OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 3, No. 5, May 2009, p. 435 - 438

Structure of ecological lead free silicate glasses

B. A. SAVA, A. DIACONU, L.-D. URSU, M. ELISA[a], I. STAMATIN[b], F. NASTASE[b], C. NASTASE[b]
National Institute of Glass, 47th Th. Pallady Av., sect.3, 032258, Bucharest, Romania
[a]*Department of Optospintronics, National Institute of Optoelectronics-INOE 2000, Atomistilor Str. 1, P.O.Box MG - 5, RO-77125, Com. Magurele, Romania*
[b]*University of Bucharest, Faculty of Physics, 36-46 Mihail Kogalniceanu Boulevard, sect. 5, Bucharest, Romania*

The paper investigates ecological glasses prepared from non-toxic raw materials. These glasses have compositions belonging to the quaternary oxide systems: SiO_2-R'_2O-R''O-$R'''O_2$, where R' is Na or K, R'' is Ca or Mg and R''' is Zr or Ti. The present work aims to replace barium and lead oxides by potassium, magnesium, zirconium and titanium oxides, in order to use such materials as lead free crystals and for other applications. Some of the characteristic temperatures, such as: vitreous transition point, low and high annealing points, softening point and also the thermal expansion coefficient between 20 and 320°C are measured. FTIR and Raman spectroscopy provide interesting structural information. The characteristic vibration modes for silicon and titanium oxide are discussed. The vitreous network forming role of zirconium oxide is put in evidence. The refraction index calculation and UV-VIS transmission diagrams are presented and discussed.

(Received March 10, 2008; accepted May 25, 2009)

Keywords: Ecological glass, Lead free glass, FTIR, Raman, UV-VIS

1. Introduction

The paper presents a structural study on some glasses from the oxide system SiO_2-R_2O-RO-ZrO_2. These materials don't contain toxic substances such as BaO, PbO, As_2O_3, As_2O_5. The vitreous system contains potassium, magnesium and zirconium oxides, for lead free crystals.

The molecular energy levels studies are based on two techniques: Fourier transform infrared absorption spectroscopy (FTIR) and Raman spectroscopy. A vibration motion is active in IR range when the dipole moment of the molecule is changed [1]. A transition is Raman active when there is a change in the molecule polarizability. FTIR and Raman spectra provide useful information about the role of zirconium oxide in the structure of those vitreous materials. UV-VIS transmission provides information about electronic transition within glass atoms.

2. Experimental

The chemical reagents used for the batch preparation were: SiO_2, Uricani; TiO_2, e.g., CHIMOPAR; zirconium silicate, e.g., Turkey, Na_2CO_3, e.g., ICD; K_2CO_3, e.g., CHIMOPAR; $CaCO_3$, e.g., CHIMOPAR; $MgCO_3$, e.g., CHIMOPAR; ZnO, e.g., CHIMOPAR; Al_2O_3 99,9%, Tulcea, and NaCl 99%, Govora.

The batch compositions (wt. %) are presented in Table 1.

The glass batch was prepared by the wet-route, using water (6 wt. %) as reaction environment, added under continuous stirring. Then, the mixture is poured into a refractory crucible (0.5 liter capacity) and it was melted in an electric Nabertherm oven, equipped with superkanthal heating elements. The glass batch was melted in alumina crucibles at 1500°C, for 2 hours. The vitreous melt was cast by pouring into metallic plates followed by annealing at 500-550ºC, for 1 hour.

Table 1. The oxide composition of the ecological silicate glasses (wt. %)

Oxide//%	CFP-1	CFP-2	CFP-3	CFP-6	CFP-7
SiO_2	73,1	72,3	72,3	67,3	67,3
MgO	3,8	0,9	0,9	0,9	0,9
CaO	5,3	1,2	1,2	1,2	1,2
Na_2O	6,2	6,1	6,1	6,1	6,1
K_2O	11,6	11,5	11,5	11,5	11,5
TiO_2			8	4	0
ZnO					4
ZrO_2		8		8	8
Al_2O_3				1	1

UV-VIS-NIR absorption spectra of CFP1, CFP2, CFP3, CFP6 and CFP7 samples were plotted by means of a Jasco V570 spectrophotometer, in the range 220-2000 nm, the spectra being acquired by the reflection technique.

IR absorption curves were recorded in the 4000 to 400 cm^{-1} range for CFP samples, using a FTIR Jasco 6200 spectrophotometer, equipped with an ATR device with variable angle, the spectra being acquired at 50 degrees angle.

Raman spectra were plotted with a Raman System 2001 Ocean Optics equipment, using a 500 mW Ga-As laser diode, emitting at 785 nm, with a resolution under 8 cm^{-1}.

3. Results and discussion

In Fig. 1 we present the dependence of the refractive index on the amount of zirconium oxide and titanium oxide. It is known that the above-mentioned oxides increase the refractive index of the final product, which is used as crystal glass. The x-axis represents the equivalent content of oxide which was calculated by the next weight % formula:

$$\% \text{ equivalent oxide} = c_1 x\%TiO_2 + c_2 x\%ZrO_2 \quad (1)$$

where, from our previous experimental data [2]: $c_1 = 1$; $c_2 = 0.5$ and x % = weight % for the oxides.
Zirconium oxide and titanium oxide have a different influence on the refractive index of the glass, i.e. TiO_2 has a two-fold increasing effect as compared to the same amount of ZrO_2.

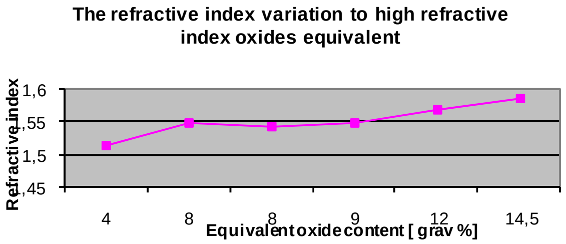

Fig. 1. The variation of refractive index versus titanium and zirconium oxides equivalent

It can be seen (Fig.1) that a high content of those two oxides leads to an important increase of the refractive index. The sample that contains 14.5 % equiv. oxide has the higher refractive index, about 1.585.

The increasing of TiO_2 and ZrO_2 amount in the glass content is restricted because of the significant crystallization tendency of SiO_2 -TiO_2 -ZrO_2 oxide system.

Fig.2 presents UV-VIV-NIR diagrams for CFP1, CFP2, CFP3, CFP6 and CFP7 samples.

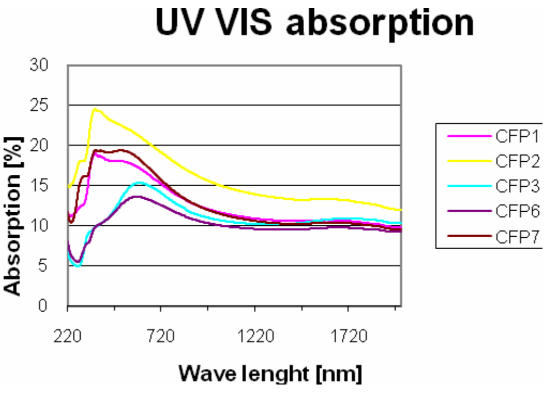

Fig.2. UV-VIS-NIR spectra of CFP1, CFP2, CFP3, CFP6 and CFP7 glass samples

It is shown that CFP1 glass sample exhibits optical absorption at about 400 nm and 480 nm. CFP2 glass sample that contains ZrO_2 exhibits a more pronounced absorption peak at 400 nm and a peak at 480 nm, which is very weak as compared to CFP1 sample. Thus, we may assess that ZrO_2 decreases the optical transmission of the ecological glass caused by its opaqueness effect. CFP7 glass sample has a similar behavior as CFP1 sample but the peak at about 480 nm is more evidenced. We may assess that ZnO counteracts the opaqueness effect due to ZrO_2 on the glass matrix. The absorption spectra of CFP3 and CFP6 glass samples are similar, presenting an absorption peak in UV domain at about 300 nm and absorption peaks in the visible range at 675 nm and 750 nm for CFP3 and CFP6 glass sample, respectively. In the case of these two samples, it is noticed a shift of the absorption peak from UV domain (CFP1, CFP2 and CFP7) to the visible range, possible due to TiO_2. All the glass samples exhibit a high optical transmission (over 80%) in NIR domain up to 2000 nm.

In Fig.3, we present FTIR plots for CFP1, CFP2, CFP3, CFP6 and CFP7 samples in the domain 500-4000 cm^{-1}.

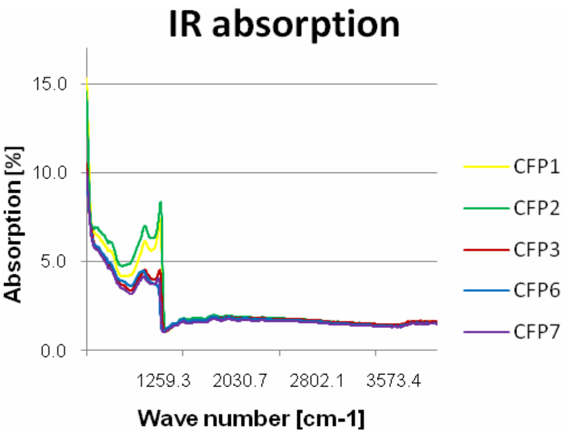

Fig.3. FTIR spectra of CFP1, CFP2, CFP3, CFP6 and CFP7 glass samples.

FTIR absorption spectra of CFP7 sample doesn't put in evidence the maximum for un-polymerized $[ZnO_6]$ group, in 460 – 468 cm^{-1} range whereas the maximum for polymerized $[ZnO_4]$ group, in 578 – 581 cm^{-1} range appears [3]. The specific maximum for polymerized $[SiO_4]$ group [3, 4] can be observed at about 1095 cm^{-1}. The peak is more pronounced for CFP1 and CFP2 samples, that don’t contain titanium oxide. Raman spectra of TiO_2-containing glass samples, CFP3 and CFP6, show vibration peaks characteristic for silicon oxide and new ones, in the region 1000-1100 cm^{-1}, attributed to Si-O-Ti bonds. CFP3 sample, which contains the most important amount of titanium oxide, exhibits new peaks at 890 cm^{-1} which could be assigned either to the vibration of Si-O-Ti bond or to the condensed $[TiO_4]$ group. This confirms that TiO_2

is a vitreous network former together with SiO_2, providing some mixed oxide network. The maxima at above 950 cm^{-1}, which are attributed to condensed – polymerized [TiO_4] group increase from CFP6 to CFP3 sample, when titanium oxide content increases.

FTIR spectroscopy also revealed specific Bu and Eu modes at about 580 and 725 cm^{-1}, for monoclinic and tetragonal zirconium oxide [5, 6], more pronounced in the case of the CFP2 sample. IR peaks at 3440 and 1625 cm^{-1} attributed to bending and stretching vibrations of O-H groups and the peaks at 1540 and 1383 cm^{-1}[7] assigned to non-bridging and bridging OH group, are not present in the analyzed samples.

Figs. 4 and 5 present Raman shifts for CFP1, CFP2, CFP3, CFP6 and CFP7 samples in the domain 100-4000 cm^{-1}. Fig.6 presents Raman spectra for two selected samples, in the domain 0-60 cm^{-1}.

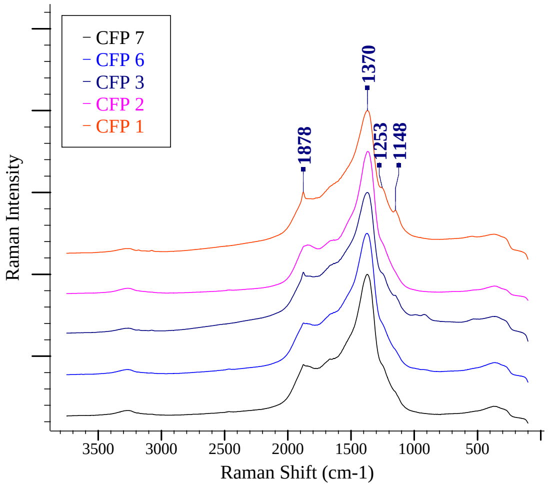

Fig. 4. Raman spectra for the lead free samples, thermal treated at 1450°C, for two hour.

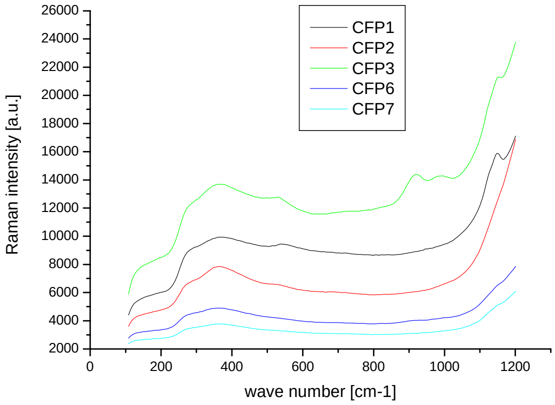

Fig. 5. Raman spectra for five samples, on 100-1200 cm^{-1} domain

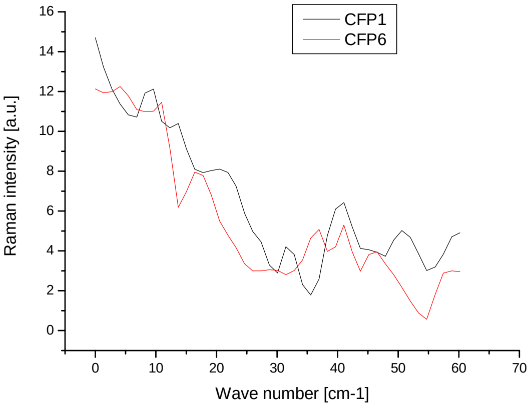

Fig. 6. Raman shift for the CFP1 and CFP6 code samples, on 0-60 cm^{-1} domain

Raman spectra reveal important shifts at about 175, 345, 1148, 1253, 1370 and 1878 cm^{-1}. The peaks located at 175 and 345 cm^{-1} are close to the maxima attributed to monoclinic phase of zirconium oxide [8].

Fig.7 shows specific maxima for zinc and titanium oxide bonds in the 200-600 cm^{-1} region [1]. Characteristic Raman peaks for Si-O-Si symmetric bending ν2 [4, 9], and for Q_2 and Q_3 species, appear in 290 – 373 cm^{-1} and 431 – 497 cm^{-1} ranges. The first peak attributed to Q3 species of SiO_2 [4, 9], at about 290 cm^{-1} is shifted to higher wave number, probably because of mixed silica and zirconia's network apparition. For CFP1, CFP2 and CFP3 samples the specific Raman maxima for asymmetric bending ν4 [9] appear in 520 – 566 cm^{-1} domain. The Si-O stretching vibrations, assigned to Q2 type tetrahedron as trimer ring are identified at 596 – 607 cm^{-1}. CFP3 sample is the only sample that presents significant peaks for Q2 species of SiO_2 tetrahedron at 920 and 990 cm^{-1}. Q3 species exhibit symmetric stretching peak at about 1150 cm^{-1}[10].

In the case of CFP7 sample, Raman active phonons of Zn-O bond can be identified as E2 type in the domain 432 - 436 cm^{-1} as well as E1 type phonons at 581 – 585 cm^{-1}.

CFP and CFP6 samples present characteristic Raman shifts, specific for Eg type vibrations of anatas titanium oxide at 195-198 cm^{-1} and 638-640 cm^{-1}. Supplementary, B1g type anatas vibrations at 397-399 cm^{-1} and also A1g type vibrations at 514-518 cm^{-1} were identified.

The sample containing ZrO_2 reveals a shift of TiO_2 Raman peaks to lower energy, which put in evidence the formation of Zr-O-Ti vitreous mixed network.

Fig.6 presents Raman peaks in the 20-60 cm^{-1} domain, attributed to different Zr-O bonds [11].

The peaks over 1200 cm^{-1} are related to the -C-O, -N-O and H-O- vibrations bands. Raman shifts from 1370 and 1878 cm^{-1} are attributed to OH group's vibrations.

4. Conclusions

In the present work, silicate glasses from the oxide systems: R_2O (R: Na, K) – R'O (R': Ca, Mg, Zn) – ZrO_2 - SiO_2 have been obtained and investigated.

UV-VIS-NIR absorption spectra revealed ZrO_2 effect to decrease the optical transmission of the glass samples as well as the counteracting effect of ZnO as regards the increasing of the optical transmission. It is noticed the shift of the absorption peaks in the red range of the visible spectrum due to TiO_2 influence.

The calculated refractive index values are closely to the experimental data for the compositions in the system based on zirconium, silicone and magnesium oxide.

FTIR transmission spectra in the range 4000-400 cm^{-1}, put in evidence ZnO_4, ZnO_6, TiO_4, TiO_6, ZrO_6, SiO_4 groups as well as Si-O-Ti and Ti-O-Ti groups.

Raman spectra in the range 0-4000 cm^{-1} show vibration peaks specific for silicon dioxide as well as for zirconium and titanium dioxide. This emphasizes the vitreous network forming role of these components in the glass host. Zirconium oxide is able to form mixed network together with silicone oxide and titanium oxide.

References

[1] B. A. Sava, A. Diaconu, M. Elisa, C. E. A. Grigorescu, I. C. Vasiliu, A. Manea, Super lattices and Microstructures, (2007).

[2] B. A. Sava, A. Diaconu, L. D. Ursu, L. Boroica, M. Elisa, C. Grigorescu, C. Vasiliu, I. Stamatin, F. Nastase, C. Nastase, A. Dumitru, XXIst Int. Cong. of Glass, ICG 2007, France, Strasbourg, CD Rom proc., H6 (2007).

[3] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th edition, Wiley- Interscience, New York (1986).

[4] P. F. McMillan, Am. Min., **69**, 622 (1984).

[5] G. Davidson, Spectroscopic Properties of Inorganic and Organometallic Compounds, 35, Royal Society of Chemistry, London, England (2002).

[6] K. McGuire, Z. W. Pan, Z. L. Wang, D. Milkie, J. Menendez, A. M. Rao, J.Nanosci. Nanotech., **2**(5), 1 (2002).

[7] H. W. Kunert, Cryst. Res. Technol., **38**(3-5), 366 (2003).

[8] H. Ortiz, J. C. Alonso, E. Haro-Poniatowski, Journal of Electronic Materials, **2**,137 (2005).

[9] B. A. Sava, T. Visan, U.P.B. Sci. Bull., series B, **69**, 1, 11 (2007).

[10] B. A. Sava, A. Diaconu, M. Elisa, C. E. A. Grigorescu, I. C. Vasiliu, A. Manea, Superlattices and Microstructures, **42**, (1-6), 314 (2007).

[11] M. Yashima, N. Ishizawa, M. Yoshimura, J. Am. Ceram. Soc., **76**, 641 (1993).

---

*Corresponding author: avabogdanalexandru@yahoo.com