THE EFFECT OF CRYSTALLIZATION ON THE BASICITY IN THE SYSTEM Li$_2$O–2SiO$_2$

CAMELIA CĂPĂȚÎNĂ, CLAUDIA MARIA SIMONESCU*

Constantin Brâncuşi University of Tg-Jiu, Engineering Faculty, 3 Geneva Street, 210152, Târgu-Jiu, Gorj, Romania
*Department of Inorganic Technology and Environmental Protection, Faculty of Applied Chemistry and Materials Science,
Politechnica University of Bucharest, 1-7 Polizu Street, 011061, Bucharest, Romania

E-mail: cam@utgjiu.ro

The paper presents the study of the crystallization influence on the basicity in the Li$_2$O · 2SiO$_2$ glass. The quantitative methods were used for the basicity determination of the oxide glasses. The Li$_2$O–2SiO$_2$ samples were thermally treated at 560°C, for 20, 30, 55, 95 minutes in presence and in absence of Cu^{2+} as indicator. The experimental results showed that when the crystallinity degree increases, the wavenumber of the Cu^{2+} absorption decreases corresponding to a higher basicity of samples. It was observed an increasing of the maximum diameter of crystallites and a decreasing of the crystallization speed with the extension of the thermal treatment time at 560°C.

INTRODUCTION

In the chemistry of melts and oxide glasses, the evaluation of the oxidic systems basicity is one of the most important problems from both the theoretical and practical point of view [1-18]. Among the approaches, concept of optical basicity, proposed by Duffy and Ingram [19], has been widely accepted and used in the field of glass science and technology. In this context, Baucke and Duffy [20] reported that the ratio of Fe^{2+} to Fe^{3+} in alkali silicate melts can be represented as a simple linear function of optical basicity regardless of the types of alkali ions in the glasses. Optical basicity was first established using ultraviolet absorption of probe ions, such as Tl$^+$, Pb^{2+} and Bi^{3+}. This idea was then extended to obtain the value from glass composition using empirically assigned basicities of oxides [21].

Basicity represents a candidate for the dominant factor of glass structure. In general, basicity of oxide glass is interpreted as an ability of electron donation of oxide ions, and oxide ions with higher basicity possess excess electrons.

These are two types of basicity, namely measured optical basicity, and calculated optical basicity [22]. Although the concept of optical basicity made a remarkable success in investigating states of glass, its limitations as "universal basicity indicator" have been recognized by the researchers. For example, Duffy and Ingram [22] presented several examples of deviations between measured optical basicity, and calculated optical basicity indicating that the environment of the site, where the probe ion is accommodated does not necessarily follow the trend that is expected from the change in the glass composition. In case of doped metal ion in glass, the doped ion tends to interact preferentially with specific sites in the glass depending on its character. An alternative measure of optical basicity is the basicity percentage (pB), which can be correlated to a series of structural characteristics (coordination number, electronegativity, Z/a^2 ratio).

In the systems Na$_2$O–SiO$_2$, K2O–SiO$_2$ and Li$_2$O–SiO$_2$ it is noticed that the basicity of the oxide systems with an equal content of modifying oxide increases in the order LiO$_2$–Na$_2$O–K$_2$O, which is in agreement with the general notions of inter-relationship between the bonding energy M–O (formation enthalpy and the acid-basic properties of the alkaline metals oxides) [23].

The basicity percentage (pB) of lithium disilicate glass (LS$_2$) can be used to determine the coordination number of the lithium ion in these kind of glasses. In the study of Radu and coworkers on the basis of basicity percentage it was established that the lithium ion coordination number in lithium disilicate glass (LS$_2$) was equal to 2 [3].

For determination of the glass basicity a quantitative method can be used. In this method was used the 3d ions charge transfer absorption [20]. The authors used Cu^{2+} as indicator ion because it is a metallic ion and powerfully influenced by the electrons donor strength of the oxygen atoms [24-28].

The linear dependence between the minimum energy at which the Cu^{2+} charge transfer takes place is expressed by relations (1) and (2). In these relations υ is peak energy, expressesed in cm^{-1}, and pB is the glass basicity [20].

$$pB = 151 - 0.00259\upsilon \qquad (1)$$

or using the relation

$$pB = 125 - 0.002\upsilon \qquad (2)$$

The Equation (1) is for crystalline phase of glass, and the Equation (2) is for the vitreous phase of glass [24, 25].

The paper presents the study of the crystallization influence on the basicity percentage in the $Li_2O \cdot 2SiO_2$ glasses which were thermally treated at 560°C, for 20, 30, 55, 95 minutes, in order to achieve a gradual crystallization of LS_2 glasses.

EXPERIMENTAL

Lithium disilicate glasses (LS_2) were prepared from: lithium carbonate and quartz with the SiO_2 content of 79.2%.

The melting was done in platinum melting pots at a temperature 1400°C for 3 hours. There were obtained glass disks with 2.5 cm diameter and 2 mm thickness. The glass disks were annealed at 250°C for 3 hours. The cooling of the disks was taking place slowly with a cooling rate by 2.5°C/min.

Simultaneously with the lithium disilicate glass, a glass with the same composition but with 0.1% at. Cu (CuO) was melted. The copper was used as indicator for the experimental determination of the basicity percentage.

The samples with a copper content as indicator are blue, and those without copper are colorless. This colour is due to Cu^{2+} ion which absorbed the visible spectrum at around 800 nm in octahedral sites in silicate glasses [18].

The lithium disilicate samples were thermally treated at 560°C, for different periods of time in order to have a gradual crystallization of the LS_2 glasses. Powder X-ray diffraction (XRD) was used to characterize the sample. Data were collected on a X-ray Diffractometer Shimadzu XRD6000 with CuKα radiation (λ = 1.54178 Å). A scan rate of $0.05°s^{-1}$ was applied to record the patterns in the 2θ range of 10-40°. The X-ray diffraction was used in order to determine the composition of crystalline phases of LS_2 glass samples, thermally treated at 560°C for 20, 30, 55, 95 minutes and for the sample, which was not thermally treated. The crystallinity degree of the samples was determined by using the same technique.

The optical absorption spectra of the present glass samples were recorded at room temperature using a double beam SHIMADZU spectrometer (model UV-3100) in the wavelength range 400-800 nm.

A digital optical microscope was used in order to determine the local topography, the crystallites shape and their crystallization speed of the partially crystallized lithium disilicate samples (LS_2).

RESULTS AND DISCUSSION

It is observed that the sample, which was not thermally treated, presents a typical diffraction pattern for a glass (Figure 1a). For the other samples, the identified crystallization peaks were exclusively assigned to the crystalline lithium disilicate from JCPDS file 72-1140 [29, 30], their intensity increasing with the thermal treatment period (Figure 1b,d). The maximum value of peaks intensity corresponds to the sample thermally treated for 95 minute (Figure 1d). In addition, X-ray diffraction (XRD) analysis showed no evidence of crystalline particles in the as-quenched glass (Figure 1a), and confirmed its vitreous character.

The use of copper in a very low quantity (0.1% at. Cu) as indicator of the crystallization process, showed no differences between the diffractograms of the $Li_2O \cdot 2SiO_2$ glass samples with and without indicator, thermally treated for 55 minutes at 560° (Figure 1c).

In order to determine the crystallinity degree of the samples, there was considered that the sample, which was not thermally treated, is completely vitreous and the sample treated for 95 minutes at 560°C is totally crystallized. It is well known that the crystal growth rate initially increases with increasing temperature and increasing of the time of thermally treatment and then decreases with further increase of temperature and time, producing a bell-shaped of growth rate versus temperature (time) [37].

For the determination method of the samples crystallinity, the Equation (3) was used [31]:

$$\%C = \frac{I_x - I_v}{I_c - I_v} \cdot 100, \qquad (3)$$

where: I_v - the area of the most intense diffraction peak for the vitreous sample (Figure 1a), I_c - the area of the most intense diffraction peak for the totally crystallized sample (Figure 1d), I_x - the area of the most intense diffraction peak for the thermally treated sample in different periods of time.

Data regarding the area of the diffraction peaks as well as the obtained results are presented in Table 1.

Figure 2 is obtained by the graphical representation of the crystallinity of the LS_2 samples, thermally treated at 560°C depending on the thermal treatment time 0, 20, 55, 95 minutes.

Table 1. Data regarding the X ray diffraction.

| Thermal treatment at 560°C for: | Method I | |
	Area of the diffraction peak (mm²):	Crystallinity (%)
0 minutes	23.2	0
20 minutes	49.9	5.35
55 minutes	63.8	22.15
95 minutes	206.5	100

The shape of the dependence between the crystallinity degree and the thermal treatment time is the same with the shape of the kinetic curve of the crystallization process for such glasses [32-37].

The optical absorption spectra of the present glass samples were recorded at room temperature using a double beam SHIMADZU spectrometer (model UV-3100) in the wavelength range 400-800 nm. Data
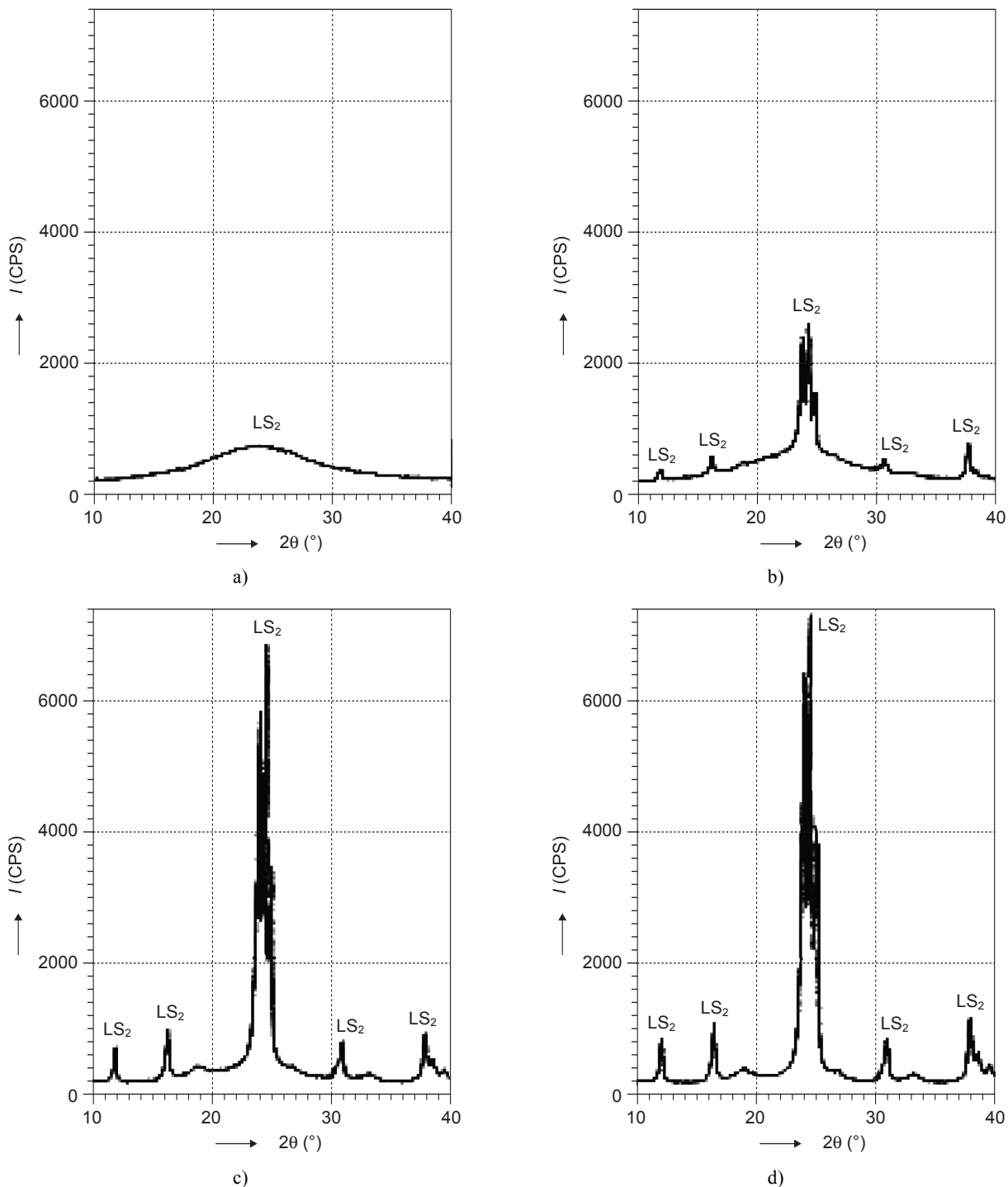
Figure 1. XRD diffraction patterns of the lithium disilicate glass not treated thermally (a) and for the LS₂ glass thermally treated at 560°C for 20 min.(b), 55 min. in presence of 0.1% Cu (c) and 95 min.(d).

obtained from these measurements are presented in Figures 3 and 4. These figures are obtained by the difference between the spectrum of the lithium disilicate glass with 0.1% at. Cu, thermally treated at 560°C for a) 0 min.; b) 20 min.; c) 30 min.; e) 95 min. and the spectrum of the glass with the same composition without indicator and not thermally treated. From these figures can be observed that the obtained curves present a pronounced peak corresponding to Cu^{2+} and a shoulder attributed to Cu^+. It was observed that, with the increase of the thermal treatment time, the peak corresponding to Cu^{2+} moves towards lower wavelengths [26].

Table 2 presents the experimental data for the wavelength number of the absorption peak of the Cu^{2+} ion (v^*), in cm^{-1}, the experimental basicity percentage and the crystallinity degree (C), for the LS_2 glass thermally treated at 560°C for different periods of time.

The crystallinity degree of the LS_2 samples thermally treated at 560°C for 0, 20, 30, 55, and 95 minutes was obtained from Figure 1 based on the interpretation of the X ray diffractograms, and the experimental basicity percentage was calculated by using the Equation (1) [24, 1].

Figure 5 presents the dependence of the Cu^{2+} absorption wavelength number (v^*) with the thermal treatment period. It is interesting to observe that the peak with maximum intensity shows a blue shift with increasing the time of thermal treatment. This kind of shift of Cu^{2+} absorption peak intensity was observed by other authors [38].
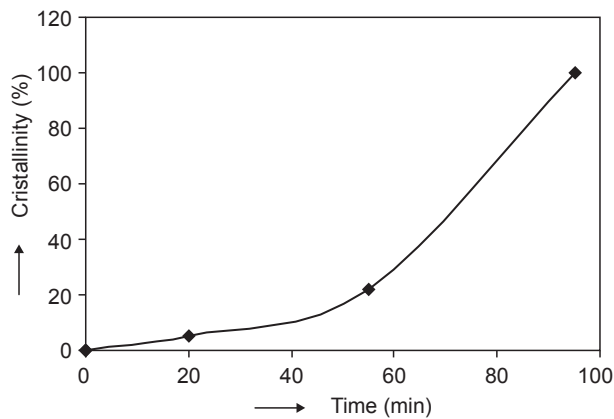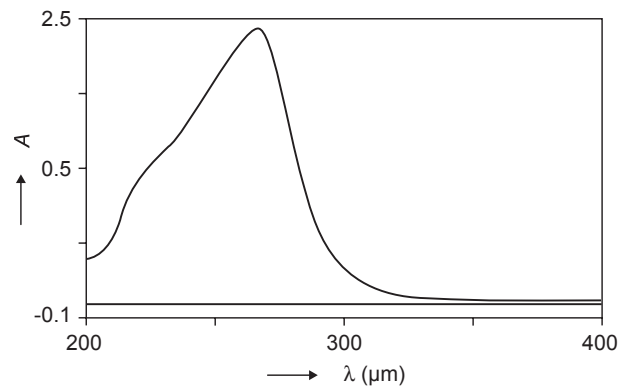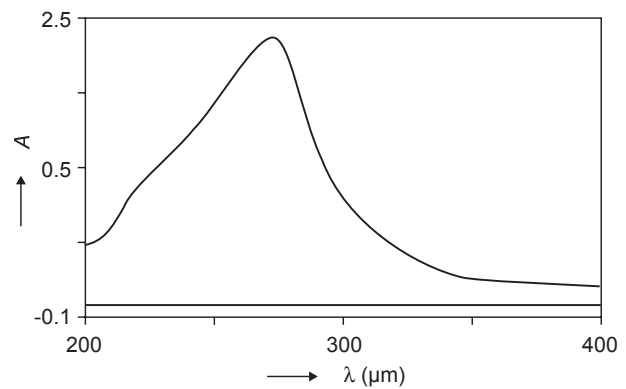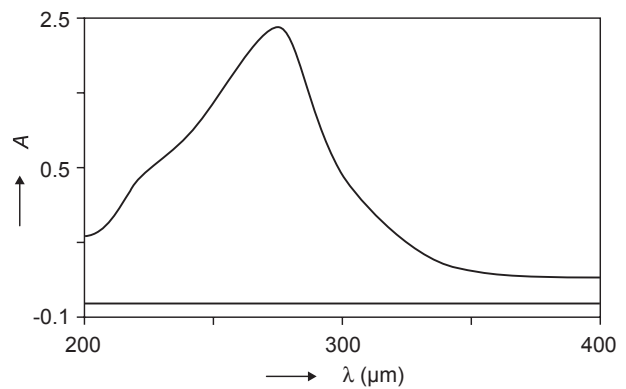
a)

b)

Figure 2. The dependence between the crystallinity degree and the thermal treatment time at 0, 20, 55, 95 minutes for the LS_2 samples thermally treated at 560°C.

c)

Figure 3. The UV absorption spectra for the lithium disilicate glass not thermally treated (a) and thermally treated at 560°C for 20 min. (b) 30 min. respectively (c).

Table 2. Experimental data regarding the studied disilicate lithium glasses.

No.	LS_2 glass thermally treated at 560°C (min)	Cu^{2+} wavenumber σ*, (cm^{-1}), for	Experimental basicity pB_{exp} (%)	Crystallinity degree C (%)
1	0	37707.39	53.34	0
2	20	36845.98	53.78	5.35
3	30	36496.35	54.23	7.5
4	55	35211.27	55.87	22.15
5	95	32786.89	59.43	100

It is observed a linear dependence between the Cu^{2+} absorption wavelength number (υ^*) and the thermal treatment time, expressed by the Equation (4). The value of the correlation coefficient (R^2) can be considered an acceptable value [23, 35]:

$$\upsilon^* = -56.282\, t + 37789; \quad R^2 = 0.9861 \qquad (4)$$

With the increase of the thermal treatment period the peak corresponding to the Cu^{2+} absorption moves towards lower wavenumbers, which, according to Equation (5) of calculation of the experimental basicity, shows an increase of the alkaline character of samples. For the calculation of the experimental basicity percentage the following equation was used:

$$pB_{exp} = [pB_{crystalline}\, C + pB_{vitreous} \cdot (100\text{-}C)]\, /\, 100; \qquad (5)$$

where: $pB_{crystalline}$ - the percentage of the experimental basicity for the LS₂ crystalline determined with the relation (1), $pB_{vitreous}$ - the percentage of the experimental basicity for a vitreous LS₂ determined by the Equation (2), C - the crystallinity degree.

Figure 5. The variation of the Cu^{2+} absorption wavelength number (υ^*) depending on the thermal treatment time at 560°C, for the synthesized lithium disilicate samples.

Figure 6. The variation of the experimental basicity percentage pB_{exp} depending on the thermal treatment time at 560°C, for the synthesized lithium disilicate samples.
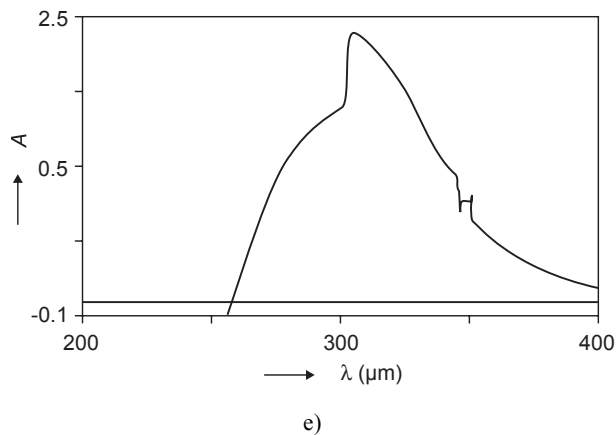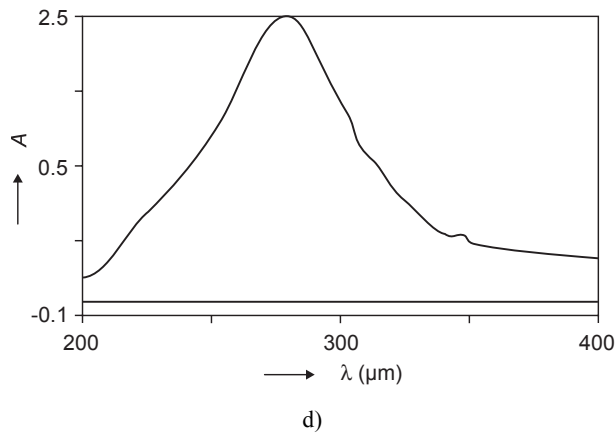

d)

e)

Figure 4. UV absorption spectra for the lithium disilicate glass thermally treated at 560°C for 55 min.(d) 95 min. respectively (e).

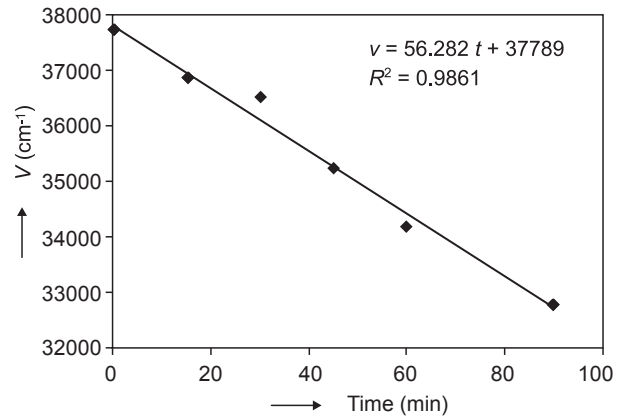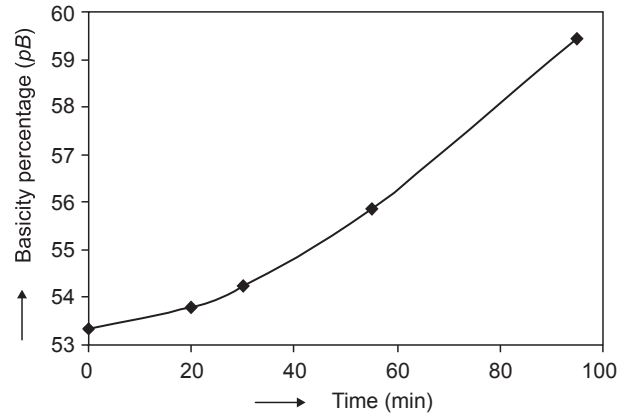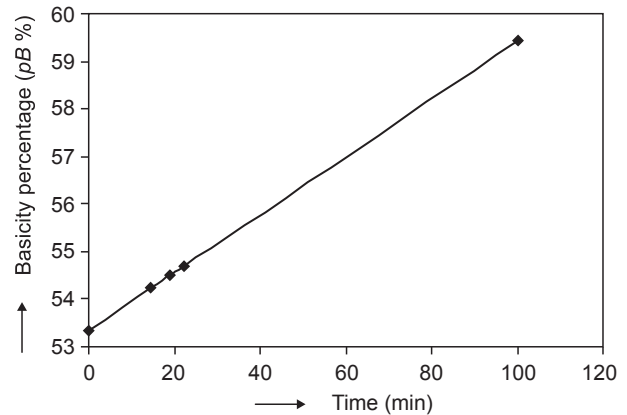Figure 7. Variation of the experimental basicity percentage (pB_{exp}) with the crystallinity degree for the LS₂ samples thermally treated at 560°C for 0, 20, 30, 55, and 95 minutes.

Figure 6 presents the dependence between the experimental basicity percentage pB_{exp} and thermal treatment time.

Figure 7 shows the variation of the experimental basicity percentage pB_{exp} with the crystallinity degree determined from X ray analysis for LS_2 samples thermally treated at 560°C for 0, 20, 30, 55 and 95 minutes.

The linear dependence between the percentage of the experimental basicity p_{Bexp} and the crystallinity degree can be expressed by the following linear relation with a very good correlation coefficient R [3]:

$$pB = 0.0609\ C + 53.342;\ \ R^2 = 0.999 \tag{6}$$

It can be noticed that once the crystallinity degree increases, the wavenumber of the Cu^{2+} absorption decreases, corresponding to a higher basicity of samples, which is situated in the general trend according to which the oxide glasses are less basic than the crystals with the same composition. One of the factors that explain this behavior is the fact that the coordination number of the cations with the oxygen (which has a pronounced basic character), increases when passing the samples from vitreous state to the crystalline one.

The crystallization dynamics was obtained by measuring the maximum diameter of the crystallites Dmax. in the four steps of thermal treatment presented in Table 3. In Figure 9 the increasing of the maximum diameter of crystallites depending on the thermal treatment time at 560°C can be seen.

The crystallization rate can be established by using the Equation (7) [30]:

$$v(t) = \frac{D_{max}(t)}{t} \tag{7}$$

where: $v(t)$ - crystallization rate; $D_{max}(t)$ - the maximum diameter of the crystallites; t - thermal treatment time.

The data obtained for the crystallization rate in function of the crystallites maximum diameter are presented in Table 3.

Table 3. Crystallization rate and maximum diameter of the crystallites.

Temperature and thermal treatment time	Maximum diameter of the crystallites D_{max} (µm)	Crystallization rate $v(t)$ (µm/min)
560°C/20min.	150	10
560°C/30 min.	180	6
560°C/55 min.	235	3.9
560°C/95 min.	280	3.1

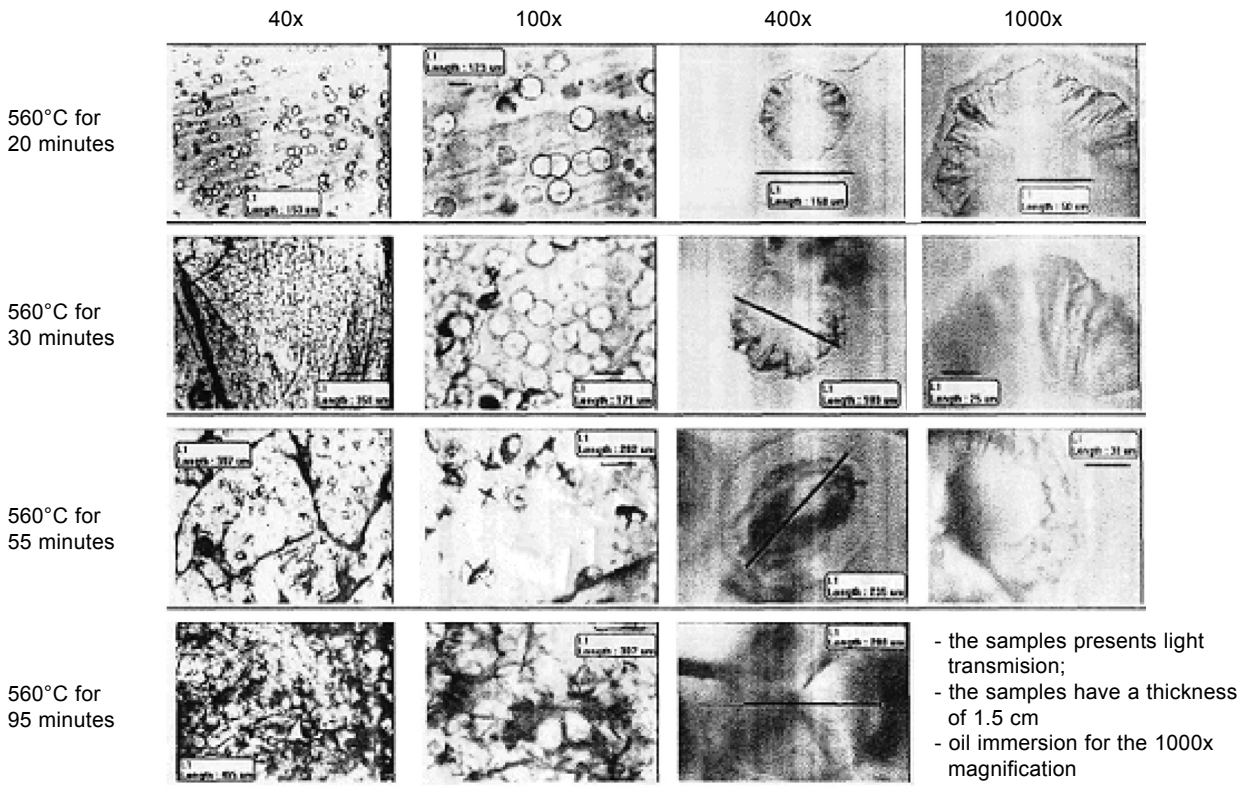Figure 8. Microtexture of the lithium disilicate samples (LS_2) thermally treated at 560°C.

It is observed a relatively normal behavior, the crystallization rate decreases with the increase of the thermal treatment time, due to a saturation effect and a densification of the crystalline structure effect in time. Figure 8 presents the microtexture of the crystallites in LS₂ samples thermally treated at 560°C for 20, 30, 55 and 95 minutes.

The relation between the maximum diameter of the crystallites of glass samples obtained at different time of thermal treatment is shown in Figure 9. Figure 10 depicts the variation of crystallization rate with thermal treatment time for the LiO_2–2SiO₂ samples.

CONCLUSION

The study shows that with the increase in the crystallinity degree the wavenumber of the Cu^{2+} absorption decreases, corresponding to a higher basicity of sam-
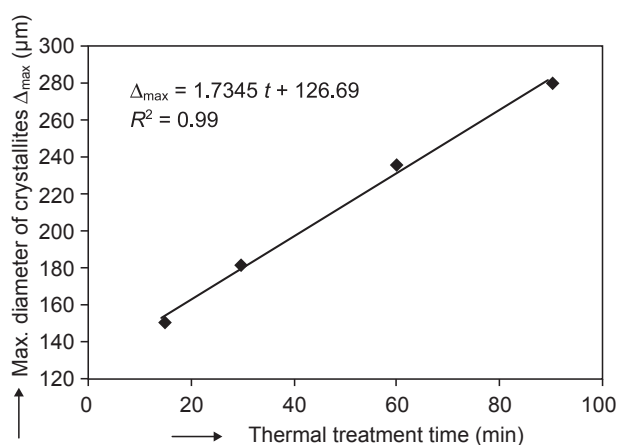
ples. This result corresponds with the general trend according to which the oxide glasses are less basic than the crystals with the same composition [26, 39].

For the system studied the increase in the maximum diameter of the crystallites and a decrease in the crystallization speed with the increase of the thermal treatment time at 560°C was observed.

Figure 9. Maximum diameter of the crystallites D_{max} versus the thermal treatment time *t*, for the analyzed samples LiO_2–2SiO₂ (LS₂).

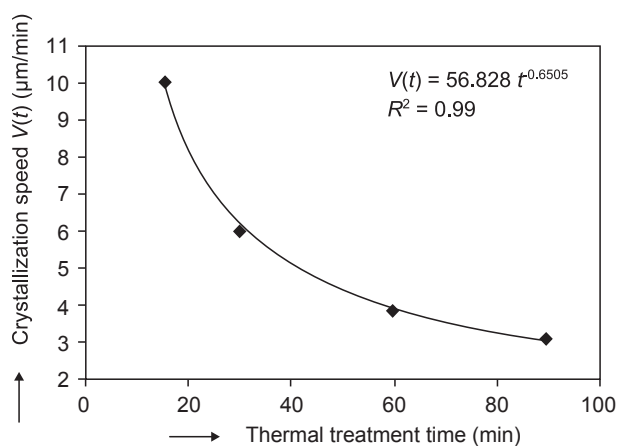Figure 10. Crystallization rate, *v(t)* versus the thermal treatment time *t*, for the analyzed samples LiO_2–2SiO₂ (LS₂).

References

1. Dima V., Baltă P., Eftimie M., Ispas V.: J.Optoelectron. Adv.Mater. *8*, 2126 (2006).
2. Nanba T., Sakida S., Miura Y.: Materials Science and Technology: Materials and Systems *1*, 535 (2006).
3. Radu D., Mazilu C., Grigoras B.: Romanian Reports in Physics *56*, 413 (2004).
4. Duffy J. A., Ingram M. D., Fong S.: Phys.Chem.Chem. Phys. *2*, 1829 (2000).
5. Nagaraja U. P., Kishore G.: Trends Biomater. Artif. Organs *18*, 158 (2005).
6. Yu B., Chen B., Yang X., Qiu J., Jiang X., Zhu C., Hirao K.: J.Opt.Soc.Am. B *83*, 256 (2004).
7. Duffy J. A.: Phys.Chem.Glasses *46*, 257, (2005).
8. Duffy J. A.: Phys.Chem.Glasses *46*, 1, (2005).
9. Duffy J. A.: J.Phys.Chem. B. *108*, 14137, (2004).
10. Duffy J. A.: J.Non-Cryst.Solids *196*, 45, (1996).
11. Kamitsos E. I., Chryssikos G. D.: Solid State Ionics *105*, 75, (1998).
12. Cachia J. N., Deschanels X., Den Auwer C., Pinet O., Phalippou J., Henning C., Scheinost A.: J.Nucl.Mater. *352*, 182 (2006).
13. Nemec L., Kloužek J.: Ceramics - Silikáty *47*, 81 (2003).
14. Chrysicopoulou P. in: Proc. Symposium Structure of Glass, p. 243, Ed. G. Kordas, Athens 2001.
15. Juodkazis S., Misawa H.: Appl. Phys. Lett. *88*, 201909 (2006).
16. Maekawa T.: J.Ceram.Soc.Japan *112*, 467 (2004).
17. Baltă P.: J.Optoelectron.Adv.Mater. *7*, 2347 (2005).
18. Thiemsorn W., Keowkamnerd K., Suwannathada P., Hessenkemper H., Phanichaphant S.: Bull. Mater. Sci. *30*, 487 (2007).
19. Duffy J. A., Ingram M.: J.Am.Chem.Soc. *93*, 6448 (1971).
20. Baucke F. G. K., Duffy J. A.: Phys.Chem.Glasses *35*, 17 (1994).
21. Sakaguchi K., Uchino T.: J.Non-Cryst.Solids *353*, 4753 (2007).
22. Duffy J. A., Ingram M. D.: Optical Basicity, in: *Optical Properties of Glass*, Eds. D. R. Uhlmann, N. J. Kreidl, American Ceramic Society, Westerville 1991.
23. Sreekanth Chakradhar R. P., Ramesh K. P., Rao J. L., Ramakrishna J.: J.Phys.:Condensed Mater. *15*, 1469 (2007).
24. Baltă P.: *Glass Technology*, Didactic and Pedagogic Publishing House, Bucharest 1984. (in Romanian)
25. Baltă P., Baltă E.: *Introduction to the Physical Chemistry of the Vitreous State*, Abacus Press, Kent 1976.
26. Solacolu S., Baltă P., Jitianu G.: Rev.Roum.Chem. *15*, 91 (1970).
27. Radu D., Mazilu C., Căpățînă C.: Rev.Chim. *56*, 399 (2005).
28. Duffy J. A., Ingram M. D.: J.Non-Cryst.Solids *21*, 373 (1976).

29. Kuzielová E., Hrubá J., Palou M., Smrčková: Ceramics - Silikáty *50*, 159 (2006).
30. De Jong, B. H. W. S.: J.Non-Cryst.Solids *176*, 164 (1994).
31. Lenhart A., Schaefer H. A.: Glastechn.Ber. *58*, 139 (1985).
32. Edward J. R., Paul A., Douglas R. W.: Phys. Chem.Glasses *13*, 131, (1972).
33. Yamaguchi S., Imai A., Goto K. S.: Scand. J.Metallurgy *11*, 263 (1982).
34. Dimitrov V., Komatsu T., Sato R: J. Ceramic Soc. Japan *107*, 255 (1999).
35. Kawazoe H.: J.Non-Cryst.Solids *42*, 281 (1980).
36. Duffy J. A, Kamitsos E. I.: Phys.Chem.Glasses *34*, 153 (1993).
37. Ray C. S., Ranasinghe K. S., Day D. E.: Solid State Sci. *3*, 727 (2001).
38. Sreekanth Chakradhar R. P., Yasoda B., Rao J. L., Gopal N. O.: J.Non-Cryst.Solids *352*, 3864 (2006).
39. Dimitrov V., Komatsu T.: J. Solid State Chem. *178*, 831 (2005).

VLIV KRYSTALIZACE NA BAZICITU
SYSTÉMU Li_2O–$2SiO_2$

CAMELIA CĂPĂŢÎNĂ, CLAUDIA MARIA SIMONESCU*

*Constantin Brâncuşi University of Tg-Jiu, Engineering Faculty, 3 Geneva Street, 210152, Târgu-Jiu, Gorj, Romania
Department of Inorganic Technology and Environmental Protection, Faculty of Chemistry and Materials Science, Politechnica University of Bucharest, 1-7 Polizu Street, 011061, Bucharest, Romania

Článek prezentuje studii vlivu krystalizace na bazicitu skla sytému Li_2O–$2SiO_2$. Bazicita tohoto systému byla charakterizována kvantitativními metodami. Vzorky skel bez i s obsahem Cu^{2+} jako indikátoru byly zahřívány při 560°C po dobu 20, 30, 55 a 95 minut. Výsledky ukázaly, že s rostoucím podílem krystalické fáze klesá vlnočet maxima absorpce Cu^{2+} iontů, což odpovídá vyšší bazicitě skla. Byl pozorován růst velikosti krystalů a pokles krystalizační rychlosti s rostoucí dobou výdrže při teplotě 650°C.