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The effect of ZrO_2 in $30K_2O$-$70SiO_2$ glass: a comparison with $30Li_2O$-$70SiO_2$

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The influence of the introduction of ZrO_2 in concentrations of up to 5 mol% into a $30K_2O$-$70SiO_2$ base glass composition has been investigated with the aid of differential thermal analysis (DTA), FT-IR spectroscopy, as well as chemical durability tests (pH, conductivity and AES-Inductively Coupled Plasma measurements) and refraction index determination. Several differences have been found by comparison with similar compositions belonging to the Li_2O—ZrO_2—SiO_2 system. The higher ionic radius and the lower field strength of K^+ with respect to Li^+ is responsible for higher stability towards crystallisation and lower chemical durability. Moreover, even though Zr^{4+} increases glass polymerisation (higher glass transition temperature, chemical durability and refraction index), the presence of high water content as highlighted by spectroscopy measurements, seems to weaken the glass structure.

1. Introduction

It is known [1] that the addition of 20 to 30 mol% of M_2O (M = alkaline metal) to pure silica glass causes the liquidus temperature to drop rapidly from 1713°C to temperatures ranging from 750 to 1000°C and the resulting liquid forms a clear glass on cooling [2]. On the other hand, the simple M_2O—SiO_2 system alone shows poor properties as regards to chemical durability and mechanical characteristics. Addition of oxides acting as network formers and modifiers can greatly improve the above mentioned properties. In particular zirconium when present as ZrO_2 in glasses posses a coordination number ranging from 6 to 9 [3]. ZrO_2 imparts increase in density, viscosity, liquidus temperature, mechanical and chemical resistance, electrical conductivity, and decrease in thermal expansion coefficient [4]. This behaviour demonstrates that zirconium ion plays a fundamental role in the glasses structure, even though the correlation existing between the structural modifications and the final glass macroscopic properties is object of recent studies [5, 6].

The purpose of this study is to focus the attention on the role played by the intermediate oxide ZrO_2 when added to a glass belonging to the K_2O—SiO_2 system. A further comparison with the behaviour of zirconia in Li_2O—SiO_2 glass has been also performed.

The compositions chosen are such to fall in a very narrow zone of the compositional triangle K_2O—ZrO_2—SiO_2 [7] characterised by a high percentage of the network former oxide SiO_2 in order to assure good technological properties. By considering the similarity between the two phase diagram K_2O—SiO_2 [8] and Li_2O—SiO_2 [2] and by analogy with an other study on the Li_2O—ZrO_2—SiO_2 system [9], the starting point to tailor the compositions has been the molar ratio K_2O/SiO_2 equal to 30/70. This ratio guarantees a good meltability and avoids the formation of crystobalite (with a significant variation in linear thermal expansion coefficient) after the crystallisation treatment.

2. Experimental procedure

2.1. Sample preparation

Maintaining constant the molar ratio K_2O/SiO_2 equal to 30/70, systems with increasing amount of ZrO_2 (in the form of $ZrSiO_4$) from 1 to 5 mol% were prepared (Table I).

The samples have been prepared by dry mixing high purity industrial reagents (K_2CO_3, Quartz and $ZrSiO_4$) in an agate mortar for 15 min to obtain an homogeneous mixture. Glasses preparation has been accomplished by melting the reagents in a platinum crucible through firing in an electric furnace at 1550–1590°C for 5 hrs. At the end of the firing cycle, the melt was poured onto a graphite mould and so quenched in air obtaining transparent and colourless glassy materials.

2.2. Sample characterisation

The obtained amorphous samples have been characterised by means of:

– differential thermal analysis (DTA) measurements (Netzsch DSC 404) both on powdered and bulk monolithic samples from 20 to 1400°C with heating rate of 10°C/min;

– FT-IR spectroscopy (Perkin Elmer 1600) on powdered samples (1 mg of samples plus 200 mg of dried

TABLE I Chemical composition (mol% of oxides) of the studied glasses

K_2O	ZrO_2	SiO_2	Sample
30.00	0.00	70.00	K30Z0S70
29.70	1.00	69.30	K30Z1S70
29.25	2.50	68.25	K30Z2.5S70
28.95	3.50	67.55	K30Z3.5S70
28.50	5.00	66.50	K30Z5S70

TABLE II Glass transition temperature, T_g, as a function of ZrO_2 content

Sample	$T_g \pm 2$ (°C)
K30Z0S70	495
K30Z1S70	500
K30Z2.5S70	535
K30Z3.5S70	520
K30Z5S70	510

KBr) in the 4000–450 cm^{-1} range. The registered spectra were subtracted of the KBr spectrum obtained in the same conditions;

– release tests in bidistilled water at 25°C both on powdered samples (grain size between 0.250 and 0.355 mm to have a weight/volume ratio corresponding to 0.5 g for 100 cm^3 of water) and on bulk material with the same weight/volume ratio. pH (Orion Mod 420A) and conductivity (Crison Basic 30) were measured after regular intervals up to 120 min. The obtained solutions were analysed by AES-ICP (Atomic Emission Spectroscopy Inductively Coupled Plasma Varian Liberty 200) to measure the content of K, Zr and Si leached;

– refraction index determination using the Becke's line method [10] on powdered samples (grain size 0.212–0.250 mm). This method is commonly employed in mineralogy for determination of the refractive index of small grains.

3. Results and discussion

DTA measurements were firstly performed on powdered samples to verify the reactivity of the material with the atmosphere which has appeared to occur at a large extent as reported by a previous work [7]. In Fig. 1 is reported the thermogram of the K30Z2.5S70 powdered sample where is evident the dehidratation phenomenon as an endothermic peak near 100°C. Because of the glass reactivity with the atmosphere, the DTA study has been continued on bulk samples. In these cases the only transformation temperature evident from the DTA curves is the glass transition temperature reported in Table II.

From the table it is evident that T_g is affected by Zr content. Being T_g a parameter related to the system viscosity and lowering when the network modifier cations content is increased, its increase can be attributed to the introduction of Zr in the glassy lattice which behaves as network former ion with 6-co-ordination number. Zr occupies a distorted ZrO_6 octahedron which shares corners with SiO_4 tetrahedra with Zr—O—Si angles close to 130° [11, 12]. A similar trend for Tg with the progressive addition of ZrO_2 is observed also by Novaes de Oliveira et al for glasses belonging to the Li_2O—ZrO_2—SiO_2 system [9].

Moreover the thermograms of the Li-containing glasses show crystallisation peaks in the range 800–900°C [13] hence it is possible to obtain glass-ceramics from correct devitrification of such glasses. This difference is due to the different nature of the Li^+ and K^+ ions. Although they have the same positive charge, the ionic radius is different, i.e., 0.78 Å for Li^+ and 1.33 Å for K^+ [14] therefore the field strength is higher for Li^+ with respect to K^+ (0.23 $Å^{-2}$ for Li^+ and 0.13 $Å^{-2}$ for K^+ [11]). Since the field strength indicates the cation capacity to attract electrons and so to arrange O^{-2} neighbours, an ion with higher field strength increases the glass capacity to form crystals [15].

In order to investigate the role played by the different cations and the kind of absorbed water in the glass structure, FT-IR spectroscopy was performed. As regards water in the glass structure a lot of studies in the literature [16–18] report the existence of different kind of water: for low H_2O content in the glass (<3 wt%) the principle species are hydroxyl groups (bands in the 2800, 2350 and 1760 cm^{-1} region) named $H_2O(II)$ and for higher H_2O content it is dissolved as molecular water (corresponding bands are 3500–3300, 2200, 1670, ≈630 and ≈200 cm^{-1}) named $H_2O(I)$.

The spectrum reported in Fig. 2 is representative of all compositions and shows the presence of bands

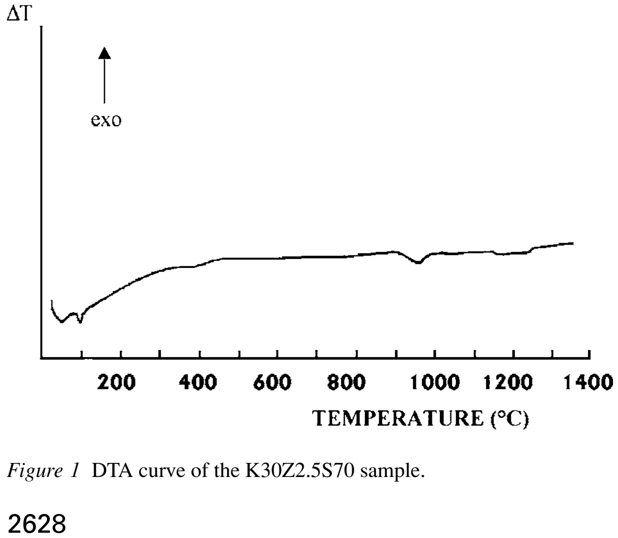

Figure 1 DTA curve of the K30Z2.5S70 sample.

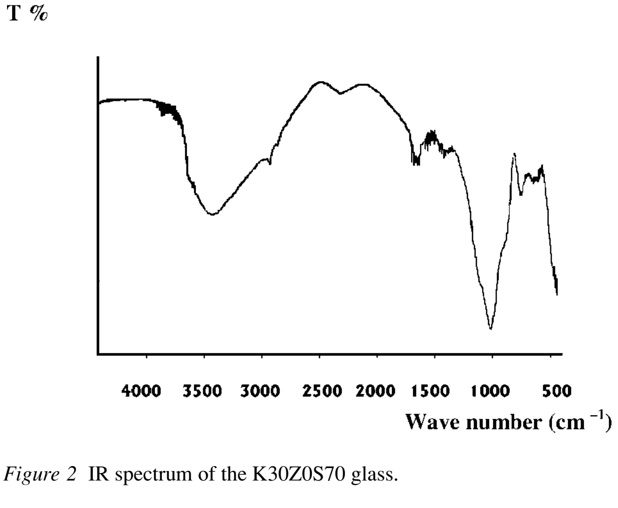

Figure 2 IR spectrum of the K30Z0S70 glass.

corresponding to $H_2O(I)$. This is molecular water entrapped in the glassy lattice which is significant for contents higher than 3 wt% and can be eliminated at 100°C [16]. The band at 1650 cm^{-1} is attributed to the bending mode and the band at 3400 cm^{-1} to the overlap of the symmetric and asymmetric stretching modes. It is very difficult to understand whether this water is present in the glass before or after the grinding process, but, even though water should be present only as a consequence of grinding and not in the bulk process, the spectroscopic results show significant surface reactivity.

The effect of the high percentage of water within the glassy lattice is highlighted by the shape and number of bands characteristic of the silicate network which are located at 1000 cm^{-1} for the stretching mode of the Si—O—Si bond and at 800 cm^{-1} for the symmetric stretching of the Si—O—Si bond and 450 cm^{-1} for the rocking of the bond Si—O—Si. In the spectra only a single band between 970 and 1030 cm^{-1} for each composition is present, instead of the two typical bands characteristic of silicate glasses containing alkaline ions, i.e., 960–980 cm^{-1} for stretching of $SiO^- M^+$ and 1050–1070 cm^{-1} for stretching of Si—O—Si [16]. This peculiar IR spectrum allowed us to classify the absorbed water as H_2O (Ib), i.e., water which weakens the glassy network and is prevalent for H_2O amount higher than 10 wt%. On the other hand, H_2O (Ia) has the action to dilute the lattice and is present for H_2O content between 3 and 10 wt%. Furthermore, another phenomenon observed is that the increasing amount of zirconium in the tailored compositions provokes a significant shift towards lower frequencies of the band at 1000 cm^{-1}, related to the Si—O—Si stretching (Table III) [17] and it has been already observed for $Li_2O—ZrO_2—SiO_2$ glasses [19]. This is probably due to the fact that the absorption at 1000 cm^{-1} is prevalently related to the stretching mode of the $Si—O^-\ Zr^{4+}$ bond. This mode is shifted towards lower frequency with respect to $Si—O^-\ K^+$ because of the higher charge and atomic weight of Zr with respect to K.

Finally, the other bands typical of a silicate network are in the range 751-760 cm^{-1} (asymmetric stretching of Si—O—Si) and 440–465 cm^{-1}; these bands are slightly lower in wave numbers with respect to those of a pure silica glass because of the Si—O—Si bond weakening due to the introduction of a modifier ion such as K^+. This low-frequency broad response which is shifted down to lower frequencies for glasses containing potassium corresponds to the localized vibration of this heavy cation. This mode corresponds to the external vibration of cations against the silica network [17].

The chemical durability in terms of resistance of glass surface to chemical agents, is an important aspect for a commercial glass in that it affects its industrial applicability. The reaction begins at the surface and spreads inwards as a result of either the diffusion of the invading elements into the glass or the break up of the glass network bonds by the attacking species [20].

TABLE III IR band position as a function of the zirconium content

ZrO_2 (mol%)	Band position (cm^{-1})
0	1018
1	1002
2.5	1001
3.5	1001
5	969

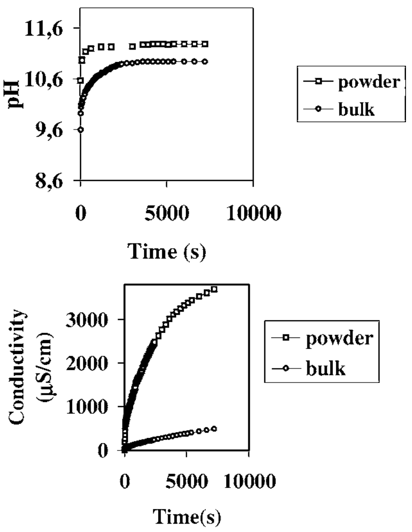

Figure 3 Comparison between pH and conductivity of powdered and bulk glass K30Z0S70 as a function of time.

In order to evaluate the amount of ions leached pH and conductivity have been measured on the powdered and bulk monolithic glasses (Fig. 3). The higher reactivity of powdered sample with respect to the bulk as a consequence of larger amount of surface area is confirmed from Fig. 3. In fact after 10 sec of contact of the powder with the reaction medium pH increases from 5.8 to 10.6 and conductivity from 9 to 193 $\mu S \cdot cm^{-1}$. The final values of pH and conductivity after 120 min are 11.3 and 3700 $\mu S \cdot cm^{-1}$, respectively. By considering this very high reactivity, the other durability measurements have been conducted only on bulk samples. Fig. 4 shows the pH and conductivity trends for the 5 glass compositions. All the glasses show low

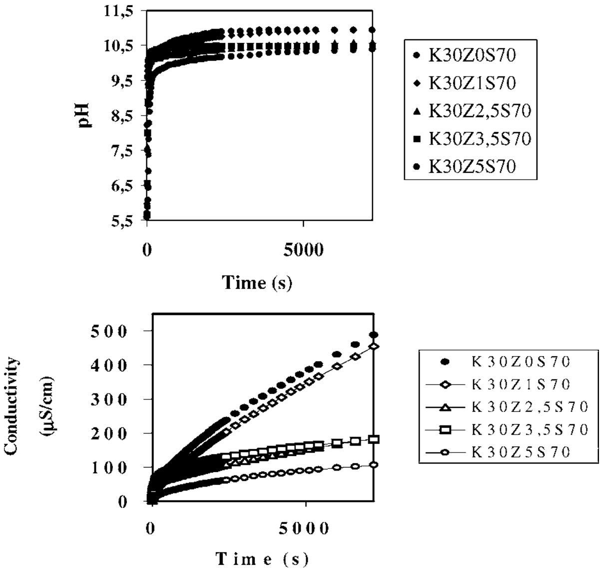

Figure 4 pH and conductivity as a function of time for the 5 prepared glasses.

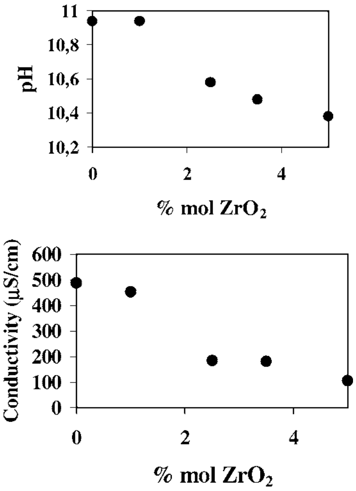

Figure 5 pH and conductivity trend as a function of ZrO_2 content in the glasses.

durability, with K30Z5S70 being the best composition which reaches 10.4 pH value in the bidistilled water after 120 min, remembering that for $pH > 9$ the SiO_2 dissolution mechanism besides the ion exchange between alkaline ion and H^+ ions of water becomes important. It is worth of note that both properties increase less for higher content of ZrO_2 in the glass; being the increase related to the leaching of the K^+ ion, it is possible to hypothesize that the ZrO_2 addition improves the durability also for these glasses as already seen in literature for the systems Li_2O—ZrO_2—SiO_2 and CaO—ZrO_2—SiO_2 [4, 6, 19]. The chemical durability improvement suggests that the glass structure becomes more dense with the introduction of zirconium confirming the network former role played by this ion. In order to better evidence the behaviour of zirconium, in Fig. 5 the pH and conductivity trend as a function of ZrO_2 content in the glass are reported.

From the chemical analysis conducted on the solutions obtained after 120 min (Fig. 6) it is evident that every oxide is less leached with the increase of ZrO_2 in the glass. As a conclusion it can be asserted that the compositions studied belonging to K_2O—ZrO_2—SiO_2 glassy system have a high surface reactivity corresponding to low chemical resistance. This behaviour is mainly due to the different nature of the K^+ ion with respect the other alkaline ions such as Li^+ and Na^+ which are used in the glass technology to enhance the raw materials fusibility and to lower the melt viscosity. Because of the large ionic radius of K^+ with respect the other alkaline cations ($rLi^+ = 0.78$ Å, $rNa^+ = 0.98$ Å, $rK^+ = 1.33$ Å) this ion has a low strength field therefore it plays a strong modifier role in the glass network destabilising the structure. The potassium dimension produces a lattice distortion together with increase of the bond length when the ion arranges near the non bridging oxygens originating by the breaking of Si—O—Si bond. This behaviour open the glassy network with respect to both a pure silica glass and a glass with the same molar composition containing as modifier ion Li^+ or Na^+ making the potassium based glass less chemical resistant than lithium based glass. The resistance enhancement shown by the addition of Zr^{4+} is due to the high strength field of this ion which is not very mobile within the lattice and does not diffuse towards outside as underlined by the release values reported in Fig. 6 less for ZrO_2 with respect to K_2O and SiO_2. The presence in the leached solution of silica suggests the glassy network desegregation because of the high pH due to the release of OH^- ions according to the reaction

$$\text{—Si—O}^-\text{K}^+ + \text{H}_2\text{O} \longrightarrow \text{—Si—O}^-\text{H}^+ + \text{K}^+ + \text{OH}^-$$

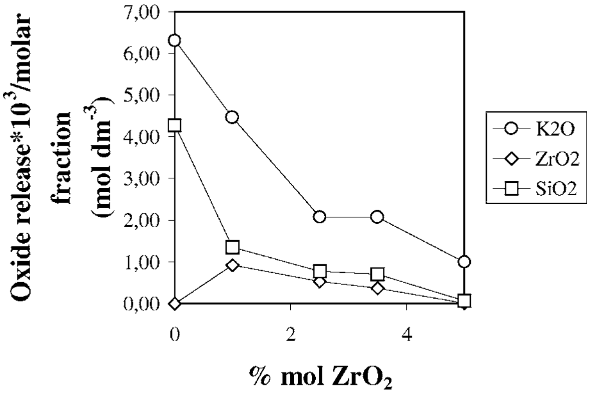

Figure 6 Release amount of oxides respect to the respective molar fraction in the glass as a function of ZrO_2 molar percentage.

TABLE IV Refraction index as a function of ZrO_2 content in glasses

Sample	n_D
K30Z0S70	1.505–1.510
K30Z1S70	1.510
K30Z2.5S70	1.510–1.515
K30Z3.5S70	1.525–1.530
K30Z5S70	1.530–1.535

As chemical durability, the refraction index is increased by ZrO_2 content as well (Table IV). This trend is known in literature [4] and it is explainable by considering the light refraction phenomenon which is related to the deviation of a light beam in a material. This deviation is due to the presence of polarizable atoms. The bond Zr—O is more polarized with respect to Si—O, therefore O^{2-} has a higher partial negative charge which provokes a higher light deviation as a function of ZrO_2 content.

4. Conclusions

The first goal of this work has been the study of a narrow compositional range of glasses belonging to the K_2O—ZrO_2—SiO_2 ternary system, which is not very well known and studied in the literature, because of the high surface reactivity of potassium containing glasses with the atmospheric humidity. As second goal, it has been helpful to study the behaviour of different alkaline ions, in particular by comparing the results achieved in this study to those reached on glasses of the same molar composition and belonging to Li_2O—ZrO_2—SiO_2. The main characteristic of the glasses investigated in this study can be summarised as follows:

- inability to crystallise differently with respect to glasses belonging to the Li_2O—ZrO_2—SiO_2 system because of the different ionic radius and the corresponding field strength of the Li^+ and K^+ ions.
- low chemical durability because of the large ionic radius of K^+ with respect to the other alkaline cations Na^+ and Li^+. This feature leads to a strong modifier role played by potassium in the glass network destabilising the structure.
- significant effect of the presence of Zr^{4+} into the glassy network. Firstly, the forming role of this ion which increases the glass transition temperature was tested. Secondly it has been evidenced the capability of Zr^{4+} to improve the chemical durability of the glasses in which it is introduced also in small percentages and in presence of a cation as K^+ with poor behaviour as regards this property. Finally, it has been confirmed also for the selected glasses belonging to the K_2O—ZrO_2—SiO_2 ternary system, the tendency of Zr^{4+} to increase the refraction index of glasses in which it is added in small amount.

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