Different roles of phosphorus in the nucleation of lithium aluminosilicate glasses

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ABSTRACT

Glasses in the Li_2O–Al_2O_3–SiO_2 (LAS) system with different $\frac{Al_2O_3}{Li_2O}$ ratio and with or without addition of P_2O_5 have been synthesized and characterized by thermal analysis. The glass structure and the phosphorus environments in the glasses and their evolutions with annealing have been studied by ^{31}P Solid-State Nuclear Magnetic Resonance (NMR) and $^{27}Al\{^{31}P\}$ D-HMQC (Dipolar Hetero-nuclear Multiple-Quantum Coherences) NMR correlation technique. The crystallization behavior has been studied by X-ray diffraction, NMR and Raman spectroscopy. The results showed a different role for P_2O_5 depending on the $\frac{Al_2O_3}{Li_2O}$ ratio. For low alumina content, P_2O_5 plays a nucleating role while it acts as crystallization inhibitor for high alumina content. These different roles are related to different local environments of the phosphorus in the as-cast glasses. Our study emphasizes the importance of POAl complexes in the crystallization of aluminosilicate glasses.

1. Introduction

Glass-ceramics are materials obtained by controlled crystallization of glasses, which is achieved by thermal treatments on parent glasses [1]. The lithium aluminum silicate ternary system is one of the most studied and a large number of materials with this composition are commercialized due to their excellent thermo-physical properties. As typical examples we can mention the near-zero thermal expansion property for β-quartz solid solution glass-ceramics used for telescope mirror, stove cooktops and firedoor applications [2, 3], or the good mechanical properties for compositions with low amount of Al_2O_3 used in the field of restorative dentistry [4]. Since the properties of the glass-ceramics are widely dependent of the nature and relative amount of crystalline phases, the control of nucleation is a key step in order to optimize the final properties. To promote bulk crystallization and obtained an uniform distribution of crystals in the material, nucleating agents such as TiO_2, ZrO_2 and P_2O_5 are typically added in the Li_2O–Al_2O_3–SiO_2 (LAS) glass composition [5-7]. In particular, phosphorus, which is classified as a typical network former in glasses, has a complex structural role that strongly impacts its solution behavior, the melt viscosity [8] or its ability to promote liquid-liquid separation and affects the crystallization mechanisms [9].

In a study on the effect of the $\frac{Al_2O_3}{M_2O}$ ratio (where M = Li, Na) on the crystallization of LAS system with P_2O_5 addition [10], different crystalline phases were reported depending on the Al_2O_3 content. Volume crystallization was observed at low Al_2O_3 amount contrary to surface crystallization observed at high alumina content. Indeed, P_2O_5 is a well-known nucleating agent for low alumina LAS compositions, yielding $Li_2Si_2O_5$ crystallization [5, 11-14]. In terms of nucleation mechanism, Headley and Loehman [15] reported that lithium orthophosphate Li_3PO_4 crystals act as heterogeneous nuclei for silicate crystalline phases (lithium metasilicate Li_2SiO_3 and lithium disilicate $Li_2Si_2O_5$ phases). Successive studies using Solid-State ^{31}P MAS-NMR gave insight on the changes around phosphorus occurring during the crystallization processes [16-18]. Indeed, MAS-NMR techniques probe the local environment around phosphorus and reveal modifications occurring in the first crystallization steps which could conceivably be missed by other techniques [19]. On a disilicate (aluminum-free) glass-ceramic composition, Holland et al. [16] reported that crystalline Li_3PO_4 was not detected by MAS-NMR before the formation of $Li_2Si_2O_5$ phases. However, recent studies revealed that a highly disordered Li_3PO_4 phase is formed concomitantly with Li_2SiO_3 crystallization [17, 18].

In aluminosilicate glasses, MAS-NMR showed that phosphorus has different environments depending on the $\frac{Al_2O_3}{M_2O}$ ratio [20, 21]. At low P_2O_5 content, a majority of PO_4^{3-} orthophosphate and $P_2O_7^{4-}$ pyrophosphate groups are observed in the glass matrix, while for increasing Al_2O_3 contents, aluminophosphate groups are formed. Recent developments in NMR provide information on the connectivity of PO_4 tetrahedra with the aluminosilicate network. Spatial proximities between P and Al were reported in systems with low amount of P_2O_5 and Al_2O_3 [22, 23] and aluminophosphate groups could be detected in such glasses. Nevertheless, such methods were not used up to now for the detailed study of the nucleation process by P_2O_5 in LAS glass-ceramics. The aim of the present work is to provide a better comprehension of the role of phosphorus in crystallization mechanisms by looking at the phosphorus environment in different LAS compositions with different $\frac{Al_2O_3}{Li_2O}$ ratios. We report a combination of characterization and spectroscopic methods to investigate the crystallization sequences and the nucleating role of phosphorus. NMR and Raman spectroscopies enable us to discuss the changes in the phosphorus environments in relation with the crystallization, showing a different behavior between the glasses containing low and high Al_2O_3 contents.

2. Experimental section

2.1. Materials

Glasses were prepared in the Li_2O–Al_2O_3–SiO_2 ternary system with addition of P_2O_5 oxide as a nucleating agent. Analytical grade precursors Li_2CO_3 (Sigma Aldrich, 99%), Al_2O_3 (Merck, 99.9%), SiO_2 (Alfa Aesar, 99.5%) and $(NH_4)_2HPO_4$ (Sigma Aldrich, 98%) were ground together, dried and melted in a Pt crucible at 1550 °C for 2 h, then quenched by immersing the bottom of the crucible into water. The glasses were ground and molten once again to ensure a good homogeneity. Table 1 reports the nominal and analyzed glasses compositions. They are located along the 74 mol% SiO_2 isopleth, with 0 or 1 mol% P_2O_5. These compositions cover a range with a ratio R = $\frac{Al_2O_3}{Li_2O}$ from 0 (Al-free) to 1.3 (peraluminous composition). The glasses are labeled as follows: LASR-Pn, where R is the ratio $\frac{Al_2O_3}{Li_2O}$ and n the mol% of P_2O_5. Transparent, bubble free, glasses were obtained excepted for the LAS0-P1, which is opalescent. For all samples, powder X-ray diffraction patterns show the characteristic broad peak of amorphous materials with no observable Bragg peaks. The glasses compositions were checked by Electron Probe Micro-Analyser (EPMA, CAMPARIS, Paris, France) with a CAMECA SX-Five apparatus equipped with five Wavelength-Dispersive X-ray Spectrometers (WDSs) for SiO_2, Al_2O_3, P_2O_5 and by Flame-Atomic Emission Spectroscopy (F-AES) with a Agilent AA280FS apparatus for Li_2O content. For EPMA, with the instrument operating at 15 kV and 10 nA, we used a 5 μm spot size. The standards

for calibration were orthoclase for silicium and aluminum, and apatite for phosphorus. 20 points were taken and obtained compositions were averaged. Glasses compositions were homogeneous according EPMA.

2.2. Differential scanning calorimetry

Differential Scanning Calorimetry (DSC) thermograms were recorded on a 404 C Pegasus calorimeter from Netzsch (Selb, Germany). All the measurements were carried out in air and heat treatments were conducted at 10 °C·min^{-1} with a bulk sample of ~50 mg in Pt crucible, using an empty Pt crucible as reference. The glass transition temperature T_g, the onset crystallization temperature T_x of the first exothermic event and the temperature of the maximum of the first exothermic event T_c are reported in Table 1 for each composition.

2.3. X-ray diffraction

X-ray diffraction (XRD) was carried out at room temperature using a diffractometer (PANalytical X'Pert PRO) with Ni-filtered CuKα radiation (λ = 1.5418 Å). Data were recorded in the 5° ≤ 2θ ≤ 80° range with a step increment of 0.016° and an interval time of 0.82 s per step.

2.4. Raman spectroscopy

Raman spectra of the glasses and annealed glasses were obtained using a Horiba LabRam HR Evolution system with Ultra-Low Frequency (ULF) module, 1800 gr/mm grating, and a 532 nm laser operating at 100 mW. A ×10 magnification objective was used for this study. Each sample was analyzed with an exposure time of 30 s (per window) with 10 accumulations and a spectral window from 5 to 2000 cm^{-1}. No temperature correction nor normalization have been used for these spectra.

2.5. Scanning electron microscopy

Scanning electron microscopy (SEM) was used to observe the microstructure of the samples. Bulk material pieces were embedded in epoxy resin, then cross sections were polished and etched with 1% HF for 30 s. They have been coated with iridium (2 nm thick) and observed using a SEM-FEG (Field Emission Gun) ZEISS LEO 1550 (Jena, Germany), at a 5 kV accelerating voltage. Observations have been done with the In-lens secondary electrons detector.

2.6. Solid-state NMR

^{31}P and ^{27}Al MAS-NMR (Magic Angle Spinning Nuclear Magnetic Resonance) spectra were recorded at 9.4 and 18.8 T on Bruker AVANCE

Table 1

Analyzed compositions (mol%) by EPMA and F-AES of the glasses investigated in this study, nominal compositions are in parentheses. Errors are typically less than 0.3% relative on SiO_2, less than 0.7% relative on Al_2O_3, less than 3% relative on P_2O_5 and 2% relative on Li_2O. R = $\frac{Al_2O_3}{Li_2O}$. T_g is the glass transition temperature, T_x is the onset crystallization temperature of the first exothermic event and T_c is the temperature of the maximum of the first exothermic event determined from the DSC curves. The error in the determination of T_g, T_x and T_c is estimated close to ± 2 °C.

Glass	SiO_2	Al_2O_3	Li_2O	P_2O_5	R	T_g (°C)	T_x (°C)	T_c (°C)	$T_x - T_g$ (°C)
LAS0-P0	74.4 (74.22)	0.3 (0.00)	25.3 (25.78)	0.01 (0.00)	0.01 (0.00)	483	659	764	176
LAS0-P1	73.6 (73.46)	0.2 (0.00)	25.1 (25.52)	1.1 (1.02)	0.01 (0.00)	477	606	635	129
LAS0.2-P0	75.7 (74.23)	4.6 (4.13)	19.7 (21.64)	0.02 (0.00)	0.23 (0.19)	507	660	832	153
LAS0.2-P1	74.3 (73.47)	4.2 (4.08)	20.7 (21.42)	0.8 (1.02)	0.20 (0.19)	509	592	646	83
LAS0.4-P0	74.5 (74.23)	7.4 (7.22)	18.1 (18.55)	0.01 (0.00)	0.41 (0.39)	536	651	770	115
LAS0.4-P1	75.0 (73.48)	7.6 (7.14)	16.4 (18.36)	1.0 (1.02)	0.46 (0.39)	548	617	639	69
LAS0.7-P0	73.6 (74.22)	10.8 (10.31)	15.6 (15.47)	0.01 (0.00)	0.69 (0.67)	594	559	769	65
LAS0.7-P1	73.8 (73.47)	10.2 (10.21)	15.0 (15.30)	1.0 (1.02)	0.68 (0.67)	614	708	840	94
LAS1-P0	74.0 (74.23)	13.2 (12.89)	12.8 (12.89)	0.003 (0.00)	1.03 (1.00)	748	852	922	104
LAS1-P1	73.7 (73.47)	13.0 (12.76)	12.5 (12.76)	0.79 (1.02)	1.04 (1.00)	736	936	1005	200
LAS1.3-P0	74.1 (74.23)	14.7 (14.43)	11.2 (11.33)	0.01 (0.00)	1.32 (1.27)	770	1080	1222	310
LAS1.3-P1	75.0 (73.47)	14.6 (14.29)	9.4 (11.22)	0.96 (1.02)	1.55 (1.27)	778	/	1234	/