Thermoluminescent trap parameters of sodium tetraborate compounds

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F Spano†, G Sanchez‡, E Caselli§|| and M E Rodriguez¶

† Gerencia de Protección Radiológica, Comisión Nacional de Energia Atomica, Avenida del Libertador 8250, 1429 Buenos Aires, Argentina
‡ Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellón I, Ciudad Universitaria, 1428 Buenos Aires, Argentina
§ Instituto de Física Arroyo Seco, Universidad del Centro de la Provincia de Buenos Aires, Gral Pinto 399, 7000 Tandil, Argentina
|| Comisión de Investigaciones Científicas de la Provincia de Buenos Aires, Calle 526 entre 10 y 11, 1900 La Plata, Argentina
¶ Consejo Nacional de Investigaciones Científicas y Técnicas, Rivadavia 1917, 1033 Buenos Aires, Argentina

Abstract. Phosphorescence measurements of γ-irradiated sodium tetraborate compounds recorded between room temperature and 420 °C have been analysed to find the trap depths involved in thermoluminescence and their frequency factors. The glow curve consists of two complex overlapping bands. From the trap depths related to the high-temperature band it is concluded that sodium atoms are involved in the thermoluminescent mechanisms as electron traps.

1. Introduction

$(M_2O)_x(B_2O_3)_{1-x}$ compounds, where $M \equiv$ alkali metal, become thermoluminescent upon irradiation with x-rays or γ-rays. Lithium tetraborate ($x = 0.33$), which is usually doped with Cu or Mn in order to increase the light output, have been extensively investigated for use in personal dosimetry owing to its tissue-like characteristics [1–8]. As to the compounds with sodium, since 1980, experiments have been carried out with undoped samples to obtain better knowledge of their thermoluminescent properties. These studies dealt with the dependence of the glow curves on the sodium content, the thermoluminescent mechanisms related to paramagnetic centres built by irradiation and the spectral composition of the light [4, 9, 10]. According to the results, undoped sodium tetraborate has thermoluminescent properties which are similar to those of undoped lithium tetraborate. For instance, the glow curves of both compounds have a low-temperature band (hereafter called band MI), which is unstable at room temperature, and a high-temperature band (hereafter called MII), which is related to paramagnetic centes due to x-radiation or γ-radiation [4] (see figure 1). The paramagnetic centres consist of a trapped hole in an oxygen atom having a hyperfine interaction with one or two boron atoms (BOHC centres) [11]. These centres are stable at room temperature. The results reported in [1, 10] indicate that, when an irradiated sample is heated at temperatures corresponding to the high-temperature band, an electron after being released from a trap, goes into the conduction band and then makes a non-radiative transition to a BOHC centre. The energy released is taken up by an impurity,

usually referred to as an activator, which in turn emits light (resonant transfer of energy). In this process a paramagnetic centre becomes non-paramagnetic. So far the nature of the electron trap centres has not been investigated. In this work we report the results of phosphorescence measurements, i.e. measurements of the intensity of the emitted light at a constant temperature as a function of time, to determine the energy of the traps. We resort to this method because it is appropriate when the bands are made up of overlapping peaks. Further phosphorescence measurements are applicable to first-order kinetics, a requirement that sodium tetraborate fulfils, because the shapes and the maxima of the bands do not depend upon the dose. Another method widely used, the initial-rise method, becomes cumbersome when a band is made up of strongly overlapping peaks, because it is necessary to ensure that the peaks lying at lower temperatures than that of the peak being investigated are annealed out. It should be pointed out that this method has the advantage of being applicable whatever the order of the kinetics. For this reason we employed it in simple cases, i.e. with the lowest-temperature peak of band MI a day after irradiation and with the lowest peak of band MII 4 weeks after irradiation, when band MI has completely disappeared at room temperature, to compare the resulting thermoluminescent parameters with those obtained from phosphorescence. We also calculated the thermoluminescent parameters of the peaks related to band MII from measurements of the intensity of the paramagnetic signal of the BOHC centres in samples that had been subjected to step anneals at different temperatures, as explained in the next section. A brief account of the methods to determine the trap depths is given in the next section. Detailed descriptions can be found, for instance, in [4, 12, 16, 17].
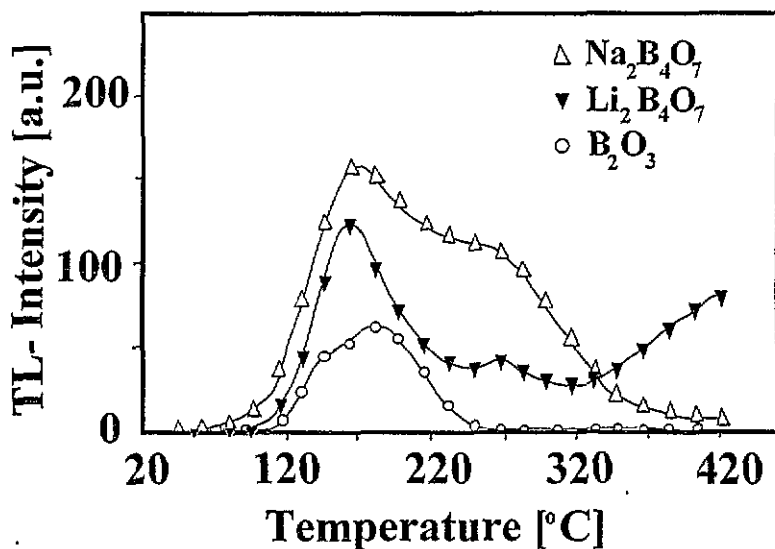

Figure 1. Glow curves of sodium tetraborate, lithium tetraborate and pure borate (heating rate, 400 °C min^{-1}) (a.u., arbitrary units) TL, thermoluminescence.

2. Materials and experimental procedures

In table 1 the impurity content of sodium tetraborate powder (Merck 6306) is shown. X-ray diffraction experiments revealed that the compounds are amorphous.

Table 1. Impurity contents of the compounds used in this work.

Impurity	Amount (g per 1000 g) of impurity in the following compounds	
	$Na_2B_4O_7$	$Li_2B_4O_7$
Al	0.3	0.1
Si	0.03	0.1
Fe	0.003	0.05
Mg	<0.0003	<0.0003
Cu	<0.001	<0.001
Ag	<0.001	0.003
Ti	0.01	<0.003
Ba	0.0001	0.0001
Sr	0.001	<0.001
Cs	<0.0003	0.001
Mn		<0.0003

For first-order kinetics the intensity of the light emitted by a sample heated at constant temperature is given by

$$I(t) = I_0 \exp[-st \exp(-E/kT)] \tag{1}$$

where the time is denoted t, with k the Boltzmann constant and E the trap depth. s is the frequency factor. Then the half-life τ, i.e. the time required to reduce the intensity to half its value at $t = 0$ (from I_0 to $I_0/2$) can be found from a plot of I versus t. From equation (1),

$$\tau = [\ln 2 \exp(E/kT)]/s \tag{2}$$

Thus, if phosphorescence measurements are performed at different temperatures and $\ln \tau$ is plotted against $1/kT$, a straight line should be obtained and the trap depth E can be determined from its slope. After having found E from equation (2) the frequency factor can be computed. It often happens that two or more peaks overlap. Then the intensity is given by

$$I(t) = \sum_i I_{0i} \exp\left[-st \exp\left(-\frac{E_i}{kT}\right)\right] \tag{3}$$

where I_{0i} and E_i are the intensity at $t = 0$ and the trap depth, respectively, of peak i. A plot of $\ln I$ versus time consists of a curve concave upwards, which for times longer than the largest half-life of the traps involved in the emission of light becomes a straight line. If the straight-line portion is extrapolated back to $t = 0$, and if the values of the intensity given by the line are subtracted from the original curve, the curve that remains represents the decay of all components except that having the largest half-life. In this way the phosphorescence curve can be resolved into its components. To obtain a better fit of equation (3) to the experimental data, we resorted to the Harwell subroutine VCO5A/AD, which performs a least-squares minimization [13]. Let us denote by $\Delta I(t)$ the difference (residual) between the experimental curve and the fitted curve, and by S the sum of squared differences at a given number of points, i.e.

$$S = \sum_{j=1}^{N} [\Delta I(t_j)]^2. \tag{4}$$

Equation (3) can be written

$$I(t) = \sum_j a_j \exp(b_j t).$$

(5)

Given estimates of the b-values found from a phosphorescence curve by the procedure outlined above and the accuracy requirement the subroutine calculates the parameters of equation (5) by minimizing S. At the beginning of a peak the intensity depends on the temperature as follows:

$$I(T) \propto \exp(-E/kT).$$

(6)

This expression holds when the intensity amounts to a few per cent of the peak intensity. By fitting a straight line to $\ln I$ versus $1/kT$ the trap energy can be found. It is apparent that this method is most easily applied to glow curves showing a single peak or several well separated peaks. When peaks overlap strongly, those peaks lying at lower temperatures than that of the peak being investigated should be annealed out, which renders the method cumbersome. Nevertheless because this method does not depend on the kinetic order of the thermoluminescent processes, we employed it in simple cases to assess the results obtained from phosphorescence measurements.

If a sample is subjected to step anneals at successively higher temperatures T_i, the ratio r_i of the ESR signal intensity after the ith anneal to that before the first anneal is given by [4]

$$r_i = \exp[-s \Delta t \gamma(T_1, T_2, \ldots, T_i)]$$

(7)

where Δt is the duration of each annealing step and γ is given by

$$\gamma(T_1, T_2, \ldots, T_j) = \sum_{i=1}^{j} \exp\left(-\frac{E}{kT_i}\right).$$

(8)

Then the ratio r_j/r_{j-1} is given by

$$r_j/r_{j-1} = \exp[-s \Delta t \exp(-E/kT_j)].$$

(9)

Therefore, if $\ln[\ln(r_j/r_{j-1})]$ is plotted against $1/kT_j$, a straight line should be obtained, whose slope is the trap energy.

The light intensity was measured with an EMI 9558QA phototube (spectral range from 165 to 850 nm), a Harshaw 2000B picoammeter and an HP 7004B plotter.

The phosphorescence measurements reported in this work were made with samples irradiated with doses ranging from 1000 to 10 000 Gy.

3. Results and discussion

In figure 1 the glow curves of sodium and lithium tetraborate are plotted. They have, as already mentioned, two bands that we denote MI and MII, and a band showing up only in lithium tetraborate. For a heating rate of $400\,°C\ min^{-1}$ the maximum of band MI of sodium tetraborate lies at about $170\,°C$ and that corresponding to band MII at about $270\,°C$. For

Table 2. Trap depths and frequency factors of the peaks of band MI and band MII.

Band MI		Band MII	
E (eV)	τ (s)	E (eV)	τ (s)
0.57	7×10^5	1.10	1×10^{10}
0.83	2×10^8	1.34	7×10^{11}
0.85	6×10^7	1.55	1×10^{13}
		1.61	8×10^{12}
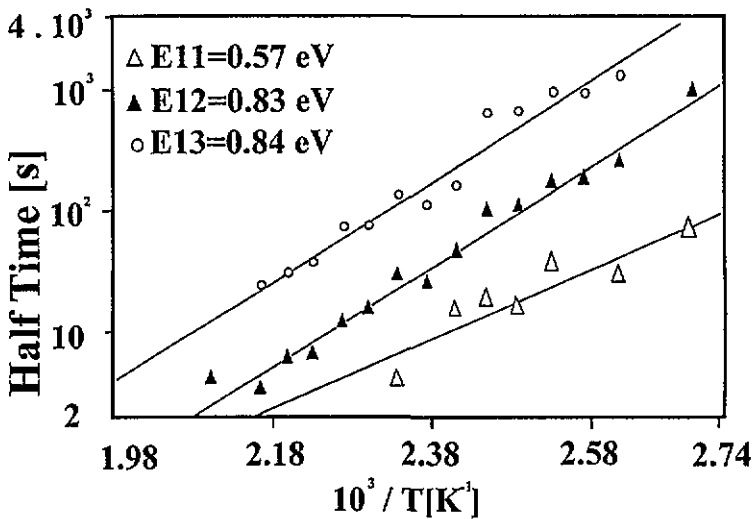
Figure 2. Half-lives of the peaks of band MI as a function of the inverse temperature.

comparison the glow curve of pure borate is shown in figure 1 as well. For pure borate, band MII does not occur, which indicates that it is related to the alkali metal [9].

As mentioned in the introduction the shapes and positions of band MI and band MII do not change with the dose. Therefore the kinetics of the thermoluminescent mechanisms are of first order. This result has been used for analysing the phosphorescence and the ESR intensity step-annealing curves. Phosphorescence measurements were performed at temperatures between 90 and 420 °C. Following the procedure described in section 2, band MI could be decomposed into three peaks having the energies and frequencies listed in table 2, and band MII into four peaks, whose trap depths and frequency factors are also listed in table 2. In figures 2 and 3 the half-lives are plotted against the inverse of the temperature together with the curves fitting the data. It is worth mentioning that the optical trap depth of sodium traps has been estimated from the radiation-induced optical spectrum to lie at about 2 eV [14], and that this value is consistent, according to the configurational coordinate model, with the thermal activation energies listed in table 2 for band MII. Thus it can be concluded that sodium atoms are probably the traps related to band MII. There are further findings lending support to this conclusion. First, according to [14], sodium atoms are electron traps stable up to 150 °C or higher. In the glow curves of sodium tetraborate taken with a low heating rate (10 °C min^{-1}), band MII appears at about 150 °C. Second, in [11], it is reported that in irradiated sodium tetraborate the majority of the electrons are
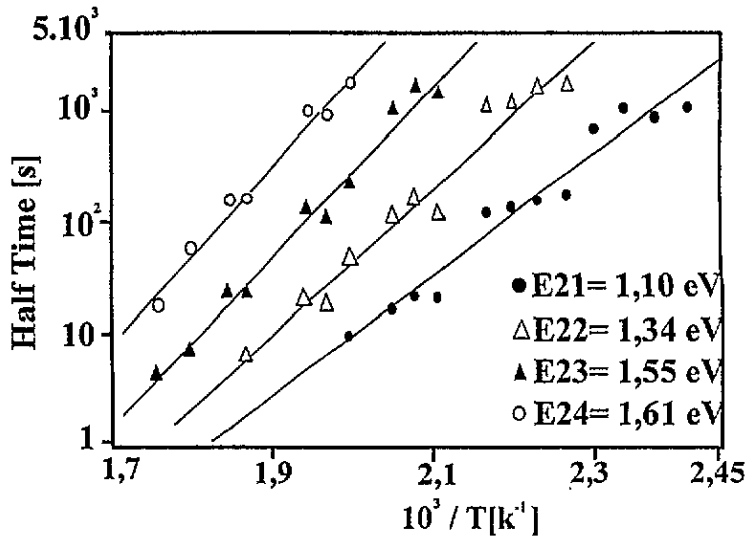
Figure 3. Half-lives of the peaks of band MII as a function of the inverse temperature.
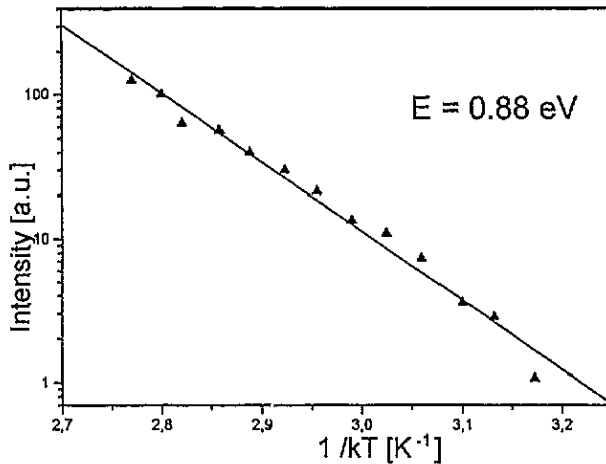

Figure 4. Initial-rise measurements for the lowest-temperature peak of band MII performed 1 d after irradiation (a.u., arbitrary units).

trapped in sodium atoms. These results indicate that sodium atoms are trap centres related to band MII, and that they are the main electron trap. Investigations performed by Kroog-Moe [15] showed that sodium atoms are coordinated by six or seven oxygen atoms with a rather broad distribution in the sodium–oxygen bond distances. Owing to its mobility the sodium ions can form clusters before, during or after irradiation, resulting in trapping sites comprising a number of cations. Thus one expects that several activation energies correspond to the sodium traps, in agreement with the several trap depths corresponding to band MII.

In figures 4 and 5 the results obtained with the initial-rise method are plotted. For band MII the trap depth of 1.13 eV agrees satisfactorily with that of 1.1 eV found from
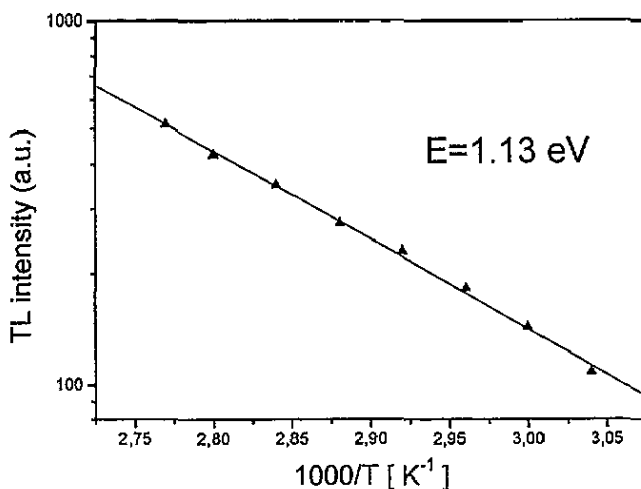
Figure 5. Initial-rise measurement for the lowest-temperature peak of band MII performed 1 month after irradiation (a.u., arbitrary units).
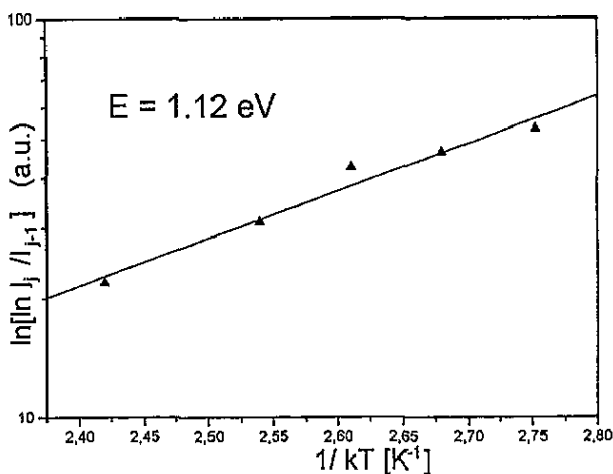

Figure 6. ESR step-annealing measurement of the lowest temperature drop of the signal intensity (a.u., arbitrary units).

phosphorescence measurements. For band MI the trap depth of 0.88 eV is found, a result that can be understood with the help of figure 1 of [4], where glow curves taken 20 min, 1 d, 3 d and 7 d after irradiation are shown. The results show that, after 1 d, band MII has faded to nearly a half its initial value, and that the band maximum has shifted to a higher temperature, indicating that the lowest-temperature peak has faded significantly. Therefore one expects that, when performing an initial-rise measurement 1 d after irradiation, one would obtain the second trap depth indicated in table 2 for band MII, i.e. 0.83 eV, a value that agrees satisfactorily with the value obtained from the initial-rise method.

The step-annealing curve of sodium tetraborate shows two temperature regions where

the ESR-signal intensity decreases significantly [4]. For the low-temperature region, which is probably related to the lowest-temperature peak of band MII, $\ln[\ln(r_j/r_{j-1})]$ is plotted against $1/kT$ in figure 6. The trap depth is 1.12 eV and the corresponding frequency factor is 6×10^9 s^{-1}. The results agree well with those obtained from phosphorescence ($E = 1.1$ eV and $s = 1 \times 10^{10}$ s^{-1}) and from the initial-rise method ($E = 1.13$ eV).

4. Summary

The trap depths and frequency factors related to the two bands forming the glow curve were found by means of phosphorescence measurements assuming first-order kinetics. This choice is justified because no shift in the band maxima occurs on changing the dose. The trap depths of band MI has been found but the traps could not be identified. On the contrary, there is evidence indicating that the trap depths connected with band MII could be ascribed to sodium atoms forming centres with different trap energies. Trap parameters found by means of the initial-rise and ESR step-annealing measurements are in agreement with those obtained from phosphorescence experiments.

Acknowledgment

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