Synthesis and Powder Ceramization in the Glass System SiO_2 -P_2O_5-Al_2O_3-MgO-K_2O

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Multicomponent, mixed-network SiO_2 -P_2O_5-Al_2O_3 glass containing MgO and K_2O as modifiers was synthesized. Fourier transform infrared (FT-IR) spectroscopy, differential scanning calorimetry (DSC) and thermomechanical analysis (TMA) were used to characterize the obtained glass. It showed high thermal stability, exhibiting no crystallization tendency in bulk form even after 24hrs. of heating at high temperatures.

It crystallized readily in powdered form when heated in the same range of temperatures. X-ray diffraction (XRD), scanning electron microscopy (SEM), coupled with energy dispersive x-ray analysis (EDX) confirmed that the first phase to crystallize was berlinite ($AlPO_4$) together with $Mg_2P_2O_7$. As temperature is increased, $Mg_3(PO_4)_2$ started to crystallize as well. The content of $Mg_2P_2O_7$ diminishes as temperature is increased. Above ~1000°C (in molten glass), only $AlPO_4$ and $Mg_3(PO_4)_2$ continue to exist, but with different morphologies.

Introduction

Until recently not much was known about glasses vitrified through conventional cooling, and containing substantial amounts of both glass network formers SiO_2 and P_2O_5. This is mainly because of differences in chemical bonds between their structural tetrahedral units SiO_4 and PO_4.

In the presence of Al_2O_3 which is able to develop strong and moreover flexible bonds whit both SiO_2 and P_2O_5, joining together the unlike SiO_4 and PO_4 tetrahedral units, the two compounds are capable of forming glasses through unconventional, special amorphosization techniques such as rf-sputtering, and only in the presence of alkali and / or alkaline earth glass modifiers, that homogeneous, stable glasses containing varying proportions of these network forming oxides can be obtained through the standard melting and cooling procedures. These multicomponent, mixed-network glasses are classified as being of non-uniform, continuous polymeric network glasses, made-up of polymerized polyhedra namely AlO_4, PO_4 and SiO_4 [1-4].

The main objective of the present study is to investigate the effects of replacing the total molar percentage content of Na_2O by K_2O in a specific glass composition [1], on its formation, properties and most importantly the crystallization behaviour.

Experimental

The glass batch having the composition 38% SiO_2, 20%Al_2O_3, 17% P_2O_5, 17%MgO and 8% K_2O (mol %) was prepared utilizing reagent-grade SiO_2, $Al(OH)_3$, MgO, K_2CO_3 and H_3PO_4 (85%). The procedures followed for the production of the clear, homogeneous, bubble-free bulk glass samples, and the methodology of their characterization, as well as their ceramization in bulk were exactly as those described in previous publications [1-2].

For glass ceramization through powdered route, bulk glass pieces were crushed, ground and sieved. The powdered portion passing through 0.15 mm and retained on 0.06 mm sieve, was collected and loosely packed into a platinum boat, and then introduced into the accurately calibrated gradient temperature furnace at its maximum temperature of 1100 °C and left to undergo heat treatment for 24 hrs.

After the heat treatment, the crystallized samples were cut into pieces matching different temperature intervals in accordance with their respective response to the heat treatment employed and its duration. Different portions representing the crystallization behaviour within certain temperature ranges were divided into yet smaller fractions for detailed identification of crystallized phases and their characterization on microstructural bases.

XRD7 (SEIFERT–FPM) x-ray diffractometer with CuKα radiation was employed for identification of crystallized phases over a 2θ value 10^{o} to 80^{o}. JCPDS cards were used for naming the crystallized phases over the whole range of crystallization. Philips XL 30 with link ISIS energy dispersive spectroscopy was also employed for morphological characterization, elemental x-ray mapping and EDX microanalysis, using ground and polished bulk samples which were etched with 2ml HF + 100ml H_2O solution for 15 sec. before being carbon coated.

Results and Discussions

Structurally, the glass under investigation is characterized by the same infrared spectroscopical features oftenly exhibited by silicate, aluminosilicate and aluminophosphosilicate glasses. As it can be seen from the FT-IR spectrum shown in figure 1, the main characteristical vibrational bands due to bridged oxygen atom stretching, bending and rocking vibrations at 1066 cm^{-1}, 715 cm^{-1} and 465 cm^{-1} respectively, are within the typical and most commonly encountered ranges of absorbance frequencies for most of the above mentioned materials [1-8].

It is quite evident that SiO_4, AlO_4 and PO_4 tetrahedral structural units constitute the network structure of the glass, in which $AlPO_4$ groups substitute for pairs of SiO_4 units within the partially depolymerized silicate network structure. The absence of a vibrational band at ~ 1280-1300 cm^{-1}, which accounts for the P=O bond, explains beyond any doubt the presence of all phosphorus in the form of PO_4 units. While the addition of Al_2O_3 to the silicate glass, should have resulted in shifting the main stretching band to yet a lower wavenumber, but the inclusion of P_2O_5 into the glass, had its effect in counterbalancing such lowering effect, simply because P_2O_5 has an opposite effect to that of Al_2O_3 [4].

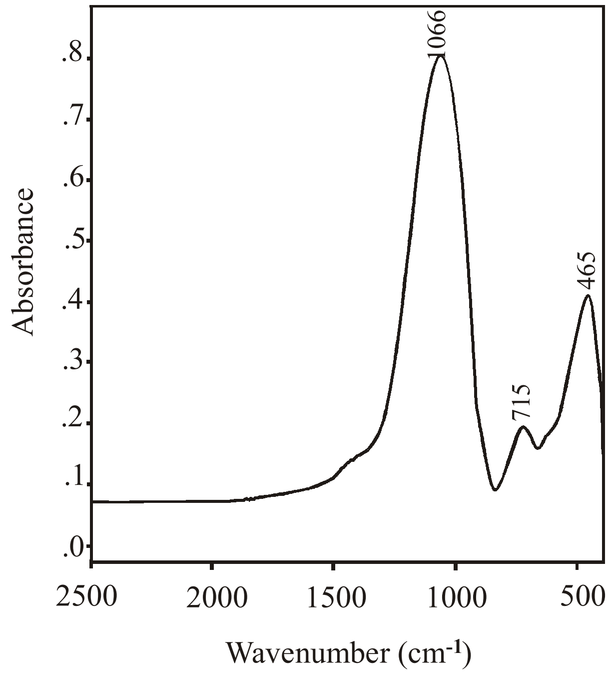

Figure 1: FT-IR absorbance spectrum for the studied glass.

The DTA curve recorded for the studied glass at a heating rate of 10°C/min., showed very diffused thermal deflection at the glass transition temperature range, with a Tg value of 696°C. The glass transformation temperature (Tg) was found to be 662 °C on the TMA curve at the same heating rate, while the glass softening temperature (Ts) was ~ 736 °C. At a heating rate of 10°C/min., and over a temperature range of 50-500 °C, the thermal expansion coefficient was determined to be ~ 4.375×10^{-6} / °C. The moderately high Tg and Ts temperatures on one hand, and the rather low coefficient of thermal expansion on the other hand, illustrate the strong interconnectivity of the glass structure imparted by the presence of $AlPO_4$-SiO_4 linkages, as well as the nature of the glass network structure being stuffed with large potassium cations which occupy the spaces between linked tetrahedra. The density of the bulk glass was determined to be 2.3898 (± 0.0001) g/cm^3.

It has long been realized that for glass formation through the normal procedure of melt cooling, certain minimum amounts of glass network modifiers, most commonly Na_2O, and for practical purposes with CaO and / or MgO are required to stabilize the network structure in the glass system P_2O_5-SiO_2, together with Al_2O_3 which acts as a buffer component between the two network formers differing in their chemical bonds and accordingly their properties, making it impossible for them to form stable glass on their own. And since glasses in the system Na_2O-MgO (CaO)- Al_2O_3-P_2O_5-SiO_2 were successfully made, and their crystallization behaviour thoroughly investigated [1-4], and because of the large radius of potassium, and the strong ionic character of the K-O bond, K_2O was selected to replace Na_2O in a specific glass composition within the above mentioned glass system which contained 17 mol.% Mg O [1].

While the Na_2O-containing glass crystallized very readily at a temperature near Tg, the K_2O-containing glass showed no sign of crystallization in bulk even after its heat treatment for 24 hrs. at temperatures as high as 1100°C. It is believed that such behaviour can be explained in light of Stoch's views summarizing the factors controlling the crystallization of multicomponent glasses [9,10]. He concluded that the flexibility of the glass structure, the number and strength of broken oxygen bonds and ionicity of modifiers within the silicate glass, are among the major factors affecting glass crystallization. Having considered that, it could be argued that the studied glass has a very poor tendency for crystallization due to the high degree of flexibility and low strength bonds as a result of the presence of potassium with its high ionicity, as compared with sodium at least.

In powdered form, whereas the sites for heterogeneous nucleation and crystal growth are so excessive, the glass crystallized readily. The platinum boat containing the loosely packed powder covered the temperature range down to ~ 820°C only. In the temperature range of ~ 820-860 °C, there was an extensive crystallization as reflected by the intensity of the diffraction peaks, and the almost complete absence of the halo-like peak indicative of the amorphous state. According to the XRD results, the crystallized phases were $AlPO_4$-high cristobalite form (JCPDS 200045), $Mg_2P_2O_7$ (JCPD 320626) and $Mg_3\ (PO_4)_2$ (JCPDS 330876). As temperature was increased to the range ~ 860-1000°C whereat the glass powder underwent partial melting, as indicated by the relatively enlarged halo-like peak, the same phases continued to crystallize, but with more content of $Mg_3\ (PO_4)_2$ at the expense of $Mg_2P_2O_7$. The amount of the latter diminished as temperature was increased.

In the melting temperature range of ~ 1000-1100°C, only $AlPO_4$ and $Mg_3\ (PO_4)_2$ coexisted in the melt. The former recystallized into well-shaped dendritic crystals, while the latter adopts a needle-like, elongated rod-like crystals as proved through SEM and EXD, figures 2 and 3.

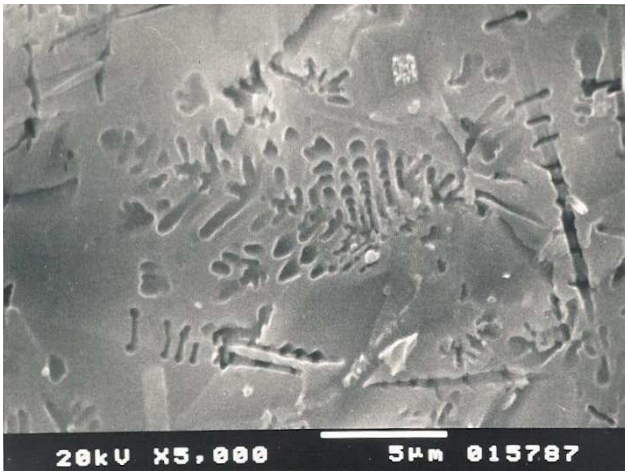

Figure 2: SEM micrograph of well-shaped dendritic $AlPO_4$ crystals

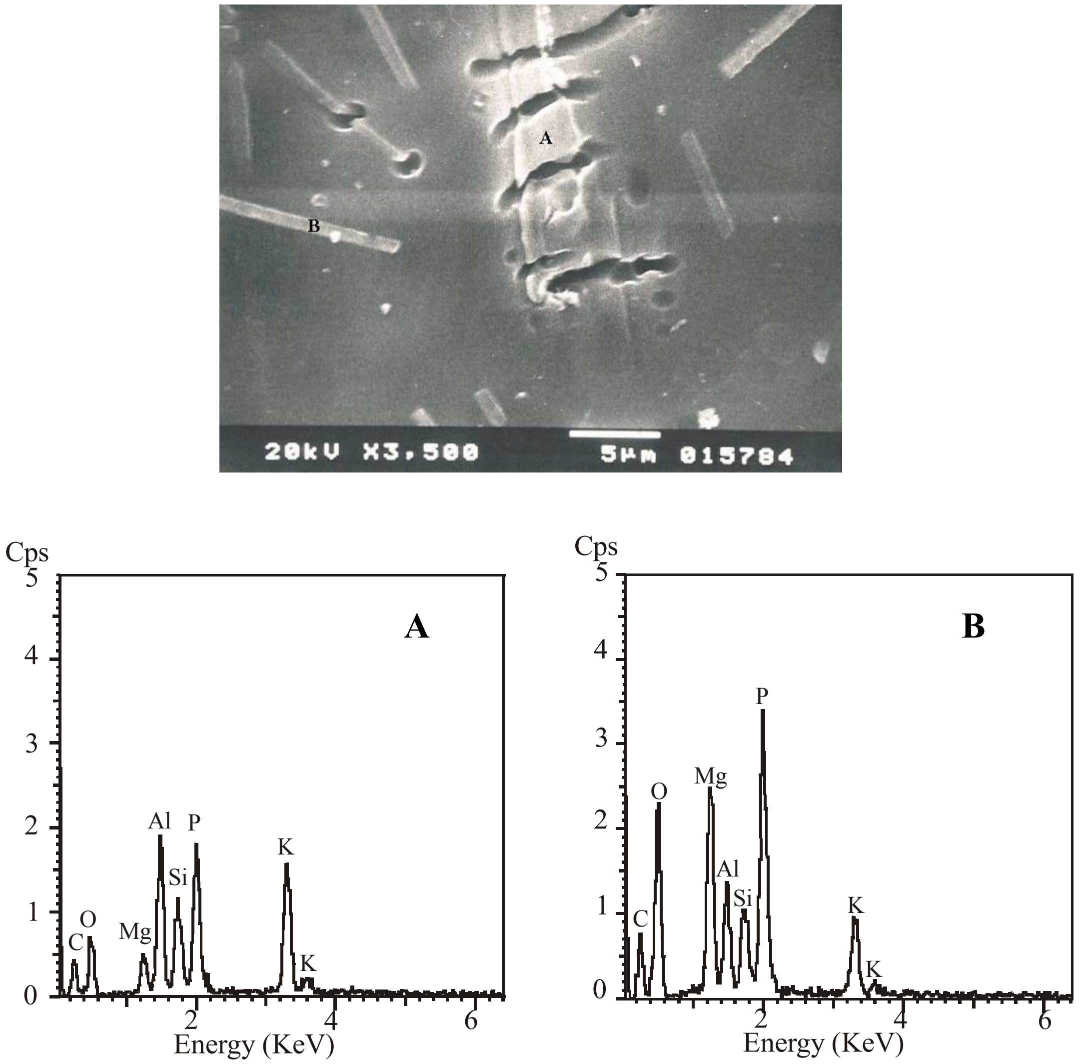

Figure 3: SEM micrograph and EDX spectra of $AlPO_4$ phase (A) and $Mg_3(PO_4)_2$ phase (B)

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