THE EFFECT OF TiO_2 ADDITION ON THE CRYSTALLIZATION OF $\text{Li}_2\text{O-Fe}_2\text{O}_3\text{-MnO}_2\text{-CaO-P}_2\text{O}_5\text{-SiO}_2$ GLASS

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Abstract The excess addition of TiO_2 to $\text{Li}_2\text{O-Fe}_2\text{O}_3\text{-MnO}_2\text{-CaO-P}_2\text{O}_5\text{-SiO}_2$ (LFMCPS), forming the $\text{Li}_2\text{O-Fe}_2\text{O}_3\text{-MnO}_2\text{-CaO-P}_2\text{O}_5\text{-SiO}_2\text{-TiO}_2$ (LFMC PST) system. The effect of TiO_2 addition on the crystallization process of LFMC PST glass was studied with differential analysis (DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM). The DTA curves shows three-stage crystallization, varies from 650°C to 850°C for different TiO_2 content. The phase in the LFMCPS glass with TiO_2 was Li_2SiO_3 , $\text{Ca}_4\text{P}_6\text{O}_{19}$, CaTiO_3 , LiFeO_2 and Li_2TiO_3 , when the sample C crystallization at 700°C for 1h. In the crystallization temperature from 750°C to 850°C at various duration time, the crystallization phases of Fe_3O_4 was detected, except the phases Li_2SiO_3 , $\text{Ca}_4\text{P}_6\text{O}_{19}$, CaTiO_3 , LiFeO_2 and Li_2TiO_3 .

INTRODUCTION

Recently, A-W glass-ceramics containing apatite and wollastonite,^{1,2} and $\text{MgO-CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-P}_2\text{O}_5$ glass-ceramic displaying a high mechanical strength,³ have been already clinically used as artificial middle ear bone, iliac bone spacer, and tooth root, etc. Hydroxyapatite and apatite and wollastonite containing glass-ceramic have also been used to fill bone defects after curettage

of bone tumors.^{4,5}

The phase containing lithium ferrite and hematite in an Al_2O_3 - SiO_2 - P_2O_5 glass matrix,⁶ and precipitation of magnetic from glasses has been studied by several workers,⁷⁻⁹ Furthermore, the crystallization of Li_2O - Fe_2O_3 - MnO_2 - CaO - P_2O_5 - SiO_2 (LFMCPS)glass have been reported.¹⁰ However, an extensive literature search showed that details of the crystallization related to the addition of TiO_2 to the Li_2O - Fe_2O_3 - MnO_2 - CaO - P_2O_5 - SiO_2 (LFMCPS) system have not been reported.

The present paper was aimed at revealing the effect on TiO_2 addition on the crystallization of Li_2O - Fe_2O_3 - MnO_2 - CaO - P_2O_5 - SiO_2 glass by using differential thermal analysis(DTA), X-ray diffraction(XRD) and scanning electron microscopy(SEM).

EXPERIMENTAL PROCEDURE

The test materials used for preparing the glasses were following analytical grade reagents: Li_2CO_3 , Fe_2O_3 , MnO_2 , CaCO_3 , $\text{Ca}(\text{PO}_4)_2$, SiO_2 and TiO_2 . Chemical compositions of the glasses were listed in Table 1. All samples obtained in 100g batches of the described composition were accurately weighed and well premixed powders. The batches were transferred into a platinum crucible and melting at 1450°C in an electron furnace for 2h. After homogenizing, the melt was cast onto a 450°C hot stainless steel plate, and transferred to an annealing furnace held at 450°C for 2h. Finally, a dark colored glass was obtained.

Differential thermal analysis was conducted in the temperature range of 25

°C to 1000°C . The 200mg powder samples (67 , 48µm) were heating in air at a rate of 10°C/min by PERKIN-ELMER 7 series thermal analysis system . Powder Al₂O₃ was used as the reference material.

The crystalline phase was identified by XRD analysis, using a Rigaku X-ray diffractometer Cu Kα radiation and a Ni filter , at a scanning rate (2θ) of 0.25°/min .

JEOL JSM-840 scanning electron microscope was to examine the surface of the polished sample, etched (5 parts HF, 2 parts HCl, and 93 parts H₂O) and coated with a thin gold film.

Table 1 Chemical composition of LFMCPST glasses (wt%)

Sample	Oxides						
	Li ₂ O	Fe ₂ O ₃	MnO ₂	CaO	P ₂ O ₅	SiO ₂	TiO ₂ (excess)
A	10	14	11	25	5	35	2
B	10	14	11	25	5	35	4
C	10	14	11	25	5	35	6

RESULT AND DISCUSSION

DTA curves from the 48-67µm size fraction of LFMCPST glass C at a heating rate of 10°C/min was shown in Fig.1. The glass transition temperature (T_g) was indicated by the base line shift at about 542 °C . The single T_g suggests the existence of compositionally homogeneous amorphous state in the as-annealed glass. The curve showed a three-stage crystallization corresponding to temperature of T_{c1}=679°C , T_{c2}=742°C and T_{c3} =832°C .

Hsi and Wang¹⁰ explored the various phases in the LFMCPST glass system as a function of crystallization temperature. For the composition (wt%) of 10Li₂O-14Fe₂O₃-

11MnO₂-25CaO-5P₂O₅-35SiO₂, the crystallization phase were triphylite after 700°C for 6h. On heating to 800°C for 1h, the specimen contained triphylite, β -wollastonite and magnetite.

Fig.1 DTA curve of glass C for a heating rate of 10°C/min.

Figure 2 illustrates the diffraction patterns of the LFMCPST glasses crystallization at 700°C for 1h, respectively. The d-spacings of the principal crystalline phase precipitated were identical to those of the Li₂SiO₃, CaTiO₃, LiFeO₂ and Li₂TiO₃ and Ca₄P₆O₉.

Fig.2 XRD pattern of sample C crystallization at 700°C for 1h.

L: Li₂SiO₃, C: Ca₄P₆O₁₉, T: CaTiO₃, F: LiFeO₂, O: Li₂TiO₃

As the crystallization temperature of sample C increases from 750°C to 850°C, and duration for 6h, the XRD pattern of $\text{Ca}_4\text{P}_6\text{O}_9$ and Fe_2TiO_5 phases to be improved and the peaks of FeFe_2O_4 phase was observed. Figure 3(a) illustrate the XRD pattern of glass B crystallization at 850°C for 6h, indicating further development of CaTiO_3 , LiFeO_2 and LiTiO_3 precipitated. Although the phase of Fe_3O_4 was first appear, but the intensity of FeFe_2O_4 is grater than that the phase of Li_2SiO_3 .

Figure 3(b) illustrate the diffraction pattern of glass B crystallized at 850°C for 24h. For the 6h and 24h, indicating that the crystallinities of the crystalline phases are the same.

Fig.3 XRD pattern of sample B crystallization at 850°C for (a) 6h, and (b) 24h, respectively.

L: Li_2SiO_3 , C: $\text{Ca}_4\text{P}_6\text{O}_{19}$, T: CaTiO_3 , F: LiFeO_2 , O: Li_2TiO_3 , A: Fe_3O_4

The SEM micrographs of glass B heat-treated at 700°C for 3h are shown in Figs.4(a) and 4(b). Crystallization is observed to start at the surface of the LFMCPST glass, and then proceeds toward the interior of glass matrix as shown in Fig.4(a), and the proceeds toward the interior of glass matrix [Fig.4(b)]. The core sections of the

sample were dark in color, and remained essentially glassy even after 2h heating at 800 °C [Fig.4(c)]. The nucleating agent TiO_2 might function as a surface active agent by reducing the interfacial free energy between the crystal and amorphous matrix.^{11,12} At the center of the large crystals which have a characteristic dendrites shape, small dark nuclei are still visible. The morphology and size of the crystallized phase change with the degree of crystallization which increases with increasing heat-treatment temperature and time [Fig.4(d)].

Fig 4 SEM micrographs of surface morphology of the crystallized glass B showing the progressive development of crystal growth : (a) heat-treated at 700 for 3h, showing the crystallized, interfacial, and uncrystallized glass region; (b) glass phase containing crystalline particles; (c) heat-treated at 800°C of 2h, showing the light dendrites phase; (d) heat-treated at 850°C for 3h, showing the polished and etched surface of fully crystallized part.

CONCLUSION

The effect of TiO_2 addition on the crystallization in $10\text{Li}_2\text{O}-14\text{Fe}_2\text{O}_3-11\text{MnO}_2-25\text{CaO}-5\text{P}_2\text{O}_5-35\text{SiO}_2$ glasses have been studied. The d-spacing of the major crystallites were precisely measured and fitted with those of the Li_2SiO_3 , $\text{Ca}_4\text{P}_6\text{O}_{19}$, CaTiO_3 , LiFeO_2 , Li_2TiO_3 and Fe_3O_4 . Crystallization started at the surface of the glasses samples and then proceed toward the interior of the glass matrix.

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