The glass-forming ability explained from local structural differences by NMR between glasses and crystals in alkali metaphosphates

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Abstract

The glass forming ability of inorganic substances has traditionally been evaluated in kinetic terms related to the rate of spontaneous crystallization of their melts, which is related to viscosity from the macroscopic point of view. However, differences or similarities between the local structures of glasses and crystals of the same composition could have an additional influence on the kinetic ability to form a stable glass or a crystal from a melt. In this work, the local structure of alkali metaphosphate glasses and crystals has been analyzed by means of ^{31}P MAS-NMR to demonstrate that the ability to form a glass is directly related to the differences between the atomic organization in the glassy states and the structure of the stable crystals at lower temperatures. This implies that chemical compositions having a similar atomic order in their glass and crystal structures will not easily develop the disordered long-range structure of glass.

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1. Introduction

The glass transition phenomenon, concerning all amorphous substances including inorganic and metallic glasses as well as polymers, undoubtedly represents one of the long standing yet unsolved questions in condensed matter physics [1]. It is generally accepted that any composition that is submitted to a quick enough cooling from its equilibrium liquid state can form a room temperature stable glass, and Langer defined well this fact through the words “escaped crystallization” [1]. This phenomenon has been explained from macroscopic properties and atomic structures approaches. From the point of view of macroscopic properties, viscosity is considered the critical factor to freeze the disordered structure of melts. From a local structural point of view, the first to wonder on the glass forming ability of inorganic oxides was Goldschmidt, who found that the ratio between the radius of the central atom to that of the oxygen should be comprised between 0.2 and 0.4. Later on, in his original work of 1932, W.H. Zachariasen postulated the four known rules that must be fulfilled by any oxide to be able to form a glass [2]. Among other more common glass-forming oxides such as SiO_2 and B_2O_3 , P_2O_5 is also able to form glass and, due to the particular chemical characteristics of phosphorus, the phosphate-based glasses present a different network structure from silicates, that is not fully polymerized and what causes great changes in their properties when compared to silicate or borate glasses [3]. Phosphate-based glasses possess a good glass forming ability and an extraordinary flexibility to allocate big cations in their networks, as well as a significant capacity to mix with second glass former elements or substitute the oxygen atoms by a variety of other anionic species. However, in the very simple case of binary alkali metaphosphate glasses ($\text{O/P}=3$) one surprisingly finds an area of very limited glass formation at the potassium composition. In this sense, the crystallization and glass-stability parameters upon heating of alkali

metaphosphate glasses has been particularly studied for LiPO_3 and NaPO_3 [4-7], while K, Rb and Cs have been rarely considered, precisely due to this lack of glass formation. There is been attempts to make appropriate relationships between the glass forming ability and the glass-stability, nonetheless with some discrepancies. For instance, Weinberg claimed that the two concepts are independent [8]. However, Nascimento et al. have concluded more recently that in certain cases, where the glasses predominantly show heterogeneous nucleation at the laboratory time-scales, glass-forming ability and glass-stability may be well correlated [9].

From another perspective, Chen et al. studied the crystallization tendency or glass-forming ability by comparison of the structural similarities in alkali diborate glasses and crystals [10]. In their work, they showed that there is a strong correlation between the structural similarities of glasses and crystals and the nucleation mechanism, being the last heterogeneous if the glass and crystal possess different structure, while it will be homogeneous if glass and crystal have the same structure.

The aim of this work was to investigate the glass forming ability of alkali metaphosphate glasses in terms of the relationships between the structure of the glasses with that of the crystalline phases formed upon crystallization from the melts, for which the structure of the glasses and the corresponding crystalline phases has been analyzed by ^{31}P Nuclear Magnetic Resonance.

2. Experimental methods

The alkali metaphosphate glasses were obtained by melting stoichiometric mixtures of reagent grade materials using porcelain crucibles. The batches were obtained by thoroughly mixing alkali carbonates and $(\text{NH}_4)_2\text{HPO}_4$, calcined at 400°C overnight and melted for 2 h at 800°C . The melts were then poured onto a pre-heated brass mold and

annealed above their respective glass transition temperature. KPO_3 and RbPO_3 compositions were obtained vitreous after pouring the melts and quickly pressing the liquids between steel plates to prevent crystallization. On the other hand, fully crystallized samples were obtained through slow cooling from melting temperatures of the corresponding liquids at a rate of 5 K.min^{-1} , followed by a 24 h treatment at temperatures below that of crystallization as determined from the DTA cooling patterns. ^{31}P Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) spectra were performed in a Bruker ASX 400 spectrometer at a frequency of 161.96 MHz. Delay times of up to 120 s were employed at a spinning rate of 10 kHz and using $(\text{NH}_4)\text{H}_2\text{PO}_4$ as reference, with a chemical shift of 0.82 ppm with respect to H_3PO_4 (85%) [11]. The spectra were simulated using *dmfit* software [12].

Differential Thermal Analysis (DTA) on cooling from metaphosphate melts were performed in a Netzsch STA 409/C analyzer using powdered samples in a platinum crucible under static air.

Viscosity data points for KPO_3 composition were obtained by using the rotation method in a cylindrical Searle type viscometer from Haake using a ME1700 sensor. Full details of the experimental procedure were given in reference [13].

3. Results and discussion

The formation of LiPO_3 and NaPO_3 glasses is completely ensured when the melts are submitted to normal quenching conditions, i.e. melts are poured and they are allowed to reach room temperature at a free pace. However, KPO_3 and RbPO_3 developed spontaneous crystallization under the same conditions of cooling from their melts. Figure 1 plots the cooling patterns as obtained from the DTA analyses of the four metaphosphate compositions. The patterns are plotted for cooling rates of 5 K.min^{-1}

except that of KPO_3 composition. While all DTA experiments were firstly obtained at cooling rates of 20 K.min^{-1} , all compositions except KPO_3 did not show crystallization peaks. Therefore, the DTA of the Li, Na and Rb metaphosphate glasses were again performed at 5 K.min^{-1} in order to attribute crystallization peaks with the aim of showing the tendency in the crystallization temperature as a function of the composition under standard laboratory melting procedures.

The starting temperatures of crystallization for KPO_3 and RbPO_3 are the highest at 750°C and 730°C , respectively; the two others being 567°C and 555°C for LiPO_3 and NaPO_3 , respectively. This clearly shows a tendency for the decrease of the crystallization temperature along with the increase of glass formation tendency.

The four metaphosphate glass compositions were analyzed by ^{31}P MAS NMR, whose spectra are shown in Fig. 2. The spectra of Li and Na metaphosphate samples present broad and symmetric resonances of typical amorphous systems centered at -22.85 ppm (width= 9.12 ppm) and -19.99 ppm (width= 7.56 ppm), respectively. Very small additional resonances between 0 and -10 ppm can be barely observed that are attributed to certain amount of less polymerized phosphate tetrahedral $[\text{PO}_4]$ units. The spectrum of KPO_3 shows two much narrower main resonances of similar intensity at -18.37 ppm and -20.03 ppm with a total width of 3.88 ppm . It is worth mentioning here that the XRD pattern of the KPO_3 glass does not show diffraction peaks, but only a broad halo characteristic of amorphous materials. The spectrum of RbPO_3 is again composed of two small resonances at ca. 0 ppm and -10 ppm and a main Gaussian-like resonance at -20.64 ppm with a width of 5.95 ppm . The chemical shift and width of the phosphorus resonances observed in the metaphosphate glasses have been represented in Fig. 3. A single value for the KPO_3 glass has been obtained as average of the two measured phosphorous sites and the width is the total measured for the two signals together. As it

can be seen, the chemical shift and width vary oppositely, showing a maximum and a minimum, respectively, as a function of the ionic radius of the modifier. It is thus clear that the KPO_3 glass represents the limit for the glass formation in the series of alkali metaphosphate glasses. Furthermore, the fact that the width of the ^{31}P resonances is reduced from lithium to potassium is representative of an increased local ordering around phosphorus atoms that peaks at a maximum for the potassium metaphosphate. This result is comparable to the one found by Suzuya *et al.* [14], who studied the structure of alkali phosphate glasses, from ultra- to metaphosphate compositions, by neutron diffraction experiments. They found that the structure factor corresponding to an intermediate length scale (Q_I) between 1.69 and 1.98 $\text{\AA}^{-1}$, first increases up to a maximum at precisely the ionic radius of K, and then decreases for Rb metaphosphate. This fact clearly shows that the glass network ordering at long distances reaches the maximum for the potassium composition in accordance with the minimum of glass forming tendency found here.

Figure 4 depicts the ^{31}P MAS NMR spectra of the four crystallized samples from a glass precursor of identical chemical composition. The spectrum of the crystalline LiPO_3 composition presents five resonances comprised between -22 ppm and -27 ppm, from five different P sites in the crystal structure. The crystal structure of NaPO_3 shows three P sites at lower field values between -15 ppm and -20 ppm. However, the KPO_3 crystals have just two narrow resonances of 0.5 ppm linewidth separated by ca. 2 ppm, at -18.1 ppm and -20.0 ppm. These two lines occur exactly at the same chemical shift that was found in the KPO_3 glass and it suggests that the same short- and medium-range structure in the two materials exist though different long-range order is developed. Also two structural sites separated by ca. 1 ppm were detected for P atoms in the RbPO_3 at -20.5 ppm and -21.5 ppm, in resonances having 1 ppm of linewidth. However, no

splitting was found in the RbPO_3 glass despite the broad signal can be simulated with two Gaussian peaks of the same area at -19.6 ppm and -21.8 ppm, being 4.8 ppm in linewidth. Hence, glass formation is more difficult to attain in the two compositions which crystal and glass structures are similar at the local scale, i.e., in KPO_3 and RbPO_3 as the two cases with two sites for P atoms. In contrast, glass formation is much easier in the other two compositions having different glass and crystal local structures. In particular, the LiPO_3 crystal composition will have a very complex structure containing five different sites for P atoms, in contrast with a disordered dynamic structure in the low temperature precursor, with a wide distribution of atomic environments for P atoms.

As it has also been seen in the NMR spectra of the glasses, the chemical shift values of the resonances seen in Li and Na crystalline samples vary according to the ionic field strength (IFS) of the alkali cations, i.e., the higher the IFS the higher the shielding on phosphorus. However, the signals of the two peaks in the K and Rb samples vary in opposite direction. The electronic shielding on phosphorus atoms is thus affected in different ways for the metaphosphates of cations with lower and higher ionic radius than K. As a consequence of the smaller ionic field strength of potassium ions, the electronic density on phosphorus reaches a maximum that is reflected on the highest chemical shift values observed.

The glass forming tendency of a melt is directly related to slow crystallization rates [9]; however, it is not known what may be the relationship with the short-range order structure of the network and its organization in the equilibrium liquid. High melt viscosities, for example, are related to lower nucleation rates as established by Tammann long ago [15]. The viscosity curves of LiPO_3 and NaPO_3 melts were determined in a previous work [13] and that of KPO_3 recently obtained by the authors

using the same methodology. The measured viscosity values of LiPO_3 , NaPO_3 and KPO_3 melts, at temperatures close to their crystallization points in Fig. 1, are 2.06 dPa.s (575°C), 1.64 dPa.s (550°C) and 0.82 dPa.s (760°C), respectively. If, however, one compares the viscosity at the same temperature, it is found that the three have quite more similar values, being 1.11 dPa.s (750°C) for LiPO_3 , 0.8 dPa.s (750°C) for NaPO_3 and 0.82 dPa.s (760°C) for KPO_3 . At this higher temperature, the three melts are thus comparable in viscosity and, therefore, in atomic kinetics. But only potassium and rubidium metaphosphates crystallize spontaneously upon further decrease of the temperature, suggesting that additional structural factors must be at work.

In a more recent work by Muñoz *et al.* [16], the authors showed a correlation between the activation energy for the viscous flow in the melt and the ^{31}P NMR parameters as determined in a series of alkali and alkaline-earth metaphosphate glasses. The viscosity activation energy, which can be seen as the rate of increase of viscosity of the melt upon cooling, resulted proportional to the ionic field strength of the modifier cation between sodium and calcium metaphosphate compositions and also to the chemical shift anisotropy of the phosphorus atoms. It was concluded that the increase of the electrostatic interactions between modifier cations and the surrounding oxygens that belong to the $[\text{PO}_4]$ tetrahedral building units of the glass networks determine not only the rate at which the viscosity of the melt will increase but also the medium-range ordering of the phosphate chains of the glass network. It is then thought that this arrangement of the phosphate chains in the melt is the lacking structural factor that determines the glass formation ability of the respective system.

4. Conclusions

It can thus be concluded that in a simple system with uncomplicated chemical compositions like in the alkali metaphosphate series, the ability to form a glass from the melt does not depend only on the viscosity of the liquid, but also on the complexity of the formed crystals. We have found that a high structural difference at the local scale between the glasses and the related crystals favors the freezing of the disordered structure of the high temperature melt, due to additional kinetic factors. Therefore, glass formation is particularly easy in LiPO_3 and NaPO_3 where the crystal structures and glass structures are extremely different. In contrast, glass formation is highly difficult in KPO_3 and RbPO_3 where glasses and crystals have a very similar short-range atomic structure.

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Figure captions

Figure 1. DTA patterns on cooling for the series of alkali metaphosphate glasses. A rate of 5 K.min^{-1} was used for Li, Na and Rb compositions while 20 K.min^{-1} was taken for KPO_3 . The temperatures of the legends indicate the temperature of on-set of crystallization.

Figure 2. The ^{31}P MAS NMR spectra of the metaphosphate glasses as obtained at 10 kHz spinning speed in a 9.4 T spectrometer.

Figure 3. Isotropic chemical shift and width of main resonances in the ^{31}P MAS NMR spectra as a function of the ionic radius of the modifier cation.

Figure 4. The ^{31}P MAS NMR spectra of the series of alkali metaphosphate crystals.

Figure 1

Figure 2

Figure 3

Figure 4