Radiation Measurements 100 (2017) 1–8

Contents lists available at ScienceDirect

Radiation Measurements

journal homepage: www.elsevier.com/locate/radmeas

Kinetic analysis and general features of thermoluminescence of B_2O_3-Li_2O-ZnF_2 glass

Sunil Thomas, M.L. Chithambo*

Department of Physics and Electronics, Rhodes University, Grahamstown 6140, South Africa

HIGHLIGHTS

- Thermoluminescence properties of B_2O_3-Li_2O-ZnF_2 glass are reported.
- Kinetic parameters including activation energy and frequency factor are reported.
- The dose response in the range 200–1000 Gy is shown.
- A possible mechanism for thermoluminescence is described.

ARTICLE INFO

Article history:
Received 15 December 2016
Received in revised form
31 January 2017
Accepted 27 March 2017
Available online 29 March 2017

Keywords:
Thermoluminescence
Borate glass
Kinetic analysis
Glow curve

ABSTRACT

The intention of this study is to explore the thermoluminescence of beta irradiated B_2O_3-Li_2O-ZnF_2 glass. The glow-curve corresponding to 200 Gy shows three peaks; two weak-intensity peaks at 60 and 243 °C and a more prominent one at 118 °C, when measured at 1 °C/s. The dose response of the main peak at 118 °C was found to be sublinear in the range 200–1000 Gy. Regarding the kinetic analysis of the main peak, the activation energy of the corresponding electron trap was evaluated as 0.96 eV and the frequency factor as ~10^{11} s^{-1}. It is proposed that the thermoluminescence in B_2O_3-Li_2O-ZnF_2 glass is due to recombination of electrons, thermally released from Zn^+ ionic defect sites, with the holes at boron-oxygen hole centres.

1. Introduction

Borate based glasses have been the subject of recent research interest owing to their low melting point, high transparency, high thermal stability and interesting optical, structural and electrical properties (Pontuschka et al., 2001; Thomas et al., 2013). It is well known that the structure of vitreous B_2O_3 is made-up of boroxol rings, each one comprising of three [BO_3] triangles attached to a common oxygen atom. There is a large vacant space among the two boroxol rings in this model and the bonds between the rings are weaker than the bonds within the rings. Therefore, when alkali/alkaline earth oxides/fluorides are added to borate glass, bonds can break but only between boroxol rings and not inside them, and the added cation tends to reduce the free space by partially occupying the vacant space (Thomas, 2015). Borate glasses with fluoride compounds as modifiers have significantly lower phonon energy and better mechanical properties (Dwivedi and Rai, 2008).

The spectroscopic and dielectric properties of B_2O_3-Li_2O-ZnF_2 glass have previously been considered (Thomas et al., 2013). The glass comprising Li_2O as the network modifier is bubble free, highly stable and moisture resistant, which facilitates systematic analysis (Sastry and Hummel, 1958; Mhareb et al., 2016). On the other hand, glasses containing Zn have high chemical stability and lower thermal expansion coefficient (Anjaiah et al., 2015). Additionally, the presence of fluorine in the glass matrix reduces its hygroscopicity (Thomas et al., 2013). The energy band gap of B_2O_3-Li_2O-ZnF_2 glass has been estimated as 3.9 eV and the glass has also been noted as a good insulator (Thomas et al., 2013). These characteristics have motivated us to study the thermoluminescence (TL) features of this glass. Since TL is a sensitive method for monitoring changes in point defects, it offers in this work, a means to explore the role of impurities in the luminescence process in the B_2O_3-Li_2O-

* Corresponding author.
E-mail address: m.chithambo@ru.ac.za (M.L. Chithambo).

http://dx.doi.org/10.1016/j.radmeas.2017.03.038
1350-4487/

ZnF_2 glass in particular and in glass in general.

TL is a process in which light is emitted from an irradiated insulator or semiconductor during heating (McKeever, 1985). The TL intensity is a function of absorbed dose in a material and is thus a basis for radiation dosimetry. The process starts with irradiation triggering ionization of valence electrons and formation of electron-hole pairs. Some of the free electrons can be trapped at certain defect sites. Subsequently heating stimulates the trapped electrons out of the trap to the conduction band. Recombination of these free electrons with the localised holes results in radiative emission. In other words, the stored energy is emitted in the form of light and the TL intensity is proportional to the dose.

With particular reference to use of TL in dosimetry, TL studies of lithium borate compounds have previously been reported by Schulman et al. (1965). A number of other TL investigations have also been carried out on borate based materials containing alkali and alkaline-earth elements (Bahri et al., 2014; Rasid et al., 2015; Aboud et al., 2014; Sudhakar et al., 2008; Reddy et al., 2005). For instance, alkaline, alkaline earth, transition metal or rare earth doped borate glasses are known to have acceptable dosimetric features (Sudhakar et al., 2008; Reddy et al., 2005). Indeed, the fact that borate glasses are suitable for application in radiation dosimetry can be understood in light of the fact that their effective atomic number is very close to that of human tissue, that is, $Z_{eff} \approx 7.42$ (Aboud et al., 2014).

The aim of this work is to report thermoluminescence of B_2O_3-Li_2O-ZnF_2 glass. In particular, we describe the kinetic analysis of the prominent peak, the only one that could be reliably analysed; we discuss its dose response, touch on its fading features, and account for the TL with reference to Zn^{2+} as the electron trap and holes at boron-oxygen hole centres as recombination sites. The overall aim of this study is to contribute to a better understanding of the luminescence process in the B_2O_3-Li_2O-ZnF_2 glass.

2. Experimental

The molar composition of the glass chosen for the study is 25 Li_2O + 65 B_2O_3 + 10 ZnF_2. The glass was synthesised by the conventional melt-quenching technique. The raw materials for this glass composition, namely, H_3BO_3, Li_2CO_3 and ZnF_2 were mixed in an agate mortar. The mixture was then transferred to a platinum crucible and placed in a muffle furnace at 900 °C for 30 min. The melt was thereafter poured onto a preheated brass plate and annealed at 300 °C for 10 h and then cooled to room temperature. Systematic procedures for the fabrication of this glass along with its optical and dielectric properties have otherwise been reported in detail elsewhere (Thomas et al., 2013).

The sample for study by TL was powdered and placed on sample discs of 10 mm diameter and 0.3 mm thickness. Prior to measurement, the sample was annealed at 500 °C for 1 h to enhance its sensitivity. The TL was measured in a nitrogen atmosphere using a RISØ-TL/OSL/DA-20 Luminescence Reader. The presence of nitrogen helps to preclude chemiluminescence and false signals from air and also improves the thermal contact between heater planchet and sample holder. All sample irradiation was done at ambient temperature using a $^{90}Sr/^{90}Y$ beta source at a nominal rate of 0.1028 Gy/s. Luminescence was detected using an EMI 9235QB photomultiplier tube through a 7 mm thick Hoya U-340 filter of transmission band 250–390 nm.

The X-ray diffraction (XRD) pattern of the glass to assess its structure was determined using an Xpert Pro PANalytical X-ray diffractometer with Cu Kα line. XRD measurements were made for 2θ values from 10° to 80°.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the XRD spectrum of B_2O_3-Li_2O-ZnF_2 glass. The pattern does not show any sharp peaks as would be expected of a crystalline material but only a broad indeterminate hump confirming the amorphous nature of the B_2O_3-Li_2O-ZnF_2 glass.

3.2. Effective atomic number

Prior to TL studies, it was of interest to estimate the effective atomic number (Z_{eff}) of B_2O_3-Li_2O-ZnF_2 glass in order to consider its suitability for dosimetric applications. The effective atomic number is given by

$$Z_{eff} = \sqrt[2.94]{\left(f_1 Z_1^{2.94}\right) + \left(f_2 Z_2^{2.94}\right) + \cdots + \left(f_n Z_n^{2.94}\right)} \quad (1)$$

where $f_1, f_2, \ldots, f_n$ are the fractional contributions of each element to the total number of electrons in the glass composition and $Z_1, Z_2, \ldots, Z_n$ are the corresponding atomic numbers of each element (Furetta, 2003). The value of Z_{eff} for the glass composition of this report, 25 Li_2O + 65 B_2O_3 + 10 ZnF_2, was estimated as 14.31. This value, which exceeds other reported Z_{eff} values of borate based glass ($Z_{eff} \approx 8$) (Aboud et al., 2014; Anishia et al., 2011; Alajerami et al., 2013), is due to the presence of Zn in the glass composition. The value 14.31 is fairly close to the effective atomic number of bone, enamel and dentine, which is ~14.11 (Koc and Ozyol, 2000; Zenobio et al., 2011). Therefore, the value of Z_{eff} for B_2O_3-Li_2O-ZnF_2 glass suggests that it may be favourable for personnel, medical and environmental dosimetry. It is also to be noted that the melting point of B_2O_3 is considerably lower than that of other compounds present in the B_2O_3-Li_2O-ZnF_2 glass. Therefore, a small loss in B_2O_3 content may have occurred in the course of melting during synthesis. Consequently, the composition of the final product may differ slightly from that of the starting one. The slight change in composition may have affected the value of Z_{eff} obtained since this was estimated from the starting composition. Similar kind of slight changes in the final composition of borate based glasses have been reported by Elkholy (2010) and Bahri et al. (2014).

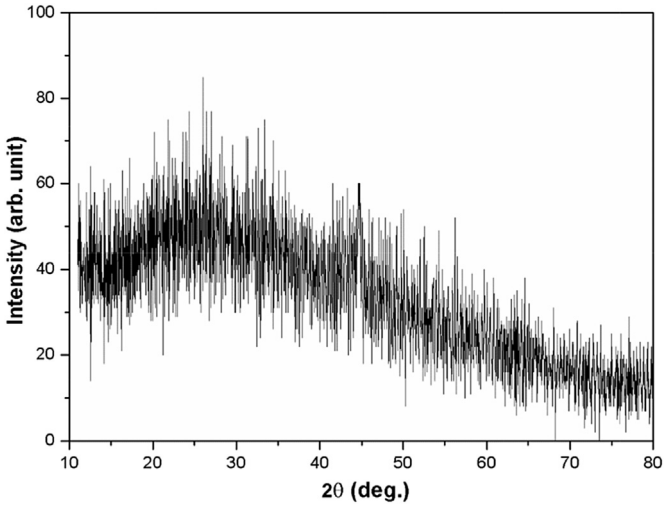

Fig. 1. X-ray diffraction pattern of B_2O_3-Li_2O-ZnF_2 glass.