD patterns and SEM images of the crystallized layers of the samples containing different amounts of TiO_2 .

4. Conclusions

Study on the crystallization of lithium–iron-phosphate glasses containing different types and amounts of nucleating agents indicates that the addition of nucleating agents could increase the tendency to bulk crystallization of the glass. However, no bulk crystallization really occurred in the glasses containing the nucleating agents. Instead, the nucleating agents enhance the surface crystallization of the lithium–iron-phosphate glass. The complex agents of TiO_2 and Cr_2O_3 show the most profound effect on promoting the surface crystallization. In addition, the nucleating stage is important when using nucleating agents to improve the surface crystallization.

Acknowledgment

This work was financially supported by National Key Scientific Instruments and Equipment Development Special Fund (2011YQ140145) and the opening projects foundation from State Key Laboratory of Crystal Material, Shandong University.

References

[1] G.P. Kothiyal, A. Ananthanarayanan, G.K. Dey, Glass and glass–ceramics, Functional Materials (2012) 323–386.
[2] D.E. Day, Z. Wu, C.S. Ray, P. Hrma, Journal of Non-Crystalline Solids 241 (1998) 1–12.
[3] D. Sola, J.I. Peña, Foamy coating obtained by laser ablation of glass ceramic substrates at high temperature, Applied Surface Science 255 (2009) 5322–5328.
[4] V.A.C. Haanappel, V. Shemet, S.M. Gross, T. Koppitz, N.H. Menzler, M. Zahid, W.J. Quadakkers, Behaviour of various glass–ceramic sealants with ferritic steels under simulated SOFC stack conditions, Journal of Power Sources 150 (2005) 86–100.
[5] K. Nagamine, K. Hirose, T. Honma, T. Komatsu, Lithium ion conductive glass–ceramics with $Li_3Fe_2(PO_4)_3$ and YAG laser-induced local crystallization in lithium iron phosphate glasses, Solid State Ionics 179 (2008) 508–515.
[6] C.P. Yoganand, V. Selvarajan, V. Cannillo, A. Sola, E. Roumeli, O.M. Goudouri, K.M. Paraskevopoulos, M. Rouabhia, Characterization and in vitro-bioactivity of natural hydroxyapatite based bio-glass–ceramics synthesized by thermal plasma processing, Ceramics International 36 (2010) 1757–1766.
[7] P. Sengupta, A review on immobilization of phosphate containing high level nuclear wastes within glass matrix—present status and future challenges, Journal of Hazardous Materials 236 (2012) 17–28.
[8] A. Marotta, A. Buri, F. Branda, Surface and bulk crystallization in non-isothermal devitrification of glasses, Thermochimica Acta 40 (1980) 397–403.
[9] P.M. Mcmilan, Glass–Ceramics (Ver.2), Academic Press, Britain, 1979.
[10] M. Erol, S. Küçükbayrak, A. Ersoy-Meriçboyu, Influence of particle size on the crystallization kinetics of glasses produced from waste materials, Journal of Non-Crystalline Solids 357 (2011) 211–219.
[11] A. Karamanov, M. Pelino, A. Hreglich, Sintered glass–ceramics from Municipal Solid Waste-incinerator fly ashes—Part I: the influence of the heating rate on the sinter-crystallisation, Journal of the European Ceramic Society 23 (2003) 827–832.
[12] M.S. Whittingham, Lithium batteries and cathode materials, Chemical Reviews 104 (2004) 4271–4301.
[13] K. Hirose, H. Tsuyoshi, Y. Benino, T. Komatsu., Glass–ceramics with $LiFePO_4$ crystals and crystalline patterning in glass by YAG laser irradiation, Solid State Ionics 178 (2007) 801–807.
[14] I. Gorzkowska, P. Jozwiak, J.E. Garbarczyk, M. Wasiucionek, C.M. Julien, Study on glass transition of lithium–iron phosphate glasses, Journal of Thermal Analysis and Calorimetry 93 (2008) 759–762.
[15] R.J. Yang, Y.H. Wang, H.L. Liu, S.Q. Liu, Study on the addition of SiO_2 into lithium–iron-phosphate glass, Advances in Materials Research 306–307 (2011) 1623–1626.
[16] R.J. Yang, H.L. Liu, Y.H. Wang, W.L. Jiang, X.P. Hao, J. Zhan, S.Q. Liu, Structure and properties of ZnO-containing lithium–iron-phosphate glasses, Journal of Alloys and Compounds 513 (2012) 97–100.
[17] J.S. Lee, C.K. Hsu, The devitrification behavior of calcium phosphate glass with TiO_2 addition, Thermochimica Acta 333 (1999) 115–119.
[18] P. Alizadeh, V.K. Marghussian, Effect of nucleating agents on the crystallization behaviour and microstructure of SiO_2–CaO–MgO (Na_2O) glass–ceramics, Journal of the European Ceramic Society 20 (2000) 775–782.
[19] G.A. Khater, Influence of Cr_2O_3, LiF, CaF_2 and TiO_2 nucleants on the crystallization behavior and microstructure of glass–ceramics based on blast-furnace slag, Ceramics International 37 (2011) 2193–2199.
[20] G. Murali Krishna, Y. Gandhi, N. Venkatramaiah, R. Venkatesan, N. Veeraiah, Features of the local structural disorder in Li_2O–CaF_2–P_2O_5 glass–ceramics with Cr_2O_3 as nucleating agent, Physica B 403 (2008) 702–710.