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**OPTICAL AND THERMOLUMINESCENT
CHARACTERIZATION OF MAGNETO-OPTICAL
TERBIUM ALUMINOSILICATE, MULTICOMPONENT
FLUORPHOSPHATE AND CuO-DOPED BOROSILICATE
SPECIAL GLASSES**

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ABSTRACT

Three special glasses were selected as examples for the study of properties which characterize the physical behavior of these materials in order to attain a better understanding of the processes leading to the special features presented by multicomponent glasses with compositions especially designed for specific purposes.

a) A magneto-optical aluminosilicate glass containing large amount of Tb^{3+} showed optical absorption (OA) bands, identified as transitions from the Tb^{3+} ground level 7F_6 to the excited states inside the optical band gap of 5.0 eV. The higher excited level bands, which are less shielded, were broadened after γ -irradiation due to their stronger interaction with charge carriers released by the ionizing radiation and trapped at available (or created) sites.

b) A multicomponent alkali earth, sodium, aluminum and magnesium fluorophosphate glass, doped with terbium and cerium, contained only the Tb^{3+} contributions to the OA spectrum,

inside a relatively clean optical band gap of 5.0 eV.

c) A CuO-doped borosilicate laser safety eye protection glass showed a very high stability of the OA spectrum of the ${}^2F_3(D) \rightarrow {}^2F_5(D)$ transition after ${}^{60}Co$ γ -irradiation, which is an important quality of the laser safety eye protection glass preserving the optical window between 16000 cm^{-1} and 28000 cm^{-1} . However, it was noticed a reduction of the band gap to about 4.2 eV, by the UV edge shift produced by Cu^{2+} ions. The AO in the visible, infrared (IR) and ultraviolet (UV) regions were measured before and after ${}^{60}Co$ γ -irradiation with exposure of 2.58 C/kg. Thermoluminescence (TL) measurements were performed of the irradiated samples.

Unitermos: vidros especiais, absorção óptica, termoluminescência.

Keywords: special glasses, optical absorption, thermoluminescence.

1. INTRODUCTION

We have selected three different examples of special glasses in order to show how different experimental techniques provide complementary informations contributing to a general understanding of the properties achieved by means of exhaustive series of trial and error processes in the glass preparation techniques seeking the optimum composition capable to satisfy some previously selected features, such as laser glasses, fiber optics and glass ceramics with several dopants.

Important applications of the magneto-optical glasses are the laser isolators, modulators and fast optical switches. In particular, a Faraday rotator can control the direction of polarization of light by applying a magnetic field along the axis of the propagating light. Although the interest for the magneto-optical applications of vitreous materials containing large quantities of rare earth ions is more recent, Robinson and Graf [1] produced aluminosilicate glasses containing Tb^{3+} , Pr^{3+} and Dy^{3+} the early as 1964. It is our scope to perform a simple characterization of the H90-45 sample of composition (wt%) 25SiO₂-12Al₂O₃-58Tb₂O₃-4.0MgO-1.0Sb₂O₃ strictly in respect to the complementary OA of visible, IR and UV regions, before and after ${}^{60}Co$ γ -irradiation with exposure of 2.58 C/kg.

The field of halide glasses, in particular the fluorides, has received an increasing attention in the last two decades [2,3]. The reason is the enormous potential of these materials for the application for the production of very low loss infrared waveguide materials. The presence of absorption peaks in the 1-4 μm wavelength range are responsible for a

considerable loss in fluoride glass optical fibers [4]. Among the impurities which contaminate the quality of these glasses are the OH⁻ (one of the most pervasive), transition metals, rare earths, CO₂ and others. In this work the OA bands due to the presence of the Tb^{3+} ion and OH⁻ before and after γ -irradiation at room temperature of the H84-114 sample of composition (wt%) 7.49 NaPO₃-16.45 MgF₂-16.38CaF₂-17.66SrF₂-11.63BaF₂-30.39AlF₃ and additional 8Tb₂O₃-0.5CeO₃ are presented and discussed.

Laser safety goggles of composition such as of the sample H85-69, (wt%) 58.58SiO₂-10.75Na₂O-7.17K₂O-12B₂O₃-2Al₂O₃-3.5CaO-6ZnO and additional 4.0CuO, must have high optical density in the range of laser emission wavelengths and sufficient transmission in the visible, so that the operator is provided with adequate protection and comfortable conditions to see clearly the beam target [5]. Certain thermal stability is also desirable, which is accomplished by the presence of boron oxide in the glass composition increasing, therefore, the bridging oxygen amount in the glass-forming network [5].

The scope of this work is to study by means of OA and TL characterization techniques how the analysed spectra of three different examples of multicomponent special glasses are more or less sensitive to the neighborhood of the local glassy matrices.

2. GLASS PREPARATION

The Tb^{3+} magneto-optical aluminosilicate glass sample H90-45 was prepared using low iron content raw materials. The batch was melted in platinum crucible at 1500°C using

stirring device in order to make the material homogeneous. After cooling to a certain temperature, the melt was poured into a preheated iron mould and then, annealed at starting temperature of 550°C followed by slow cooling to room temperature by turning off the furnace. For fluoride glass preparation, either anhydrous metallic fluorides or metallic oxides can be chosen as raw materials. The fluorides of most metals are available and their purity should be 99.99% or better. The conversion of oxides in fluorides is obtained by reaction with either NH_4HF_2 or CCl_4 . The alkali metal and some transition metal fluorides are highly moisture sensitive, but others such as BaF_2 are less so. Eventual excess of oxygen in the melt can lead to precipitation of metallic oxides which can serve as nucleation sites for crystallization of glass. The characterization of some properties was carried out of the sample H84-114, fused in platinum crucible at 850°C. The CuO-doped borosilicate glass H85-69 was melted in platinum crucible at 1420°C. The boron oxide was used in order to increase the bridging oxygen content to improve the thermal stability of the material of the glass[5], since additional contribution of vibration modes are provided to its specific heat [6,7]. The presence of Na_2O increases the UV transmittance, in addition to the usual glass-modifier function.

3. IRRADIATION AND PHYSICAL MEASUREMENTS

Samples of dimensions 1.0 x 1.0 x 0.17 cm were cut and polished for the OA and IR measurements.

The OA spectra of the visible and UV regions were taken using a Carl Zeiss spectrophotometer mod. DMR 21 and the IR measurements were carried out with a Jasco IR-700 spectrophotometer, before and after ^{60}Co γ -irradiation with exposure of 2.58 C/kg. In order to perform the TL measurements, powdered samples were provided, which were sieved to obtain separate amounts of grains of dimensions of 0.074 mm and 0.177 mm, respectively. The TL curves were obtained by heating the γ -irradiated samples with linear temperature slope of 2°C/s from 50 to about 350°C using Harshaw mod. 2000A equipment.

4. RESULTS AND DISCUSSION

All the OA bands observed in Fig.1, measured before and after ^{60}Co γ -irradiation (exposure of 2.58 C/kg at room temperature) of the H90-45 sample with thickness of 1.6 mm, are due to transitions from the Tb^{3+} excited states to the ground level $^7\text{F}_6$. The optical band gap of about 5.0 eV was evaluated from the UV absorption edge. The first peak, observed at 4600 cm^{-1} was identified as a resolved line from the term $^7\text{F}_2$. The following band, observed at 5300 cm^{-1} is attributed to a superposition of two lines ($^7\text{F}_1$ and $^7\text{F}_0$, respectively) [8]. An isolated absorption line was found at the mid-gap region of 20400 cm^{-1} attributed to the $^5\text{D}_4$ term. The $^5\text{D}_4$ Tb^{3+} level is usually labeled as A, and the following ones, of increasing energies, are respectively labeled by the subsequent alphabet letters. It follows a clean interval from 20400 cm^{-1} to 26200 cm^{-1} , before it is found the next transition, which is correspondent to the

first of a series of adjacent levels B, C, D, E, F, G, H and I, visualized by the partially resolved lines observed along the interval of 26200 cm^{-1} to 29400 cm^{-1} [8]. This interval is also coincident with the end of the UV absorption band tail. The next line of J is clearly seen at 31400 cm^{-1} and an additional bump of the band-edge, at 33000 cm^{-1} , is attributed to the transition from the K level.

The observed effect of the γ -radiation on the Tb^{3+} lines was an increasing sensitivity in function of energy of the successive lines of the spectrum. The Tb^{3+} OA lines of lower energies, namely the transitions to the $^7\text{F}_2$, $^7\text{F}_1$, $^7\text{F}_0$ and $^5\text{D}_4$ (A) levels from the ground state were not affected by the 2.58 C/kg exposure of ^{60}Co γ -radiation. The following lines (transitions from the B,...,I levels) were clearly broadened. Finally, the lines located on the UV band-edge (transitions from the J and K levels) were completely smeared out. We suggest that the observed behavior can be explained on the basis that the electrons populating the higher excited levels are located farther from the nucleus and are, therefore, less shielded so that they are more sensitive to the local electrical field from the charge carriers released by the ionizing radiation and trapped at neighboring available (or created) sites.

The IR spectrum of the H90-45 Tb^{3+} -aluminosilicate glass sample (Fig.2) shows the expected OH⁻ line centered at about 3500 cm^{-1} [9] and an additional feature centered at about 2600 cm^{-1} , which was attributed to the Tb^{3+} $^7\text{F}_4$ term [4,8]. The expected position of the Tb^{3+} $^7\text{F}_3$ level is to be centered at about 3400 cm^{-1} , which is practically

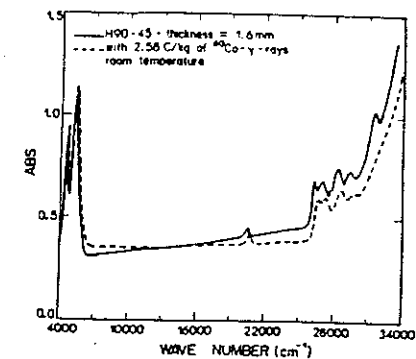


Fig. 1. OA spectra of the H90-45 glass sample taken before (solid line) and after (dashed line) γ -irradiation at room temperature.

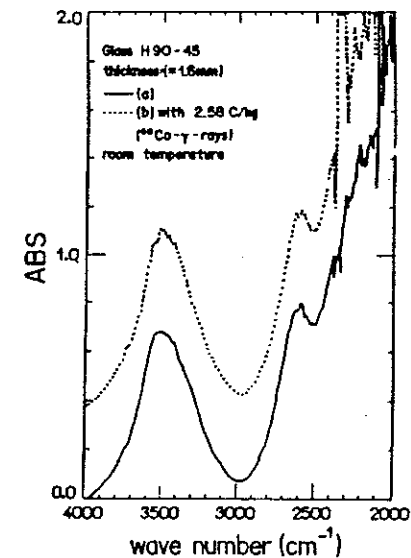


Fig. 2. Infrared absorbance of the H90-45 glass sample measured before (solid line) and after (dashed line) γ -irradiation at room temperature.

coincident with the OH line. In this case, it is impossible to evaluate the amount of the contamination of the sample due to the high nominal amount (58 wt%) of Tb present in the glass composition.

A TL intensity curve was obtained by heating the γ -irradiated sample to 350°C, where appears a single peak at 320°C as shown in Fig. 3. As the electron-hole recombination in oxide glasses occurs mostly below room temperature [10-13], the TL observed at higher temperatures is attributed to the radiative recombination of thermally released holes with transition or rare earth ions, previously reduced by photo-electrons released by the previous irradiation. The

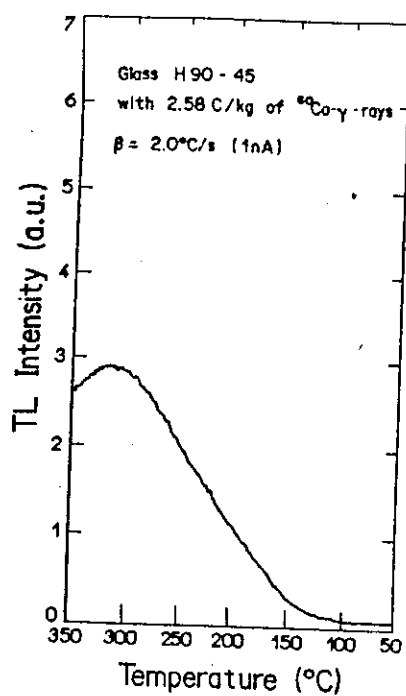


Fig. 3. TL intensity curve of the H90-45 glass sample after γ -irradiation at room temperature.

occurrence of a single peak suggests that only one kind of ion involved in the recombination. Further investigations are in progress for a more detailed description of the involved reactions between electrons, holes and impurity ions.

The OA spectra of the H84-114 sample, having 1.7 mm of thickness, were measured before and after ^{60}Co γ -irradiation with exposure of 2.58 C/kg at room temperature (Fig. 4). It is seen here that the gap is relatively clean, except for a set of weak Tb^{3+} absorption lines. From the UV absorption band

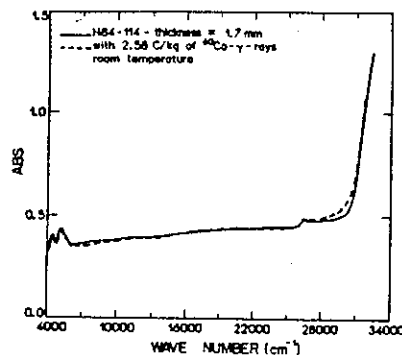


Fig. 4. OA spectrum of the H84-114 sample, before (solid line) and after (dashed line) γ -irradiation at room temperature.

edge a value of the optical band gap of about 4.3 eV could be estimated.

The present irradiation conditions produced very little effect on the OA spectrum: the UV absorption band edge remained unchanged and so occurred with the Tb^{4+} bands shown at 4600 cm^{-1} (${}^7\text{F}_6$), 5200 cm^{-1} (${}^7\text{F}_1$ and ${}^7\text{F}_0$, respectively) and 20400 cm^{-1} (${}^3\text{D}_4$).

The only difference which could be detected was the rounding of the peaks of the successive lines ranging from 26200 cm^{-1} to 29400 cm^{-1} . It is seen that the Tb^{3+} lines from higher excitation levels were more affected by the radiation. This effect is that probably the outer excited electrons are more sensitive to the local changes occurred by the action of the electrical field produced by charge carriers released by the ionizing radiation and trapped at sites available (or created) at the neighborhood.

Typical fluoride glasses exhibit the OH⁻ peak [5] centered at about 3450 cm^{-1} and phosphate glasses [14], about 2860 cm^{-1} . However, the IR spectrum of the H84-114 fluorophosphate sample (Fig. 5) shows a broad rounded peak at about 3150 cm^{-1} , an intermediate position. The uniformity of this line suggests that the glass matrix is mainly a uniform combination of structural units common to both fluoride and phosphate glasses. Another superposition expected is the Tb^{3+} absorption by the term ${}^7\text{F}_3$ expected to be observed at 3400 cm^{-1} . From the spectrum, it is clear that the OH contribution of the present sample is predominant.

Fig. 6 shows the TL intensity curve taken after the sample was γ -irradiated at room temperature. At least two peaks were observed at 155 and 250°C, respectively. As the radiation-induced

shallow electron centers are ordinarily unstable above room temperature, the more stable self-trapped holes are expected to be released precisely at the same temperature range of the observed TL [15]. The thermally released holes are then attracted by the ions with local unbalanced negative charge, trapped during the γ -irradiation process. As the TL curve of the present glass shows more than one peak, at least two species of ions are involved in the process. A more detailed investigation assuming the participation of previously reduced Tb or Ce ions is in progress.

The OA spectrum of the H85-69 sample (thickness = 1.4 mm) remained unchanged after Co γ -irradiation at room

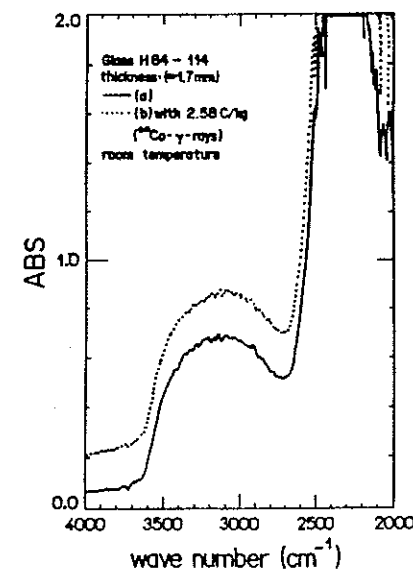


Fig. 5. Infrared absorbance taken before (solid line) and after (dotted line) γ -irradiation of the H84-114 glass sample at room temperature.

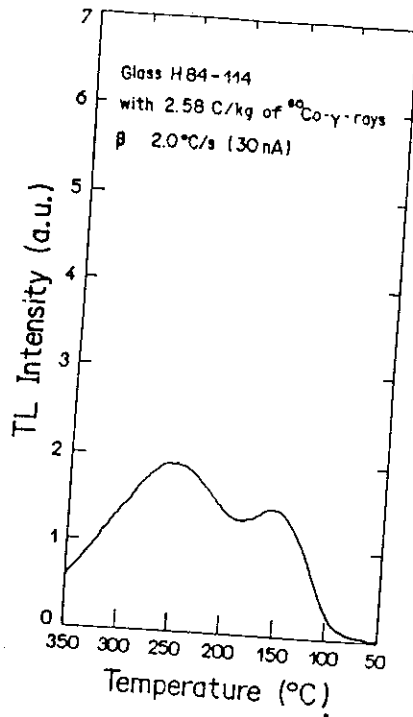


Fig. 6. TL emission curve of the H84-114 glass sample after γ -irradiation at room temperature.

temperature and exposure of 2.58 C/kg (see Fig. 7). The observed stability is an important quality for a laser safety eye protection glass. The broad band at about 9000 cm^{-1} is the well known ${}^2\Gamma_3(D) \rightarrow {}^2\Gamma_3(D)$ transition of the Cu^{2+} (d^9) ions occupying either octahedral or tetrahedral sites in the borosilicate glass. The UV edge shift was produced by Cu^{2+} ions, which also exhibit a charge

transfer band near 0.23 μm , so that the apparent band gap was reduced to about 4.2 eV. The optical window between 16000 cm^{-1} and 28000 cm^{-1} exhibits a particularly low optical absorption. A relatively low content of OH contamination is shown in the IR spectrum of the H85-69 borosilicate glass (see Fig. 8). The hydrogen impurity is always present in glasses due to the incomplete elimination of water from the melt. Although water molecules are absent in glass [9], OH and hydrogen-bonds are always present in most glasses. A relatively low content of OH contamination is shown in the IR spectrum of the H85-69 borosilicate glass (see Fig. 8). However, it is interesting to notice the presence of two broad bands located at about 2850 cm^{-1} and 3500 cm^{-1} , respectively. The actual nature of the lower energy band, although attributed also to OH, is not yet well understood. In our opinion both are from OH, associated respectively to borate and to silicate glass forming structural units. The weak narrow absorption at 2350 cm^{-1} is the well known CO_2 line.

It was noticed the absence of TL of the γ -irradiated sample. This is an evidence that at the present concentration, the Cu^{2+} ions behave as luminescence killers, so that all the electrons promoted to the conduction band recombine non-radiatively without affecting the copper ion oxidation state, in a similar way as it was previously reported about a model of the luminescence quenching of a Fe-doped aluminoborate glass [15]. This is the basis of the great stability of the Cu^{2+} optical absorption in spite of the exposure to γ -irradiation, one of the important features of the present glass.

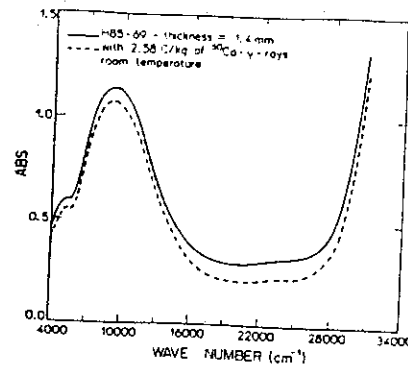


Fig. 7. OA spectra of the H85-69 glass sample taken before (solid line) and after (dashed line) γ -irradiation at room temperature.

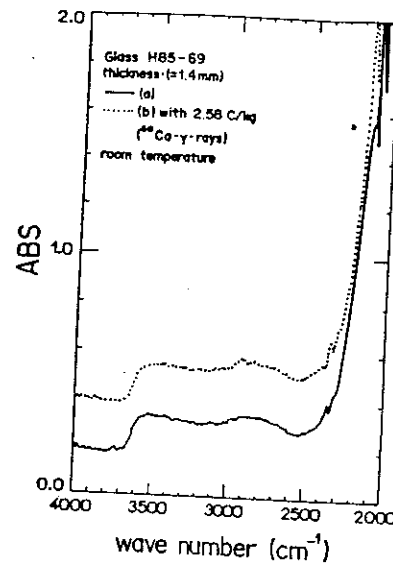


Fig. 8. Infrared absorbance of the H85-69 glass sample before (solid line) and after (dotted line) γ -irradiation at room temperature.

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7. DADOS BIOGRÁFICOS

Noelio Oliveira Dantas, nasceu em Campo do Brito. Estado de Sergipe, em 14 de março de 1961. Formou-se em Física pela Universidade Federal de Sergipe, em 1985. Obteve o título de Doutor, direto, isto é, sem antes fazer Mestrado, pelo Instituto de Física da Universidade de São Paulo (IFUSP), em 1993. Atualmente é Professor Adjunto I do Departamento de Ciências Físicas (DECIF) da Universidade Federal de Uberlândia (UFU). Suas principais áreas de atuação e de interesse dentro da grande área da Física da Matéria Condensada são: crescimento e caracterizações óptica, elétrica e termoluminescente de novos materiais isolantes (vidros especiais crescidos pelo método de fusão e cristais iônicos naturais) e semicondutores (vidros especiais semicondutores crescidos, também, pelo método de fusão e heteroestruturas semicondutoras crescidas por MBE).

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