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Determination of the kinetic parameters of BeO using isothermal decay method

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HIGHLIGHTS

- Kinetic parameters of BeO were determined.
- Isothermal decay method was used.
- Frecuency factor not agree with those obtained by other methods.

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ABSTRACT

Most of the existing methods for obtaining the frequency factors make use of the trap depth (activation energy) making some assumptions about the order of the kinetics. This causes inconsistencies in the reported values of trapping parameters due that the values of the activation energy obtained by different methods differ appreciably among them. Then, it is necessary to use a method independent of the trap depth making use of the isothermal luminescence decay (ILD) method.

The trapping parameters associated with the prominent glow peak of BeO (280 °C) are reported using ILD method. As a check, the trap parameters are also calculated by glow curve shape (Chen's) method after isolating the prominent glow peak by thermal cleaning technique. Our results show a very good agreement between the trapping parameters calculated by the two methods. ILD method was used for determining the trapping parameters of BeO. Results obtained applying this method are in good agreement with those obtained using other methods, except in the value of the frequency factor.

1. Introduction

The development of new thermoluminescent (TL) materials for use in radiation dosimetry requires having a deeper understanding of the trapping parameters (Azorin et al., 1993; Azorin, 2014) (i.e., the activation energy or trap depth, the kinetic order and the frequency factor). This can be achieved by analyzing the glow curve obtained after exposing the material to ionizing radiation in order to excite electrons from the valence band to the conduction band and back to metastable states in the band gap above the Fermi level (Stoebe and Morgan, 1984). Then, by heating, electrons can be released from their traps and recombine with trapped holes emitting light.

There are many different methods to determine the trapping parameters (Azorín, 1986; Shrivastava et al., 2012). Most existing methods for obtaining frequency factor make use of the previous determination of the activation energy by making some assumptions about the order of the kinetics. This means that there are inconsistencies in the reported values of the trapping parameters due to significant differences in activation energy values obtained by different methods. Then, it is necessary to use a method that is independent of the determination of the trap depth.

The isothermal luminescence decay (ILD) is an effective, reliable and versatile technique for the evaluation of trapping parameters because there are no prerequisite conditions and can be applied not only for first and second order kinetics but also for general order kinetics (Moharil, 1984).

This paper reports studies on Be0 in the field of the kinetic parameters, which are important in the general description of the

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physical characteristics of a thermoluminescent material. As a check, the trap parameters are also calculated by glow curve shape (Chen's) method (Chen and McKeever, 1997).

1.1. Isothermal decay method

In this method, TL response is recorded as a function of time while the sample is held at a constant temperature. The isothermal decay of luminescence is generally referred to as phosphorescence (Manam and Sharma, 2005).

There are various methods, which use the isothermal decay curve for determining the order of the kinetics one of them uses the change in the slope of the isothermal decay-curve with time (Moharil, 1984), and the other uses the area under the isothermal decay plot (Furetta et al., 2007).The second one however presents two experimental concerns. The first is that the criteria for choosing which pair of temperatures to use is not obvious and the question of whether any pair can produce similar results remains open. The second point is that this method requires that the total area under an isothermal decay-curve be known, which in practical terms, calls for an extended measurement time. The dilemma here is that a prolonged measurement, while necessary and suitable to accurately an isolated peak, may cause simultaneous loss of signal from several peaks, particularly where such peaks are closely overlapping (Chithambo and Niyonzima, 2014). On the other hand, improperly approximating the total area would then inevitably introduce inaccuracies in the determination of E. The main advantage of the first method is that it gives an estimation of the order of kinetics also, and is perhaps the only method unaffected by temperature dependent factors such as frequency factor and quantum efficiency. Then, we decide to use the first method.

The TL intensity equation for the first order kinetics is:

$$I = -\frac{dn}{dt} = nse^{-\frac{E}{kT}} \tag{1}$$

where I is the intensity at any instant, n is the number of populated traps at any instant, E (eV) is the trap depth, s (s^{-1}) is the frequency factor, T (K) is the temperature and k ($eV \cdot K^{-1}$) is the Boltzmann constant.

The solution of intensity equation for the isothermal case:

$$I(t) = n_0 se^{-\frac{E}{kT}} e^{-ste^{-\frac{E}{kT}}} \tag{2}$$

where n_0 is the initial concentration of the trapped electrons.

Therefore, for the first order case, plot of ln[I (t)] vs t should yield a straight line of slope $e^{-\frac{E}{kT}}$.

$$ln\ I = -\left(se^{-\frac{E}{kT}}\right)t + \left(ln(n_0 s) - \frac{E}{kT}\right) \tag{3}$$

For general order kinetics the TL intensity equation is:

$$I = -\frac{dn}{dt} = n_0 s' e^{-\frac{E}{kT}} \tag{4}$$

where $s' = \frac{s}{n_0^{b-1}}$is the pre-exponential factor and b is the order of kinetics.

The solution of intensity equation for the isothermal case:

$$\left(\frac{I_0}{I}\right)^{\frac{b-1}{b}} - 1 = se^{-\frac{E}{kT}}(b-1)t \tag{5}$$

So for the general order case, plot of $(I_0/I)^{(b-1)/b} - 1$ vs t should yield a straight line where I_0 is the intensity at $t=0$ and $1 < b \leq 2$. The experimental data are tested by choosing different test values of b, among which the value of b that gives the best fit as straight line corresponds to the order of kinetics.

The slope of this straight-line is:

$$(b-1)se^{-\frac{E}{kT}} \tag{6}$$

The determination of slope (m) of straight line plots of $(I_0/I)^{(b-1)/b} - 1$ vs t at different temperatures will give the value of frequency factor from the following relation:

$$\left(\frac{I_0}{I}\right)^{\frac{b-1}{b}} - 1 = mt + B \tag{7}$$

The frequency factor value is obtained from the following equation:

$$s = \frac{1}{(b-1)} \frac{m_2^{\frac{T_2}{T_2 - T_1}}}{m_1^{\frac{T_1}{T_2 - T_1}}} \tag{8}$$

where m_1 and m_2 are the slopes corresponding to the temperatures T_1 and T_2 respectively.

Now to find the thermal activation energy (E) a graph ln[$m(t)$] vs $1/T$ should be plotted, which is a straight line. The slope $m = -E/k$ of this straight line graph will give the value of thermal activation energy (E).

$$ln(m(t)) = -\frac{E}{kT} + ln(s(b-1)) \tag{9}$$

2. Materials and methods

The ILD method is based on recording the decay of the luminescence intensity with time at a constant temperature (Azorín et al., 2007). In this method three temperatures are selected on the rising side of the glow peak whose parameters are to be determined. After irradiation of the sample to suitable radiation dose, it is heated to one of the selected temperatures and the decay of the luminescence intensity is measured, at a constant temperature, as a function of time. This procedure is repeated for two other temperatures. Then experimental data are tested to find the order of kinetics.

Disc shaped BeO ceramics, commercially available in the undoped form under the commercial name Thermalox 995 manufactured by Brush Beryllium Co., Elmore, OH, USA with total contents of impurities not exceeding 0.5%, with dimensions: diameter 4 mm and thickness 1 mm, were used in the TL measurements.

Before the determination of kinetic parameters, samples were submitted to thermal annealing treatment at 600 °C during 30 min in order to erase any remaining information.

TL readings were made on a Harshaw TLD Reader Model 3500 integrating the signal from 20 up to 400 °C using a heating rate of 5 °C s^{-1}. All TL measurements were made in a nitrogen atmosphere in order to reduce the thermal noise resulting from the heating planchet of the TL reader. Dosimeters were irradiated at room temperature using $^{90}Sr/^{90}Y$ beta source ($E_{MAX} = 2.28$ MeV) at an absorbed dose of 100 mGy.

In order to calculate the trapping parameters corresponding to 280 °C glow peak, three temperatures namely 270, 275 and 280 °C were chosen and decay of luminescence intensity with time at these temperatures were recorded for samples irradiated at an absorbed dose of 100 mGy for times from 10 to 120 min.

In first order kinetics, a plot of ln(I) against t will result in a straight line of slope $se^{-E/kT}$.

In the case of general order kinetics a plot of $(I_0/I)^{(b-1)/b} - 1$ against t should be a straight line. In this case, the experimental data are tested by choosing different test values of b, among which the value of b that gives the best fit as straight line corresponds to