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Photoluminescence and thermoluminescence properties of SnO_2 nanoparticles embedded in Li_2O-K_2O-B_2O_3 with Cu-doping

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Cu-doped borate glass co-doped with SnO_2 nanoparticles is fabricated by melt quenching. The structure and morphology of the samples are examined by X-ray diffraction and field emission scanning electron microscopy. Up-conversion enhancement is observed in the photoluminescence (PL) and thermoluminescence (TL) intensities of the glass. PL emission spectra are identified in the blue and green regions, and a fourfold increase in emission intensity may be observed in the presence of embedded SnO_2 nanoparticles. The glow curve is recorded at 215 °C, and fourfold increases in TL intensity are obtained by addition of 0.1 mol% SnO_2 nanoparticles to the glass. Higher TL responses of the samples are observed in the energy range of 15–100 KeV. At energy levels greater than ∼0.1 MeV, however, flat responses are obtained. The activation energy and frequency factor of the second-order kinetic reaction are calculated by the peak shape method.

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Borate glass is a favorable host for different metals (e.g., transition and rare earth metals) and an interesting material for application in strong nonlinear optics, quantum electronics, and large electronic band gaps because of its lattice, chemical, and environmental stability, as well as mechanical robustness^{1–9}. Borates are attractive candidates as host lattices in thermoluminescence dosimetry (TLD)^{4–8}. In recent years, borate glass has become the subject of intensive investigations because of its technological and scientific importance. It is a promising material for many applications because of its high sensitivity, very low cost, easy handling, and facile preparation\(^{11,8}\).

Magnesium tetraborate, barium betaborate, and lithium tetraborate are three borates commonly used in TLD\(^{9}\). Lithium triborate (LiB_3O_5) has recently received significant research attention because of its TL properties. The effective atomic numbers of lithium triborate and lithium tetraborate are very close to that of biological tissue, which indicates that these compounds are more significant than others for medical and personnel dosimetry usage\(^{10}\). Many studies have been conducted to investigate the TL properties of borates, such as Li_2B_2O_7:Cu\(^{11}\), Li_2B_2O_7:Cu,In,Ag\(^{12}\), Li_2B_4O_7:Cu,Ag,P\(^{13}\), Li_2B_4O_7: Mn\(^{14}\), Li_2B_4O_7:Mn, Si\(^{15}\), and Li_2K_2B_3O_5:CuO, MgO\(^{16}\). In this letter, the photoluminescence (PL) and TL properties of borates, including dose response, glow curve, energy response, and kinetic parameters, are determined and explored in detail.

Powder samples composed of 20Li_2O-10K_2O-(70-x) B_2O_3-xCu, where x=0, 0.05, 0.1, 0.25, 0.5, 0.75, and 1.0 mol%, and 20Li_2O-10K_2O-(69.9-y) B_2O_3-0.1Cu-ySnO_2, where y=0.05%, 0.1%, and 0.5%, were prepared (see Table 1) by melt quenching. SnO_2 nanoparticles were synthesized by the sol-gel method\(^{17}\). The batch mixture (15 g) was prepared using raw material powder (99.99%-purity, Sigma-Aldrich, Germany). The powder was placed in a porcelain crucible and mechanically mixed with each sample for approximately 30 min to obtain a homogeneous mixture. The mixtures were melted in a platinum crucible in an electric furnace set to 1100 °C for 30 to 60 min, depending on the time required for the resultant product to become clear and homogeneous. When the required viscosity had been achieved, the samples were quenched in steel plates, annealed at 400 °C for 3 h, and then cooled to room temperature. The structure of the samples was analyzed by X-ray diffraction (XRD) to confirm their amorphous nature. The morphological analysis of the samples was performed by field emission scanning electron microscopy (FE-SEM). Optical absorption spectra were examined at room temperature using a Shimadzu 3101 ultra-violet-visible-near-infrared (UV-Vis-NIR) spectrophotometer in the range of 200–2000 nm. PL spectra were obtained using a Perkin Elmer LS55 luminescence spectrophotometer. The linear accelerator Primus (LINAC Primus) at the Department of Radiotherapy and Oncology, Hospital Sultan Ismail, Johor Bahru, Malaysia, was used to irradiate the samples with photons of very high energy at different dose rates. A TLD-Reader 4500 from Harshaw Company was used to measure TL at the Malaysian Nuclear Agency.

The XRD pattern of a borate glass sample doped with SnO_2 nanoparticles is shown in Fig. 1. The pattern reveals that the glass is completely amorphous because of the presence of diffuse peaks and the absence of sharp Bragg peaks. Several sharp peaks appear in the current host, and their presence may be attributed to overlapping peaks. Sn species, particularly Sn\(^{4+}\), is abundant in the prepared host samples. The reactivity of Sn with other...
The luminescence intensity is a result of radiative recombinations between electrons, which are released from the electron center upon heating and an antibonding molecular orbital of the nearest oxygen hole center. TL emission in the borate glasses is usually possible only at low temperatures because of this recombination process\textsuperscript{20}. During heating, electrons confined in metal ions are released and become trapped by holes in recombination centers, resulting in the production of TL light\textsuperscript{21}. Figure 4 shows the glow curves of glass samples with different SnO\textsubscript{2} concentrations after photon irradiation with 1 Gy at 6 MV. After 24 h of irradiation, the glow curve was recorded at 20 °C/s and annealing temperature of 400 °C. The maximum TL peak of the samples appears at 215 °C, and the highest TL response is observed in glass with 0.1-mol% SnO\textsubscript{2}. A nearly fourfold increase in TL intensity is obtained when 0.1-mol% Cu-doped lithium potassium borate is co-doped with 0.1-mol% SnO\textsubscript{2}. Such behavior is attributed to the creation of new traps and recombination centers when SnO\textsubscript{2} nanoparticles are added to the Cu-doped sample.

A TLD detector exhibits a linear relationship between TL intensity and absorbed dose. The light emitted by a TLD material represents the sum of contributions of different peaks, resulting in a linear dose characteristic\textsuperscript{22}. The samples were exposed to 6-MV radiation with 1 Gy at 6 MV. After 24 h of irradiation, the glow curve was recorded at 20 °C/s and annealing temperature of 400 °C. The maximum TL peak of the samples appears at 215 °C, and the highest TL response is observed in glass with 0.1-mol% SnO\textsubscript{2}. A nearly fourfold increase in TL intensity is obtained when 0.1-mol% Cu-doped lithium potassium borate is co-doped with 0.1-mol% SnO\textsubscript{2}. Such behavior is attributed to the creation of new traps and recombination centers when SnO\textsubscript{2} nanoparticles are added to the Cu-doped sample.

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constituent elements having K than both samples show a flat response at energy levels greater. The results are shown in Fig. 6. The figure indicates that response to an absorbed dose of 0.2 mGy, and the with and without co-doping with SnO (30–800 keV). The TL responses of Cu-doped samples to early with increasing dose up to 4.0 Gy. Figure 5 reveals that the TL intensity increases linearly with the photon dose. TL responses increase linearly with increasing dose up to 4.0 Gy.

The TL responses of the borate samples at various photon energies were also determined for low-energy photons (30–800 keV). The TL responses of Cu-doped samples with and without co-doping with SnO2 were recorded after exposure to an absorbed dose of 0.2 mGy, and the results are shown in Fig. 6. The figure indicates that both samples show a flat response at energy levels greater than ~0.1 MeV, which is the case for all materials with constituent elements having K-edges of less than 1 keV. Higher responses due to the dominance of the photoelectric effect are observed in the energy range of 15–100 keV. The photoelectric component of the mass energy absorption coefficient of a certain element varies approximately as Z^2. The TL responses of co-doped samples are consistently slightly higher than those of samples doped with only Cu.

One of the main objectives of a TL experiment is to extract data from an experimental glow curve, or a series of glow-curves, and use these data to calculate various parameters associated with the charge transfer process of the material under study. These parameters include the trap depth, E, the frequency factor, s, and the order of the kinetic reaction. The peak shape method was employed to determine the kinetic parameters of the samples. The activation energy is given by

\[ E_\alpha = C_\alpha \left( \frac{kT_M^2}{\alpha} \right) - b_\alpha (2kT_M), \]  

where α can be either τ=T_M - T_1, δ=T_2 - T_M, or ω=T_2 - T_1. T_M corresponds to the maximum temperature, and T_1 and T_2 respectively represent the half TL intensity temperatures at low and high regions of the peak. T_M, T_1, and T_2 of glass co-doped with SnO2 are 215, 136, and 310 °C, respectively, as shown in Fig. 7. The values of C_α and b_α depend on the parameter selected for analysis[29]. If γ is used, i.e., α is replaced by γ, then

\[ C_\gamma = 1.510 + 3.0(\mu - 0.42), \quad b_\gamma = 1.58 + 4.2(\mu - 0.42). \]  

On the other hand, if δ is used:

\[ C_\delta = 0.976 + 7.3(\mu - 0.42), \quad b_\delta = 0. \]  

If ω is used:

\[ C_\omega = 2.52 + 10.2(\mu - 0.42), \quad b_\omega = 1. \]  

The geometric shape factor, μ = 0.546, is very close to the theoretical value for a second-order kinetic reaction, μ = 0.52 τ, δ, and ω are 79, 95, and 174, respectively. Table 2 reveals that the C_α and b_α depend on τ, δ, or ω. The activation energy for the second-order kinetic reaction was determined using the peak shape method, and results from Eq. (1) are presented in Table 3.

| Table 2. Values of C_α and b_α Depending on τ, δ, or ω for Co-doped SnO2 |
|-----------------------------|----------------|---|---|
| Values | τ | δ | ω |
| C_α | 1.88 | 1.895 | 3.805 |
| b_α | 2.109 | 1.895 | 3.805 |

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<th>Table 3. Activation Energy of Glass Samples Co-doped with SnO2</th>
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<td>Chen’s Method</td>
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The doping concentration of SnO2 nanoparticles is high from 15 to 100 KeV but flat beyond 0.1 MeV. The activation energy and frequency values obtained by the peak shape method are 0.35 and 2.6×10^4, respectively.

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