

LITHIUM COORDINATION MEASUREMENT IN THE LITHIUM DISILICATE GLASSES

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Abstract: The structure of the oxide vitreous systems is characterized at a first structural level, by the type and the proportions of the constitutive ions, by the coordination number of the cations in relation with the oxygen, by the internuclear distances and the angles between the formed chemical bonds. Concrete structural information can be gathered by utilizing different experimental techniques (x-rays or neutrons diffraction, XPS, MAS-NRM, 3Q-MAS NRM, etc.). For the alkali-silicate glasses generally exists a series of data reported in literature, but in fact there are fewer results referring to the Li⁺ ion coordination in glasses from the Li₂O-SiO₂ system.

In this work, an attempt of determining the coordination number of the Li⁺ ion in the lithium disilicate glass (LS₂) is presented by using a globalizing structural characteristic - the basicity percentage (pB). This is experimentally determined from spectroscopic measurements. The experimental data processing shows a coordination number for Li⁺ in LS₂ glass equal to 2, value found in other literature reports too.

Key words: coordination number, lithium disilicate glass, and basicity percentage

INTRODUCTION

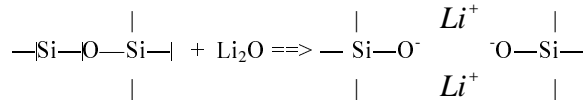
One of the important structural characteristics of the oxide vitreous systems is the coordination number of the constituent cations. If for the crystalline oxide systems it's easier to establish the cations coordination, in the case of vitreous oxide substances the existing data are less certain. Using modern methods of analysis (MAS NMR), there could be established the coordination of the constituent cations for certain types of glass. Li⁺ ions are very different from the other alkali ions in the way they influence the structure of the glasses. This way, Li⁺ has the smallest ionic radius $r(\text{Li}^+) = 0.78 \text{ \AA}$ of all the other alkali ions. The ratio $r(\text{Li}^+)/r(\text{O}^{2-}) = 0.59$ which shows the possibility that lithium may present the coordination numbers (CN)=4 and 6 in relation with the oxygen. By comparison, for the other alkali ions $\text{CN} \geq 6$.

At the same time, Li⁺ is characterized by the biggest values for the field strength (0.23) and for single bond strength Li-O (150, 5kJ/mol). In exchange, its polarizability (0,03) is much smaller compared to the other alkali ions (0,24 for Na⁺ and 2,40 for Cs⁺). The particular character of Li⁺ is also sustained by the fact that the distance cation-oxygen is the smallest (2,10 Å) for CN=6, respectively 1,97 Å in Li₂O·2SiO₂ glass [1].

Also, having the highest electronegativity (Pauling), the Li-O chemical bond presents the most prominent covalent character. All these data confirm the fact that of all

alkali ions Li^+ presents the greatest capacity of interacting with oxygen ions from the $[\text{SiO}_4]$ tetrahedral, which form the basic network of the glasses' structure from the $\text{M}_2\text{O}-\text{SiO}_2$ system ($\text{M}=\text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$).

Stereo chemically speaking, adding Li_2O to a SiO_2 glass determines the replacing of bridging oxygen, which assures the connection of 2 $[\text{SiO}_4]$ tetrahedral with two non-bridging oxygen's:



But this qualitative description cannot bring information referring to the real coordination number of lithium in relation with the oxygen. In this moment, concrete data regarding the coordination of cations in different vitreous systems can be obtained only by experimental determinations.

Using the x-rays diffraction method, Warren and his partners [1] have demonstrated for the first time, later other researchers have also demonstrated [1], that in the majority of alkali silicate glasses the Si coordination in relation with the oxygen is 4. At the same time values have been attributed for the coordination number of alkali cations too. Unfortunately, this evaluation must be considered with certain prudence, because of some approximations implied by the used methods.

In time, the refinement of the x-ray diffraction methods as well as the utilization of the new methods (neutron diffraction, MAS NMR, XPS, 3Q-MAS NMR) have supplied interesting results regarding the CN for the cations from different oxide vitreous systems. In such way, Angeli and his partners [1], using 3Q-MAS NMR technique, have shown that in the glass of $\text{Na}_2\text{O} \cdot 5\text{SiO}_2$ composition the CN for Na^+ is between 2 and 10, although CN=6 has the maximum apparition frequency. The authors also show that CN for Na^+ has different values varying with the oxide composition of the glasses in the $\text{Na}_2\text{O}-\text{SiO}_2$ system, respectively with acidic-basic character.

A similar conclusion is reported by Hoppe [1] for glasses from the $\text{MeO}-\text{P}_2\text{O}_5$ system ($\text{Me}=\text{Mg}, \text{Ca}, \text{Zn}$). This way, for more basic glasses, characterized by a higher $\text{MeO}/\text{P}_2\text{O}_5$ ratio, the CN decreases for the cations in relation with the oxygen.

In this context, somewhat surprising Hannon and his partners [2] by using the neutrons diffraction method, establish for Li^+ in the $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ a $\text{CN} \approx 2$.

In this work an attempt to establish the coordination number of the Li^+ in the LS_2 glass is presented, on the basis of some spectroscopic basicity determinations.

1. Experimentally

The raw materials used for obtaining the vitreous lithium disilicate were: lithium carbonate (p.a.) and quartz (99% SiO_2). To prevent losses through volatilization during the melting, excess lithium carbonate was used and an intermediary stage was introduced during which the raw material mixing was calcined at 800°C in platinum capsules. The raw materials' mixing was melted for 3 hours in platinum crucibles at 1300°C in an electric furnace. The melting was cooled in air between two sheets of steel preheated, resulting 2.5cm in diameter and 2mm thick disks. The samples were annealed at 250°C for 3 hours, the cooling taking place slowly at the same time with the electric furnace.

The chemical analysis for the obtained glass showed a composition very close to that of the lithium disilicate. (Table 1)

Table 1

The composition resulted from analyzing the obtained lithium disilicate.

Lithium disilicate composition (mass%)	SiO ₂	Li ₂ O
Calculated	80.00	20.00
Analyzed	79.22	20.78

Simultaneously with the lithium disilicate glass, a glass of the same composition but with 0,1 % at. Cu was melted, which was used as indicator for the experimental determination of the basicity percentage.

The differential thermal analysis for the obtained glass was made using a platinum crucible system and the reheating rate of 10°C/min. The fine ground glass powder was also analyzed with the help of the x-ray diffraction, using CuK_α radiation and a dispersion angle 2θ varying between 10° and 60°.

Using a SHIMAZU UV-VIS spectrophotometer with 2 beams, the (-logT) extinctions for the lithium disilicate glass samples with 0,1% at. Cu was obtained, compared to the glass samples of the same composition but without indicator. The curves obtained present a prominent maximum corresponding to Cu²⁺ and a shoulder attributed to Cu⁺. The measurement was repeated 3 times with different glass samples.

2. Results and discussions

The vitreous transition temperature T_g, determined with the help of the differential thermal analysis for the lithium disilicate sample powder was 467±1°C and the temperature corresponding to the crystallization maximum T_c=598°C. The thermogram is presented in fig. 1.

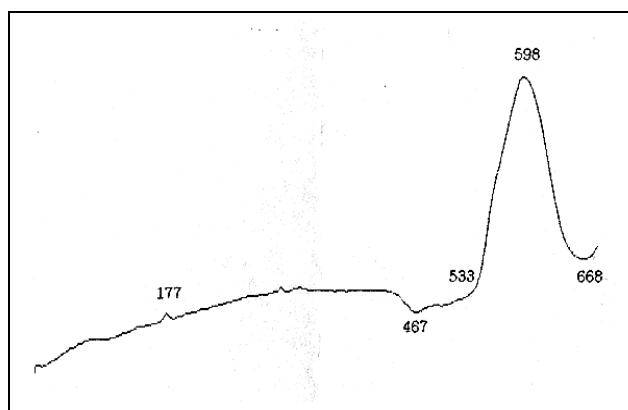


Fig.1- Lithium disilicate obtained glass thermogram

The x-ray diffraction for the obtained lithium disilicate sample has shown the fact that it is completely vitreous as it can be observed from the fig. 2 diffractogram.

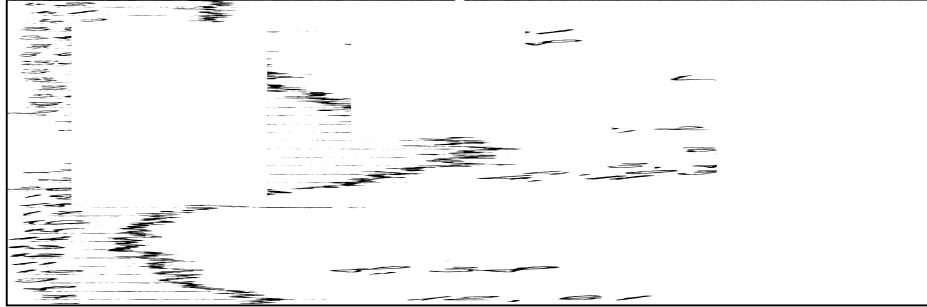


Fig.2 - Lithium disilicate glass diffractogram

Experimentally determining the basicity degree

One of the first methods of measurement and calculation of the acido-basic character is Duffy and Ingram's defined optical basicity[3]. An alternative measure is the basicity percentage (pB), which also correlates to a series of structural characteristics (coordination number, electronegativity, Z/a^2 ratio, etc.), including optical basicity.

As experimental method of determining the glass basicity was used Balta's proposed quantitative method [4] which uses the 3d ions charge transfer absorption. Cu^{2+} was chosen as indicator ion, the experimental measure utilized as measurement of the basicity is the minimal energy expressed as wave number, at which the Cu^{2+} charge transfer takes place. A dependency of pB with the wave number $\nu(\text{cm}^{-1})$ was obtained with the form:

$$\text{pB} = 151 - 0.00259 \nu; \quad (1)$$

Using the wavelengths obtained for 3 pairs of samples (in fig. 3 one of the absorption curves is presented) the values of the experimental basicity were calculated with the help of the relation 1. At the same time, taking into account glass basicity (pB) and oxides basicity (pB_i) calculation relations (2) and (3) [5], lithium coordination in the studied glass was determined. The coordination number of the silica used in calculations is 4. The results are presented in table 2.

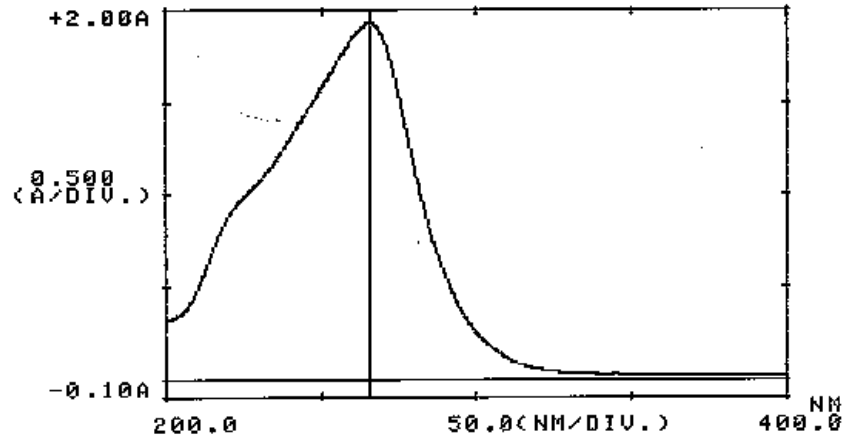


Fig.3 - UV absorption specter for the copper obtained by the difference between the specters of the lithium disilicate glass with 0.1% at. and the specter of the glass of the same composition without indicator

$$pB = \sum_{i=1}^n C_i \cdot pB_i \quad (2)$$

in which:

c_i is the gravimetric ratio of the oxide i ;
 pB_i the basicity percentage of the oxide i .

$$\lg pB_i = 1,9(NC_i)^{0,02} - 0,023P_i/NC \quad (3)$$

in which:

NC_i – is the cation coordination number in relation with the oxygen,
 P_i – the ionization potential of the cation i in the given valence state.

Table 2
 Experimental data regarding the studied lithium disilicate glasses

Pair of glasses of LS ₂ (with and without indicator)	Wave length for Cu ²⁺	Media of wave length for Cu ²⁺	Experimental basicity percentage (pB _{exp.})	Coordination number for Li (NC _{Li})
Sample 1	266	267.13	54,04	1,93
Sample 2	267			
Sample 3	268,4			

After the mediation of the wavelength for the three pairs of LS₂ glasses, one obtained a lithium ions coordination number approximately equal with 2.

3. Conclusions

The paper presents a determination method for the coordination number of the lithium ion in the lithium disilicate glass (LS₂) using the basicity percentage (pB) experimentally determined from spectroscopic measurements.

The result is in accordance with the data presented by Hannon and co. which are giving the same NC=2 for the lithium ion in the lithium disilicate glass using the neutron diffraction method.

Aknowledgements to Prof.Dr.Eng. Petru Baltă for the support in pB experimental determination.

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