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Optical and luminescence properties of silicon doped alumino-phosphate-sodium glass system

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ABSTRACT

Transparent thermoluminescent alumino-phosphate-sodium glass system of $15Al_2O_3$-$35P_2O_5$-25CaO-$25Na_2CO_3$ (all in mol%) doped with different concentrations of SiO_2 were prepared by conventional melt quenching technique. X-ray diffraction (XRD) studies checked the amorphous nature of the prepared glass. Fourier Transform Infrared (FTIR) of the glass system was investigated to find the effect of SiO_2-dopant concentrations on the absorption spectra in comparison with that of bulk sample (without dopants). Direct and indirect energy band gaps (E_{opt}) were determined and found to be in the range of 2.47–3.65 eV for m = ½ and 2.24–3.3 eV for m = 2. Refractive index (n) for each E_{opt} value vary from 2.42 to 2.55 and from 2.32 to 2.63 for the direct and indirect transition, respectively. Urbach energy values of the newly prepared glasses are found to be from 0.57 to 0.98 eV. In addition, effect of UV exposure on thermoluminescence (TL) sensitivity was also examined for $APCNSi_5$ (contains 500 ppm SiO_2 concentration) and a linear response to dose was obtained, indicating that this type of glass is promising as a TL dosimeter within the UV range.

1. Introduction

Because of the technological relevance of glasses, more efforts are required for deep insight into the structure-properties relationship searching for new materials to be used in various applications. In comparison with crystalline systems, glasses are applicable materials in many fields due to its flexibility in size and shape, and can be doped by different activator with considerable homogeneity [1–3]. So, a variety of glass matrices such as oxides, fluorides, silicates and oxyfluorides have been investigated to obtain a variety of their optical properties [4–6]. Glass is transparent to visible light and at the same time, absorbing ionizing radiation and neutrons, which eligible it to be used as a radiation shield [7–9]. Radiation detection, using the thermo-luminescent (TL) properties of glass material, is one of its beneficial applications [10–14]. Such as those based on aluminum oxide are considered as one of the most promising materials used in the field of radiation dosimetry [15–22]. The desirable properties of Al_2O_3 such as the high thermo-chemical stability, their excellent optical properties and high: transparency [23], dielectric constant [24,25], refractive index [26] increased attempts to improve its sensitivity via various dopants such as Si. On the other hand, phosphate glasses display special optical properties including wide bandwidth emission spectrum, high gain density and good chemical durability. An increase in the glass transition temperature and a decrease in thermal expansion coefficient can be obtained by introducing Al_2O_3 with phosphate into glass network, which results in increasing the cross-links between PO_4 tetrahedral [27]. In order to reduce the melting temperature and expedite the glass homogenization, Na_2O can be added reducing defects and bubbles [28].

TL properties of newly prepared alumino-phosphate-sodium glass system doped with SiO_2 (APCNSi) were studied as gamma dosimeters where, $APCNSi_5$ showed the best in sensitivity [21]. Therefore, the objective of this work is to throw off light into the optical properties of $15Al_2O_3$-$35P_2O_5$-25CaO-$25Na_2CO_3$ (all in mol%) doped with SiO_2 at different concentrations by recording XRD, FTIR and UV–VIS spectra. Additionally, its good dosimetric characteristics in gamma detection directed our efforts towards testing them in luminescence spectroscopy within UV range.

2. Material and methods

2.1. Glass preparation

Alumino-phosphate-sodium glasses with molar composition of

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Table 1
Concentrations of SiO_2 in (ppm) in bulk sample $15Al_2O_3$-$35P_2O_5$-25CaO-$25Na_2CO_3$ (all in mol%).

Sample	SiO_2 concentrations in (ppm)
APCN	0
$APCNSi_1$	100
$APCNSi_5$	500
$APCNSi_{10}$	1000
$APCNSi_{50}$	5000
$APCNSi_{250}$	25,000

$15Al_2O_3$-$35P_2O_5$-25CaO-$25Na_2CO_3$, shortly written as APCN, doped with SiO_2 were prepared using the conventional melt-quenching technique. The bulk sample was prepared from regent grade hygroscopic powders of aluminum oxide Al_2O_3 (15 mol%, its MW is 101.96 g/mol.), phosphorus oxide P_2O_5 (35 mol%, its MW is 141.94 g/mol.), calcium oxide CaO (25 mol%, its MW is 56.0774 g/mol.) and sodium carbonate Na_2CO_3 (25 mol%, its MW is 105.99 g/mol.). Each batch contained nearly 8 g of mixture-forming glass. The thoroughly mixed batch was placed in a 50 ml porcelain crucible baked into the programmable electric furnace (Eurotherm808P) at temperature rang 1200 °C for about 1 h until the batch to be melted. The resultant melt is poured into a hot stainless steel mold and subsequently annealed at 300 °C for 1 h and at 25 °C for 24 h in order to remove thermal strains and then allowed to cool to room temperature. Dopant powders of SiO_2 are thoroughly mixed with the appropriate amount of the regents of the basic materials with different concentrations as shown in Table 1.

2.2. Measurements

The amorphous nature of the glass system under study was checked by X-ray diffractoemeter (using GNR, APD2000 Pro diffractormeter at $\lambda = 1.5405$ Å). FT-IR spectrum was recorded in the range of 200–4000 cm^{-1} (using, BURKER Tensor 27 spectrometer). UV–Visible absorption spectra of the samples (with 2 mm thickness) were measured using UVS-2700 spectrophotometer in the spectral range of 190–1100 nm with a resolution of 5 nm. $APCNSi_5$ chips were irradiated with a UV source to check their TL-sensitivity with different exposure times. TL sensitivity of $APCNSi_5$ chips was checked using 4500TL reader at NIS, Cairo, Egypt. All these measurements were carried out at room temperature.

3. Experimental

The powder XR diffraction analysis (using GNR, APD2000 Pro diffractormeter at $\lambda = 1.5405$ Å) of APCN newly prepared glass confirms the amorphous nature of samples in region $5^0 \le 2\theta \le 80^0$ with 0.04 deg./min scan rate, 39.9 kV operating voltage and 29.87 mA electrical current. That means the lack of the long ring of the periodic order in the glass system is found. The structure of the glass was studied using FT-IR spectroscopy. FT-IR spectrum was recorded in the range of 200–4000 cm^{-1} (using, BURKER Tensor 27 spectrometer) and the structure of the glass system were analyzed.

UV–Visible absorption spectra of the samples (with 2 mm thickness) were measured using UVS-2700 spectrophotometer in the spectral range of 190–1100 nm with a resolution of 5 nm. Each sample was shinning with a fixed wavelength from the light source, then its absorption (or transmission) intensity against a background was detected. The wavelength was varied slightly using a diffractometer, and the process was repeated until the absorption ratio for a spectrum of wavelengths was obtained.

$APCNSi_5$ chips are polished and cut into 1 mm thick to be used in the planchet of TL- Harshaw reader 4500. Chips irradiated with a UV rays at different exposure times and their TL-sensitivity were readout using TL- Harshaw reader 4500.

4. Theory/calculation

4.1. UV–VIS spectrometry

Light in visible, near ultra-violet and near infrared regions were used in UV–VIS spectrometry to cause electronic transitions in the target. Two types of optical transitions, i.e. direct and indirect, occurred at the absorption edge [29]. The absorption coefficient, below and near the edge of each curve was determined at different wavelengths using the relation:

$$\alpha(\upsilon) = \frac{1}{d}\ln(I_0/I) \tag{1}$$

where I_o and I are the intensities of the incident and transmitted beams, respectively, and d refers to the thickness of each sample. Optical band gaps can be calculated using absorption spectra for direct and indirect transitions of all prepared glass samples.

The absorption edge which can be observed in the UV–VIS region is divided into two regions depending on the absorption coefficient (α) of the amorphous materials:

- A first region where $\alpha < 10^4\ cm^{-1}$ (known as Urbach tails) depends exponentially on the photon energy as given in the following equation:

$$\alpha(\upsilon) = \overline{\alpha}(\upsilon)\exp(h\upsilon/\Delta E) \tag{2}$$

where, $\overline{\alpha}(\upsilon)$ is a constant and ΔE is the width of band tail energy.

- The second region in $10^4 \le \alpha \le 10^6\ cm^{-1}$ depends on the following equation:

$$\alpha(\upsilon) = B\left(\frac{(h\upsilon - E_{opt})^m}{h\upsilon}\right) \tag{3}$$

where B is a constant, E_{opt} is the optical band gap energy, and m has values 1/2, 3/2, 2 and 3 which characterizes the indirect allowed, indirect forbidden, direct allowed and direct forbidden of the transition processes respectively. By plotting $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ as a function of photon energy hν, optical band gaps for indirect and direct transitions can be determined respectively. The respective values of E_{opt} were obtained by extrapolating to $(\alpha h\nu)^{1/2} = 0$ for indirect transitions and $(\alpha h\nu)^2 = 0$ for direct transitions [30].

The refractive index (n) of the samples are evaluated from the optical band gap values (E_{opt}) for the direct and indirect allowed transition using the following relation derived by [31,32,44];

$$\frac{n^2 - 1}{n^2 + 2} = 1 - \sqrt{\frac{E_{opt}}{20}} \tag{4}$$

4.2. TL-response parameters

Kinetic parameters such as trap depth (E) or the activation energy, the energy required for releasing an electron from the trap into the conduction band and the frequency factor (s), which expresses the product of the number of times an electron hits the wall and the wall reflection coefficient, considering the trap as a potential well, which were obtained after excitation. Whole glow curves of the irradiated materials contain overlapping glow peaks that can separate from each other using different programs.

Computer Glow Curve Deconvolution (CGCD) is one of the most important methods to determine trapping parameters from TL glow curves and the commercial software PeakFit v.4.12 program is a simple but convenient, powerful tool in extracting the two most important intrinsic trapping parameters, namely activation energy, E, and the frequency factor, s, of the TL peaks [33], and this program was used in the present calculations.

In addition, E and s parameters can be calculated by applying Chen's