Optical constants determination in thin films lead-free vitreous coatings.

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The optical constants ***n(E)*** and ***k(E)*** of thin films lead-free vitreous coatings have been determined. The extinction coefficient ***k*** was measured in the VIS/UV range using absorption techniques and the real part of the complex index of refraction ***n*** was calculated by using the Kramers-Kronig analysis. The sample was prepared from recycled soda-lime glass and melting anhydrous boric oxide in varying proportions, and then deposited on (100) MgO substrates for optical measurements. These measurements shown an optical energy gap about 3.2 eV and high values of ***n*** and ***k*** in the ultraviolet region, as reported for vitreous materials doped with PbO.

Keywords: Optical characterization, thin films, optical gap, vitreous coatings.

1. Introduction

Most of the optical applications of soda lime glasses are based on the knowledge of the optical constants. Soda lime glasses are well-known materials whose uses ranges from crystal windows to complicated optical apparatus. Current use of these particular oxide glasses is based on their good transmission in the optical region of the spectrum. Absorption in the visible region results from the superposition of the tails of the electronic and vibrational transitions of the atoms and contributions from added impurities [1].

The index of refraction depends on the chemical composition of the glasses. Changes in the optical constants are in many cases very weak and very precise methods are necessary to determined them. There are many methods for optical characterization of thin films ranging from complicated computational techniques to ingenuous experimental arrangements [2-4].

In this work a different approach is presented based in the work of Forohui and Bloomer [5,6] which used the dispersion relations for the determination of the index of refraction real *n* and complex *k*. Additional experimental data were obtained from the transmission spectra to completely determine the optical constants. Thin films samples were prepared from recycled soda- lime glass and melting anhydrous boric oxide in different stoichiometries.

2. Experimental details

Samples were prepared from melting recycled soda lime glass lead-free and anhydrous boric oxide ($Na_2B_4O_7$) in varying proportions. For the vitreous coatings, the Rhodes criterion was used, which states for every component the mol number *vs* the liquid temperature. In our experiments the liquid temperature ranged between 815 and 980 °C.

Based on the transparent soda lime glass lead- free composition (Na_2O CaO $6SiO_2$), four different stoichiometries of transparent glass and anhydrous boric oxide were chosen to satisfied the Rhodes criteria [7]. Unitary formulas contain basic and acid oxides acting like network formers, being different from conventional glass compositions.

The samples for optical transmissions measurements were deposited on (100) MgO substrates and melting was undertaken in a programmable cylindrical furnace in air atmosphere. For the measurements of optical absorption spectra, a Lamda UV/VIS spectrometer was used over the wavelength range (250nm- 900 nm).

To assure the accuracy in the absorbance, a baseline scanning was performed before each sample measurement and a subtraction of the baseline was taking during each measuremente. Absorption measurements were carried out at room temperature. The absorption coefficient α, are derived from the absorbance spectrum using the thickness reduced method [8].

3. Theoretical Considerations.

a. Determination of the absorption edge and optical gap.

The absorption edge of a non-metallic material, crystalline or non-crystalline, is determined by the fundamental absorption [9]. When electron-hole interactions are neglected, the density of states profile is well shaped and is proportional to some power of the energy. Relations between the energy and absorption can be written as the following equation, proposed by Tauc [10]:

$$a(\hbar w) = B\frac{(\hbar w - E_g)^2}{\hbar w} \qquad (1)$$

where α is the absorption coefficient, ħω the photon energy, *B* is a constant and E_g the optical gap.The absorption coefficient at the higher energy side of the absorption edge are used to fit Tauc equation finding the optical gap E_g of these glasses by plotting $(a.\hbar w)^{1/2}$ against ħ*w*.

b. Determination of the complex index of refraction k.

The optical properties of any medium can be described by the complex index of refraction, $N = n\text{-}ik$. For the determination of n and k absorbance or transmittance can be performed.

The extinction coefficient k can be obtained from the absorption coefficient using the expression $a = 2wk/c$. To determine the index of refraction a different approach can be carried out. Theoretically, when the complex part of the index of refraction k as function of $E = \hbar w$ is known, $n(E)$ can be determined, the equations used to calculated this dependence are the Kramers-Kronig relations. Forohui and Bloomer [5,6], deduced an expression based on a one- electron model extended to amorphous materials. In this paper we used this approach based in the following equation,

$$n(E) - n(\infty) = \frac{1}{p} P \int_{-\infty}^{\infty} \frac{k(E') - k(\infty)}{E' - E} dE' \qquad (2)$$

where P denotes Cauchy´s Principle value integral.

Using the consideration proposed by Forohui and Bloomer, $n(E)$ is then found by:

$$k(E) = \frac{A(E - E_g)^2}{E^2 - BE + C} \qquad (3)$$

and

$$n(E) - 1 = \frac{B_0 E + C_0}{E^2 - BE + C} \qquad (4)$$

where

$$B_0 = \frac{A}{Q}\left[-\frac{B^2}{2} + E_g B - E_g^2 + C\right] \qquad (5)$$

$$C_0 = \frac{A}{Q}\left[(E_g^2 + C)\frac{B}{2} - 2E_g C\right] \qquad (6)$$

$$Q = \frac{1}{2}(4C - B^2)^{1/2} \qquad (7)$$

Therefore if E_g, A, B, C, B_0, C_0, are determined from the experimental data and using a nonlinear least-square curve-fitting program, the real part of the index of refraction n can be calculated.

4. Results and discussion.

Fig. 1 shows the absorption for our glasses: B_2O_3- R_nO_m (R_nO_m: SiO_2, CaO, Na_2O). The general characteristic of these spectra is that they are composed of an almost flat baseline (absorption negligible) and a steep cut off (big absorption). UV absorption edge positions of these glasses depends on the chemical compositions, they shift to bigger energy values, as the amount of anhydrous boric oxide is incremented. The effect is remarkable on glass formers. Any glass former like B_2O_3 shifts the UV edge to longer wavelengths or smaller

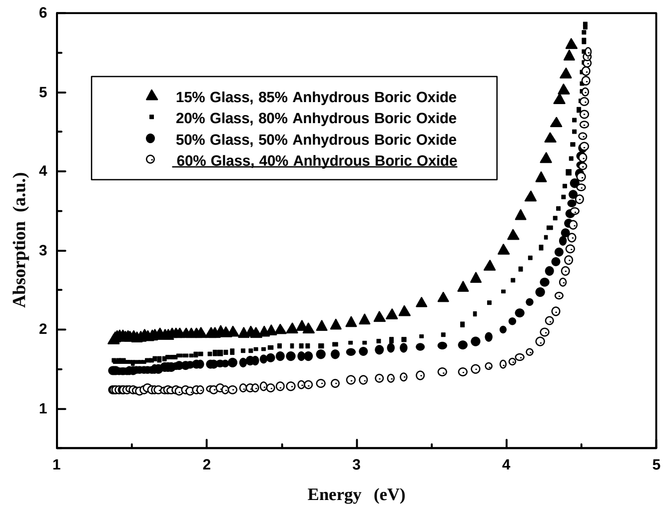

Fig. 1. Absorption spectra for different chemical compositions of recycled glass and melting anhydrous boric oxide

energy values, which indicates that B_2O_3 acts like glass former instead of a network modifier. Our results show also, that the content of anhydrous boric oxide is critical in order to get a very good absorption at the UV edge.

Chemical composition of 60% recycled glass and 40% anhydrous boric oxide, is expected to have very good transmission properties at the visible part of the spectrum and a big absorption at the UV energies, which makes this type of glasses adequate to be used as ceramics coatings.

Fig. 2 shows the absorption coefficient for these glasses with chemical composition of 60% recycled glass and 40% of melting anhydrous boric oxide and the square root rule from the Tauc equation for non-direct transitions (eq. 1). This data fitting is significantly good, as reported for various authors [11], which indicates that the assumption of a parabolic approximation is valid and the energy gap E_g corresponds to the transitions from the bottom of the valence band to the top of the conduction band [9,10]. For this composition the value obtained of E_g was 3.2 eV.

Fig. 3 shows the $n(E)$ and $k(E)$ spectra from 400 nm to 280 nm, calculated using experimental data from the absorption spectra and the method suggested by Forohui and Bloomer. Calculations were made around the absorption edge and the optical gap = 3.2 eV. They show big values for n and k in this region, like those found in vitreous materials doped with PbO.

5. Conclusions.

Absorption spectra have been obtained for glasses: B_2O_3- R_nO_m (R_nO_m: SiO_2, CaO, Na_2O) obtained melting recycled glass lead- free and anhydrous boric oxide in varying proportions. As the content of B_2O_3 is increased, the absorption edge is shifted toward higher energies.

At the high energy end of the absorption edge, data of the absorption coefficient fits the Tauc's square-root rule relation very well, specially for the chemical composition:

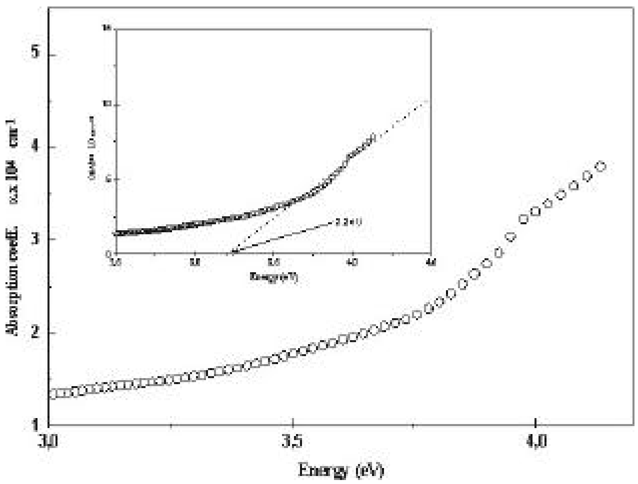

Fig. 2. Absorption coefficient and a square- root fitting of glasses: B_2O_3- R_nO_m (R_nO_m: SiO_2, CaO, Na_2O) for composition: 60% recycled glass and 40% melting anhydrous boric oxide.

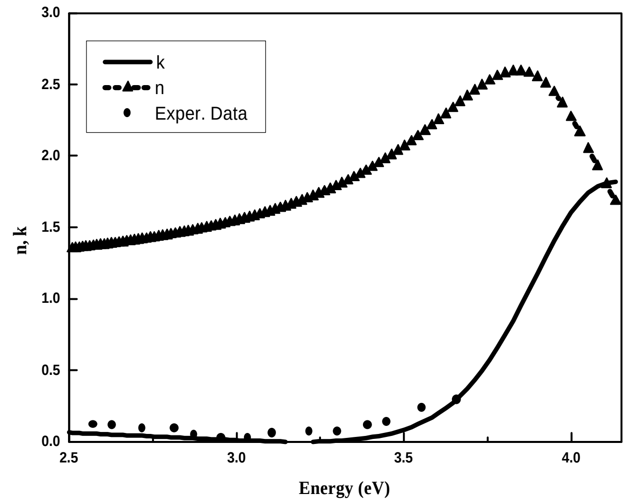

Fig. 3. The n(E) and k(E) spectra from 400 nm. – 280 nm. for Glasses: B_2O_3- R_nO_m (R_nO_m: SiO_2, CaO, Na_2O) for composition: 60% recycled glass and 40% melting anhydrous boric oxide.

60% recycled glass and 40% melting anhydrous boric oxide. For the same glasses the spectra *n(E)* and *k(E)* were calculated using the Forohui and Bloomer method.

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