

Micro-Raman Spectroscopy Studies of the Phase Separation Mechanisms of Transition-Metal Phosphate Glasses

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[Glass-ceramics are materials prepared by controlled devitrification of a glass resulting in crystalline phases. The homogeneity of the glass, along with the controlled development of crystals, led to a glass-ceramic with a uniform grain structure free from porosity. Production of porous glass-ceramics involves leaching of soluble phases to achieve a porous structure formed by the insoluble phases, with potential applications in the fields of nanotechnology and integrated chemical systems. Here, glass/ceramic interfaces of niobo-, vanado- and titano-phosphate glasses were analyzed by micro-Raman spectroscopy. The intrinsic spatial resolution of micro-Raman spectroscopy was helpful in evaluating the multiphase nature of the systems as well as for identification of devitrification mechanisms: spinodal-type separation or crystallization. Interface-controlled crystallization –surface crystallization by heterogeneous nucleation– has been evidenced for the niobophosphate and vanadium-phosphate glasses considering that the interface composition remained unchanged as the crystallization front advanced. In the titanophosphate glasses, a continuous change of the composition of the phases with time, occurs until the equilibrium phases are attained. This behavior is typical of spinodal-type phase separation. Both phase separation mechanisms were monitored by micro-Raman spectroscopy.]

INTRODUCTION

Porous materials are extremely important in the fields of nanotechnology, integrated chemical systems, and reactions performed in confined environment due to cooperative interactions. There is an increasing interest in designing and developing porous materials with stable porous textures for high-temperature separation and catalytic applications. A template-free route for preparation of advanced functional porous support is the controlled devitrification of a glass resulting in crystalline phases followed by a leaching step. Phase transformation in glasses can occur either by spinodal separation or crystallization. In spinodal separation, a continuous change of composition occurs until equilibrium values are attained and the interface is initially very diffuse but sharpens gradually¹. In crystallization, the composition of the second phase remains unaltered in time and the interface between the phases is always sharp during the growth. In this paper we employed the intrinsic spatial resolution of micro-Raman spectroscopy in evaluating the multiphase nature of the system as well as for identification the devitrification mechanism in niobo-, vanado- and titano-phosphate glasses.

EXPERIMENTAL PROCEDURE

Glass samples of nominal composition 6Li₂O-18Nb₂O₅-43CaO-33P₂O₅ (LNCP), 6Li₂O-18V₂O₅-43CaO-33P₂O₅ (LVCP) and 6Li₂O-24 TiO₂-39CaO-31P₂O₅ (LTCP) (mol%) were prepared by melting reagent grade raw materials in a platinum crucible at 1350 °C for 1 h under air. Melts were poured onto carbon plates and annealed at 550 °C for 1 h. Phase transformations were carried out at 830, 600 and 7600 °C, respectively, for different times. The Raman spectra were recorded on a Renishaw System 3000 Raman Imaging Microscope

(ca. 1 μm spatial resolution) using a He-Ne laser (632.8 nm) and 8 mW of power before the entrance optics. SEM was performed by using a JEOL JSM T-300 Microscope.

RESULTS AND DISCUSSION

The presence of a glass/ceramic interface in the niobophosphate glass, after heat treatment at 830 $^{\circ}\text{C}$ for 2 min, (Fig.1a) suggested the occurrence of crystallization. The Raman spectrum of region (A) in Fig. 1b is very similar to that recorded for the original glass, suggesting that this region presents a glassy characterⁱⁱ. At the nucleated region [Fig. 1, region (B)], the spectrum presents a band at 914 cm^{-1} (typical of short Nb-O bonds in glass structures) and a band at 1047 cm^{-1} , assigned to P-O stretching from $\beta\text{-Ca}_2\text{P}_2\text{O}_7$. At the interface [Fig. 1, region (C)], the intensity of the band at 914 cm^{-1} decreases as that of the band at 1047 cm^{-1} increases and two new $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ bands at 739 cm^{-1} and 487 cm^{-1} are observed. At the crystalline region close to the interface [Fig.1, region (D)], the band at 914 cm^{-1} is no longer observed, and only those assigned to $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ are seen. At the crystalline region distant from the interface [Fig.1, region (E)], the Raman spectrum is rather different from that recorded for region (D). Bands at 1016 cm^{-1} [$\nu(\text{P-O})$], 990 cm^{-1} [$\nu(\text{P-O})$], 805 cm^{-1} [$\nu(\text{Nb=O})$], 462 cm^{-1} , 376 cm^{-1} and 289 cm^{-1} , the last three assigned to the [$\delta(\text{O-P-O})+\delta(\text{O-Nb-O})$] deformation, indicate the presence of $\alpha\text{-NbPO}_5$. At the region (E), in Fig. 1, the most intense $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ bands (1047 cm^{-1} and 739 cm^{-1}) appear as weak signals, as a result of the presence of the very strong Nb=O band at 805 cm^{-1} . As the crystallization front advances, the interface composition remains unchanged, providing evidences of interface-controlled crystallization.

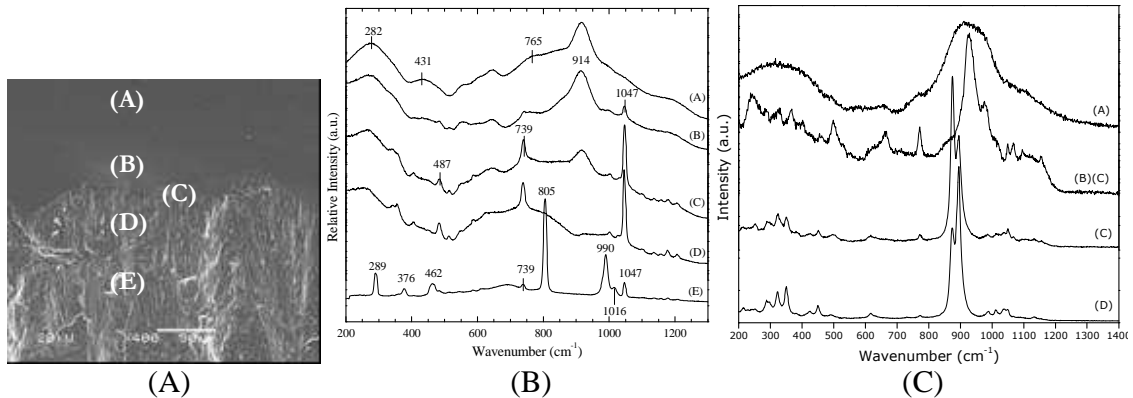


Figure 1 – (a) SEM image of the glass/ceramic interface obtained after thermal treatment of LNCp and LVCP glasses and Raman spectra of the analyzed regions of (B) LNCp and (C) LVCP glasses systems.

The glass/ceramic interface observed in Fig.1a is similar to that obtained for LVCP glass system after thermal treatment at 600 $^{\circ}\text{C}$ for 5 min. The Raman spectrum of region (A) in Fig. 1c is similar to that recorded for the original glassⁱⁱⁱ. Spectra of regions (B) and (C) are similar and indicate the nucleation of different phases. The Raman spectra of regions (D) and (E) present two bands at 880 and 900 cm^{-1} assigned to $\beta\text{-Ca}_2\text{V}_2\text{O}_7$ ($\text{V}_2\text{O}_7^{4-}$ groups) and $\beta\text{-Ca}_3(\text{VO}_4)_2$ (VO_4^{3-} groups), respectively. In region (D) the band of $\text{V}_2\text{O}_7^{4-}$ groups is more

intense while in region (E) the band of VO_4^{3-} groups is more intense indicating the phase transition. The increase of $\beta\text{-Ca}_3(\text{VO}_4)_2$ amount allows the preparation of porous glass-ceramic with small pores due to the solubility of this phase in acidic medium.

In LTCP glass system, the phase transformation occurs by spinoidal decomposition^{iv v}. Fig. 2a show that the interface is very diffuse and Raman spectra confirms compositional variation for samples with identical devitrification times (Fig. 2b) and a continuous composition change until the equilibrium value is attained (Fig. 2c), which occurs after 5 min of thermal treatment. The spinodal decomposition of LTCP glass yielding the $(12-x)\text{LiTi}_2(\text{PO}_4)_3 + (13-2x)\beta\text{-Ca}_3(\text{PO}_4)_2 + x\text{Li}(\text{TiO})\text{PO}_4 + 3x\beta\text{-Ca}_2\text{P}_2\text{O}_7 + x\text{TiO}_2$ (where $0 \leq x \leq 6$) depends on the thermal treatment conditions.

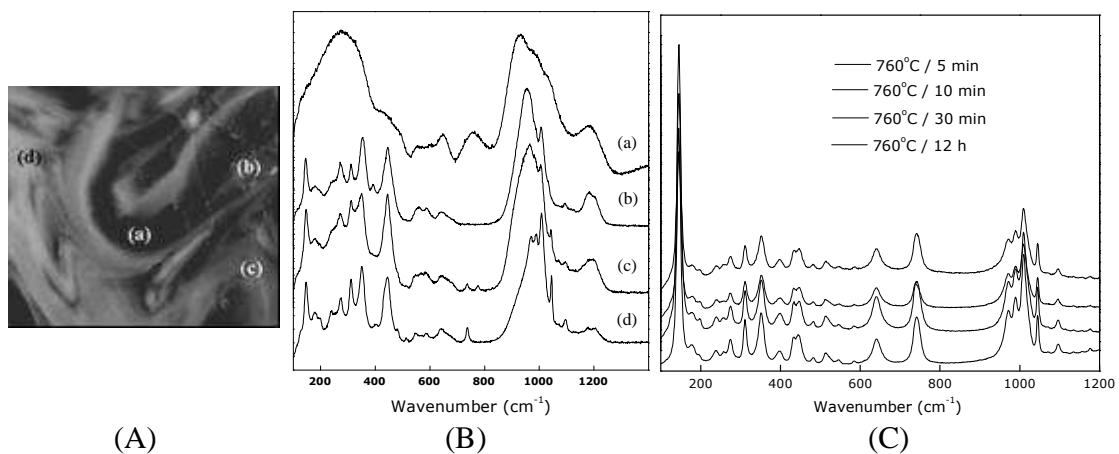


Figure 2 - (A) Optical microscopy image of the diffuse interfaces obtained after 2 min of the thermal treatment of LTCP glass and Raman spectra of the (B) regions of the Fig. 1a and at (C) different times of thermal treatment.

CONCLUSION

The micro-Raman spectroscopy was applied as a powerful tool for investigation of phase transformations as a function of time of thermal treatment of glasses, allowing the evaluation of multiphase nature of the samples as well as monitoring phase transitions and identification of the devitrification mechanism: spinodal-type separation or crystallization.

ⁱ Strnad Z, in *Glass-ceramic materials* (Elsevier, Amsterdam, 1986).

ⁱⁱ Mazali, I.O., Barbosa, L.C., Alves, O.L., *J. Mater. Sci.* **39**, p. 1987-1995 (2004).

ⁱⁱⁱ Mazali, I.O., Alves, O.L., *J. Braz. Chem. Soc.* **15**, p. 464-467 (2004).

^{iv} Hosono, H., Abe, Y., *J. Non-Cryst. Solids* **190**, p. 185-197 (1995).

^v Gimenez, I.F., Mazali, I.O., Alves, O.L., *J. Phys. Chem. Solids* **62**, p. 1251-1255 (2001).