DEVELOPMENT OF MAGNESIUM TETRABORATE
AS A MATERIAL FOR
THERMOLUMINESCENCE DOSIMETRY

by

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Magnesium tetraborate is a candidate phosphor for a laser-heated thermoluminescence (TL) dosimetry system which is under development. Near tissue-equivalent radiation absorption properties and reported sensitivity to low radiation doses offer advantages over commonly employed LiF phosphors.

Sintered wafers suitable for routine measurement were prepared. The effects of powder preparation conditions and activator concentration on TL sensitivity were investigated. Samples with additional impurities (co-doped samples) were prepared in order to increase sensitivity through coactivation or sensitization effects. TL emission spectra were employed to evaluate the effects of co-doping.
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INTRODUCTION

Widespread use of radioactive material and devices which generate high energy radiation coupled with the potential adverse health effects of radiation exposure gives rise to a need for some means with which to monitor the exposure of personnel. Such an assessment of exposure is known as personnel dosimetry. Among the physical effects of radiation on matter which is employed in dosimetry is thermoluminescence (TL), the thermally stimulated emission of light following previous exposure to high energy radiation such as x-rays or gamma rays. TL dosimetry makes use of the fact that the intensity of the emission is linearly proportional to the absorbed dose over a useful range of doses.

While many materials exhibit TL, some are particularly well-suited to personnel dosimetry. An important consideration when selecting materials is the similarity of the radiation absorption properties of the material with those of human tissue. Such properties are governed by a parameter known as the effective atomic number ($Z_{\text{eff}}$). For tissue, $Z_{\text{eff}} = 7.4$. Magnesium tetraborate, MgB$_4$O$_7$, has $Z_{\text{eff}} = 8.4$. Another important parameter is the TL sensitivity, the TL emission intensity per unit dose per unit mass. MgB$_4$O$_7$ is a particularly sensitive TL material, it will show a TL emission after low levels of exposure compared to other TL materials. For these reasons, magnesium tetraborate doped with lanthanides is a candidate for the dosimetric material in a laser-heated thermoluminescence dosimetry system which is under development.
TL signals are measured by rapid heating of the material (1-10 °C/sec) while simultaneously recording the intensity of the emitted light. This procedure is called readout. A trace of the intensity plotted against temperature is known as the glow curve of the material. For dosimetry it is desirable for the glow curve to exhibit a single, sharp maximum or glow peak, and that this peak occur at a temperature greater than 200°C.

The objective of this research is 1) to develop a preparation procedure for MgB₄O₇ that will maximize its TL sensitivity as well as provide a stable glow peak suitable for dosimetry and 2) to prepare MgB₄O₇ by this procedure in sufficient quantity (500 g) to support investigation of other dosimetric properties of the material.
II. LITERATURE SURVEY

Several factors complicate the application of thermoluminescence to personnel dosimetry, and in turn have consequences for the evaluation of the suitability of a given material for dosimetry. First, physical effects other than the absorbed radiation dose and heating cycle of the readout procedure influence the intensity of the TL emission. Second, theories of thermoluminescence, which are based on the band theory of solids, indicate that certain experimental precautions need to be taken in order to achieve useful results. Third, limitations of the instrument used for readout affect the accuracy of the measurement, and need to be considered in the development of the dosimetric material. Related literature discussing these factors is reviewed below, including reports of the observation of their effects in MgB$_4$O$_7$.

Furthermore, the dosimetric properties of a material are, like other material properties, related to the structure and chemical composition of the material, and are thus influenced by the manner in which the material is prepared. While various aspects of the relation between the TL emission and the structure of the material have been explored, the relationships have not been clearly delineated. However, the history of the preparation of MgB$_4$O$_7$ reveals some correlation between certain processing steps with features of the TL emission.
A. Factors governing the TL emission intensity

While TL is the result of exposure to high energy radiation and subsequent heating, the intensity of the TL emission is influenced by other factors, some inherent in the material, some due to the material's environment. These effects include nonlinearity, energy dependence, thermal fading, optical fading, light- and UV-induced signal, phototransferred thermoluminescence, and thermal quenching. Successful evaluation of the dosimetric properties of a material requires awareness of these effects, and exercise of appropriate experimental safeguards.

1. Factors inherent in the material

Nonlinearity (or supralinearity) refers to the deviation of the emission intensity vs applied dose curve from a linear relationship. Clearly, a deviation from linearity may make dosimetry impossible, at the very least it will complicate calibration. Nonlinear dose response has been demonstrated in MgB$_4$O$_7$:Dy by several investigators using different radiation sources. However, the nonlinear response is confined to high doses, with the linear response occurring in a range suitable for dosimetry. The wide linear range is also well-documented. When evaluating the suitability of a material for dosimetry, the radiation doses employed should be in the linear range for the material, so that comparisons can be made between samples without the interference
of nonlinear responses.

In most TL materials, the intensity of the emission for a given dose of radiation varies with the energy of the radiation employed. This is due to the variation in energy absorption by the material with the energy of the radiation. This effect is called energy dependence (18). This effect is of exceptional importance for personnel dosimetry, as the energy absorption of the dosimetric material should be as close as possible to that of tissue. MgB$_4$O$_7$:Dy is such a material (4). The energy dependence of the TL emission of MgB$_4$O$_7$:Dy has been investigated extensively (2, 3, 13, 15, 29). The dependence has also been calculated from mass absorption coefficients (24). Reports of the energy dependence which do not indicate whether it was calculated or measured can also be found (17, 27, 28). Energy dependence of the emission bears on the evaluation of material in that direct comparison of the sensitivity of samples cannot be made unless identical radiation has been employed.

2. Effects of the environment

Thermal fading is the loss of intensity of the TL signal over the time between irradiation and readout which is attributed to heat (18). It is so named because the fading varies with storage temperature. Numerous studies of thermal fading in MgB$_4$O$_7$:Dy have been reported (1, 2, 3, 13, 15, 17, 23, 24, 28, 29, 30). Two factors emerge from an examination of the reported fading
data: 1) That the thermal fading becomes more pronounced with increasing storage temperatures and that 2) the fading is rapid in the hours immediately following exposure but levels off and is slow thereafter. In fact, the fading has been fitted to an exponential equation (1). This implies that when evaluating the exposure of personnel, the readout value needs to be corrected to allow for fading. The leveling off of the fading curve suggests the possibility of using post-irradiation heat treatments to minimize fading effects. A heat treatment applied immediately after irradiation will result in rapid fading, with the intention that only the signal elements which are less susceptible to fading will remain. Several heat treatments have been recommended. When evaluating the sensitivity of a TL material, the effect of fading should be minimized by reading the sample as soon as possible (ideally immediately) after exposure.

Optical fading is the loss of TL intensity attributed to exposure of the dosed material to optical wavelength light such as fluorescent room lighting, UV lighting, or direct sunlight (18). Documentation of the effect of optical fading in MgB$_3$O$_7$:Dy is more recent than studies of thermal fading, and the reported optical fading is generally more pronounced (12, 22, 23). As with thermal fading, the consequences for dosimetry are clear. It is imperative that in both dosimetry and the evaluation of the sensitivity of TL material, irradiated material should be kept shielded from optical wavelength light between exposure and readout.
A further complication is presented by light- and ultraviolet-induced signal in the materials. Visible light and ultraviolet radiation have been shown to produce a TL response in otherwise unirradiated MgB$_4$O$_7$ (22, 23, 30). Clearly, light- or UV-induced signals will distort the evaluation of a radiation dose. This adds further importance to the need to shield dosimeters from optical signals during service. Likewise, it would be desirable to prevent light or UV exposure during the preparation and evaluation of dosimetric material.

Phototransferred thermoluminescence (PTTL) is the thermoluminescent response that is exhibited by irradiated materials if they are subsequently exposed to UV light. This effect can be observed whether the UV exposure is before or after readout (18). A relatively recent paper reports the occurrence of this effect in MgB$_4$O$_7$:Dy and claims that the intensity of the emission during the second readout is proportional to both the initial radiation exposure and the total energy of the UV exposure (30). This indicates the possibility of a second evaluation of the radiation dose. The consequences for evaluation are similar to those from fading effects, that is, the sample must be shielded from UV light at all times.

It is clear from the above discussion that the evaluation of the sensitivity of a TL material is not merely a matter of irradiating the material and recording the intensity of its thermally stimulated emission. Awareness of nonlinearity and energy dependence are important, and choice of radiation energy
and dose must be made accordingly. The material also needs to be screened from the effects of visible and UV light and those of temperature. Furthermore, the presence of PTTL indicates that the TL emission intensity is the product of the total thermal and radiation exposure history of the sample, so that a valid direct comparison is possible only if the sample histories have been kept identical.
B. Thermoluminescence theory

Several models based on the band theory of solids have been proposed to explain the occurrence of the TL emission and describe the behavior of its intensity vs temperature relationship. Differential equations describing the kinetics of the emission mechanism within the models have been derived and for many models solved by various techniques. Experimental methods which provide data for the calculation of the parameters which appear in the solutions have been developed. More than one model leads to a set of equations which requires a considerable amount of sophistication to solve, and all the methods of analysis require specialized equipment and careful control of experimental conditions. Unfortunately, such analysis offers almost no insight into a means by which the sensitivity of the material may be improved. For this reason, a full discussion of TL theory will not be presented, but rather an overview sufficient to demonstrate the current level of accomplishment. McKeever (18), on whose treatment this discussion is almost wholly dependent, presents a more comprehensive review.

One important aspect of all TL models is that they clearly illustrate the essential role of crystalline defects in thermoluminescence. Correlation of the concentration of particular defect species with the intensity of the emission would lead quite directly to various processing steps which could be taken to improve the sensitivity of the material. However, there is no straightforward way to relate the intensity of the TL
emission to a particular atomistic process involving a particular species. Other techniques for the evaluation of the defects present must be employed. Again unfortunately, only two groups of materials, the alkali halides (especially LiF) and the silica polymorphs (especially quartz) have been investigated extensively enough to make any correlation, and even there the relationships cannot be said to be completely understood (18).

1. TL models and TL analysis

The "simple model" discussed by McKeever (18), which has been widely used, will be presented here.

The model is based on the band theory of solids, which in turn is based on quantum mechanics. Solutions to the Schroedinger equation for a periodic distribution of potentials (a reasonable model for a crystalline solid) produce the result that only certain ranges of energy values, called bands, are possible for the electrons in the solid. The forbidden ranges between these bands are termed band gaps. In an insulating crystal (one with negligible electrical conductivity), the allowed energy levels are completely occupied by electrons up to the maximum level of the highest energy band (the valence band). For electron transport to take place, the electrons must find sufficient energy to occupy a level above the band gap (in the conduction band). One way for the electron to achieve such energy is by the absorption of radiation.
TL theory postulates that there are available energy states within the band gap. These states are due to defects in the crystal. Electrons may occupy these energy levels and cease to be available for transport. Such energy levels are known as traps.

Radiation incident on the material will be absorbed by the electrons, which will then enter the conduction band. Some of the electrons will lose energy and occupy trap levels. If the solid is subsequently heated, the electron may absorb sufficient thermal energy to leave the trap and once again enter the conduction band.

Two possibilities exist for the loss of energy on the part of an electron to assume a lower state. The energy could be dissipated as heat through phonon creation, or emitted as electromagnetic radiation via photons. In the first case, since the electron cannot assume any levels in the forbidden zone, enough phonons must be created simultaneously to dissipate energy equal to that of the band gap. The probability of such an occurrence is low. This makes phonon energy dissipation across the band gap unlikely.

The second case is the phenomenon known as luminescence. When an electron returns to the valence band, it recombines with any empty orbital there known as a hole. Holes are generated when electrons absorb energy from incident radiation. After creation, holes are free to migrate through the valence band.
According to the simple model, there exist levels in the forbidden zone where holes can become trapped in a similar fashion to electrons. The model further supposes that, during the heating cycle, luminescence occurs when electrons freed from traps are transported through the conduction band until they recombine with a trapped hole. Thus the energy level where the hole is trapped is called a recombination center.

The TL process can be described by first order ordinary differential equations which express the time rate of change of concentration for holes and electrons at the various levels. Solution of these equations require either simplifying assumptions, the use of numerical methods, or both. Solutions have been achieved which include two key parameters: the energy depth of the trap (the energy difference between the trap level and the bottom of the conduction band), and one known as the frequency factor, which is related to the probability of detrapping at a given temperature. These parameters are characteristic of a given peak in the glow curve of a material, and their evaluation from experimental data is not always straightforward.

The simple model involves a single electron trapping level, a single hole trapping level (or recombination center), ionization of electrons directly from the valence band to the conduction band, thermal detrapping of electrons only, and recombination of electrons in the conduction band with trapped holes. Within the context of band theory, many other energy states and transfer
processes are possible, including distributions of trapping levels, hole detrapping, and transitions directly between "forbidden" levels. Many such additions have been introduced as alternative models for TL, resulting in more complicated equations and additional solution parameters. The additions reviewed by McKeever (18) include distributions of levels, the addition of a deep trapping level known as a thermally disconnected trap, and alternative models which permit hole detrapping and transport or transitions within the band gap. For all cases the next step after solution of the equations is the design of an experiment which will permit the evaluation of the parameters in the solution. This process is known as thermoluminescence analysis.

However, as stated earlier, TL analysis seems to have very little to offer in the way of information which is useful in improving the performance of TL materials. The following quote from McKeever probably best illustrates this situation.

Of course, arriving at values for these parameters does not necessarily mean that we fully understand them, or that we are knowledgeable about the defect model with which they are associated. (Indeed, having calculated say, E and s, there is often a temptation to ask 'so what?'.)

With this in mind, the discussion of TL analysis will be minimal.
The primary source of TL data is the glow curve. The experimental difficulties of obtaining accurate data for a particular glow peak fall into two broad categories. First, it is highly unlikely that a glow curve for a TL material will display a single, well-resolved glow peak. Therefore, most TL analysis procedures focus on isolating the signal from a peak under study from the other peaks in the glow curve. According to the manner in which this is done, the technique is referred to as a partial- or whole-curve analysis, a peak shape method, a peak position method, curve fitting, or isothermal analysis. The second difficulty encountered is that of accurate measurement and control of sample temperature. The combination of an insulating material with its correspondingly low thermal conductivity, the need for a heating rate of several degrees Centigrade per second (to produce a strong signal), and simultaneous measurement of light output make accurate temperature control a challenge, and poor temperature control is a frequently offered explanation for TL data irregularities (18).

Some results of TL analysis have strong implications for other TL experiments, however. First, the solution for the equations for the simple model show that the temperatures at which glow curve maxima occur are strongly influenced by the heating rate. Furthermore, the solution procedure depends on the assumption of a linear heating rate. In the magnesium tetraborate literature, there are several differing reports of the emission maximum temperature. Not all these reports include
the corresponding heating rate. It may be safely said that the only reports of value are those which include this information. But, apparently even then the reported value may not be reliable, due to a further difficulty outlined by McKeever (18).

He illustrates this problem with the case of LiF:Mg. He employs a "heating rate plot" of $\ln(T_m^2/\beta) vs 1/T_m$ where $\beta$ is the heating rate and $T_m$ the temperature at which the maximum emission occurs. According to the theory, all data points should fall along the same straight line. A similar plot employing data from the MgB$_4$O$_7$ literature appears in fig. 1. According to McKeever, poor temperature control is one immediately obvious explanation for the scatter in the data. However, for the case of LiF:Mg this is not an adequate explanation for all the scatter. McKeever makes the observation that the TL emission of LiF:Mg is a function of the entire radiation exposure and thermal history of the sample. For accuracy's sake, the same must be assumed for MgB$_4$O$_7$. Therefore, TL data for two samples should only be compared when their histories have been kept identical.

B. Point defects and TL

The presence of energy levels within the band gap are due to point defects in the material, and the defect structure of a material determines its TL characteristics. Indeed, TL is one technique which is used in the characterization of point defects. However, the correlation of particular glow curve characteristics with particular defects is not obvious, and other techniques must
Heatng Rate Plot for MgB$_4$O$_7$

Fig. 1 "Heating rate plot" for MgB$_4$O$_7$. According to McKeever (18), first-order kinetics dictate that the plot be a straight line.
However, the correlation of particular glow curve characteristics with particular defects is not obvious, and other techniques must be employed in conjunction with TL.

To date no study of the defect structure of MgB₄O₇ and its influence on the TL emission has been published. However, one particular defect type which has long been associated with luminescence processes in general is that of an impurity, particularly lanthanide atoms. The lanthanide ions have a distribution of electron energy levels which provide for radiative electron-hole recombination that is characteristic of the ion (11). For this reason the lanthanides are widely used as activating elements for luminescent materials of all kinds. In the case of magnesium tetraborate, dysprosium, thulium, and terbium have been commonly employed (15, 17, 27, 32), and the TL emission spectrum has been shown to display the characteristic emission lines of these elements. Quite clearly, the improvement of the sensitivity of MgB₄O₇ would include finding the optimum concentration of such an impurity element.

When the emission spectrum of a phosphor contains features which are characteristic of a dopant, the dopant is referred to as an activator (33). Additional dopants which are necessary for the luminescent emission to occur but which may or may not influence the characteristics of the emission spectrum are referred to as co-activators. An impurity which absorbs energy and transfers the energy to the activator is known as a sensitizer (31). There is a distinction between this process,
sensitized luminescence, and the phenomenon of sensitization in thermoluminescence.

As discussed by McKeever (18), sensitization in TL is the increase in sensitivity of a TL material which is observed following the absorption of radiation. That is, if a TL material is exposed to radiation, then subsequently exposed to a second irradiation at a variety of doses, upon readout the material will prove to be more sensitive to the lower doses of the second irradiation. Sensitized luminescence, and sensitizer, are defined as in the above paragraph by Blasse (5). It is thus possible to have a sensitizer for a TL emission, but the term would only be appropriate if energy transfer between the sensitizer and activator were known to occur. An impurity which increased the TL sensitivity of a phosphor, but not by energy transfer, would properly be called a co-activator.
C. TL Instrumentation

One important aspect of the application of a TL material to personnel dosimetry is the instrumentation which will be employed to stimulate and record the TL emission. TL instrumentation consists of essentially two units, a device to control the material temperature and one to measure the TL signal.

As already mentioned, temperature control is of critical importance in TL measurements. Accurate measurement of sample temperature is fundamental to temperature control. In most TL heater systems the measurement device is a thermocouple which measures the temperature of an electrically resistive heating element, not that of the sample (18). Whether the heating element temperature is an accurate reflection of the sample temperature depends on the thermal contact between the element and the sample, the thermal conductivity of the sample, sample thickness, and the heating rate of the readout. Thermal contact between the element and the sample can be improved by the use of a high thermal conductivity medium (18) or some device to apply pressure and thus force the two into more intimate contact. (14). As to sample thickness, McKeever claims that in his experience a thickness of \( \leq 0.3 \text{mm} \) is adequate. The selection of a heating rate must involve a compromise between the need for an intense signal and the need to prevent a thermal gradient across the sample.

The light output of the emission is almost always measured
with a photomultiplier tube (18). One feature of the photocathode of most photomultipliers is that its sensitivity varies with wavelength. To improve the signal for a dosimetric measurement, it is desirable to have a material whose emission spectrum closely matches the response of the photomultiplier tube. Most commercially manufactured photomultipliers have their sensitivity maxima in the 300-500 nm region of the electromagnetic spectrum, thus an emission wavelength in this region is desirable.
D. MgB$_4$O$_7$ Preparation

MgB$_4$O$_7$ was first identified as a phase in the MgO–B$_2$O$_3$ system in 1964 by Kuzel (16), who performed an x-ray structural analysis. Two earlier studies of the phase equilibria in the system, cited by Kuzel, had mistakenly identified the compound as MgB$_2$O$_4$. Subsequently, the phase equilibria of the system was re-examined by Mutluer and Timucin (20), who determined that MgB$_4$O$_7$ melts incongruently to liquid B$_2$O$_3$ and Mg$_2$B$_2$O$_5$ at 995 degrees Celsius. In 1980 Morris et al (19) published a refinement of the crystal structure.

Unlike many TL dosimetry materials, MgB$_4$O$_7$ has not been subject to a great deal of scrutiny and can still be considered to be under development. The history of the synthesis of MgB$_4$O$_7$ for dosimetry from its first appearance in the literature through the present is brief enough to facilitate and incoherent enough to justify a comprehensive review.

Toryn et al introduced MgB$_4$O$_7$ as a dosimetric material in 1973 when they reported on the TL of Tb-activated compounds in the MgO–B$_2$O$_3$ system (32). Samples were prepared by firing MgO, B$_2$O$_3$, and Tb$^{3+}$ in alumina crucibles at varying molar ratios and firing temperatures. X-ray diffraction analysis revealed MgB$_4$O$_7$ in all samples, but always with other phases. The presence of MgB$_4$O$_7$ in a sample was correlated with a glow peak of 170°C at a heating rate of 3°C/s.
In 1974 Kazanskaya et al (17) performed a similar study using Dy as a dopant. Magnesium carbonate, boric acid, and dysprosium nitrate were fired in quartz crucibles. The effects of mole ratio ($\text{MgO:B}_2\text{O}_3$) and activator concentration on sensitivity were examined. A mole ratio of 1:2.5 and an activator concentration of 4 milligram-atoms of Dy per mole of base material was found to be the optimum, but it should be noted that concentrations of 0, 0.4, 4, and 40 were the only ones examined. Of particular interest is that the results were compared to LiF, with MgB$_4$O$_7$ being as much as 20 times as sensitive. The authors also noted that sintering at temperatures near the melting point improved the sensitivity of the material.

Paun et al reported a study employing a variety of elements as activators in 1977 (24). Boric acid and magnesium carbonate were employed as starting materials, fired in silica crucibles. Sm, Ce, Mn, Zn, Pb, Ag, Li, Na, K, and Cs were examined as activators. The results reported indicate that in general the rare earths were more efficient activators than the alkalis or the transition metals, with the notable exception of lithium. Lithium-activated samples displayed a signal intensity in the same range as those doped with rare earths. An optimal concentration of 0.5 % mole was found for all activators. In addition to the activator results, the authors also reported that sintering conditions of 900°C for 4.5 h resulted in the strongest signal.

In 1979 Lakshmanan et al (17) reported an investigation of
the dosimetric characteristics of MgB₄O₇:Dy, basing their sample preparation on previously reported results, with some exceptions. Magnesium carbonate, boric acid, and dysprosium oxide were used as starting materials, with mixing performed using a dilute nitric acid solution. The Dy concentration was 0.5 mole %, A firing temperature of 950°C (as compared to 900 or 1000°C) was found to be optimal, with all firing times being 2 h. The authors also stated that cooling the samples with flowing argon gas improved the sensitivity.

Interest in MgB₄O₇ as a TL dosimeter appears to have increased with the reports of material produced by Prokic (27, 28). While such material is commercially available, it is unfortunate that particulars of its synthesis and development are not. However, both of Prokic's publications provide a few clues. The 1980 paper indicates that dysprosium and thulium make efficient TL activators, with dysprosium-activated samples having a sensitivity seven times higher than LiF TLD-100. Also, sintered material is more sensitive than powders. Furthermore, the author reports that she used a second, undisclosed element to improve the sensitivity. This element is called both a sensitizer and a coactivator, with no apparent distinction between the terms. The use of this element is reported to have caused the TL emission spectrum of the Tm-activated samples to shift from the blue to the green-yellow band while not having any effect on the spectrum of the Dy-activated samples. Portal (25) states that this element is yttrium, citing Prokic's 1980 paper as his source, but there is no such indication in the report.
The 1982 paper, while making similar claims to the 1980 paper and equally lacking in experimental data, contains a number of items of interest. First, in addition to Dy and Tm, Tb, Yb, Ce, Eu, and Sm were used as dopants, with Ce, Yb, Eu, and Sm showing negligible TL emissions. This is in interesting contrast to Paun et al, who reported that Ce and Sm were among the most efficient of the activators that they studied. The TL emission spectra for Dy and Tm appear as illustrations, with emission maxima at 478 nm and 570 nm, and 450 nm, respectively, while the Tb-activated TL emission spectrum is reported to have maxima at 380 nm and 545 nm. The samples employing the sensitizer are said to have TL emission spectra that are "typical" of the activating atoms. The author also reports that improved sensitivity "can only be achieved by the proper choice of type, chemical form, and concentration of coactivator." A similar comment is that "By using starting materials in a specific chemical form and by applying our special method of TLD preparation, it was possible for us to stabilize the trapping centers..." Lastly, it is interesting to note that Prokic reports that Mn and Cu quench the rare earth activated emission, while Paun had studied Mn as an activator.

Pradhan et al (26) prepared MgB$_4$O$_7$ from MgCO$_3$, H$_3$BO$_3$, and Dy(NO$_3$)$_3$ by firing in a platinum crucible in an air atmosphere at 930°C for 2 h. They also obtained Dy-activated samples "supposed to contain an undisclosed sensitizer" prepared by Prokic. The authors recorded the emission spectra of both samples and found them to be identical.
Ogunleye et al (23) employed sintered discs of $\text{MgB}_4\text{O}_7$:Dy, 4.5 mm in diameter and 9 mm thick, in a study of the suitability of the material for low-dose measurements. The discs were obtained from the Harshaw Chemical Company, whom the authors cite as stating that the discs were prepared with a single activator only.

In summary, to date $\text{MgB}_4\text{O}_7$ has been prepared by solid state reaction using a variety of materials as refractory vessels. The mole ratio which produces the maximum emission has been reported to be $2.5 \text{B}_2\text{O}_3$ to $1 \text{MgO}$. This is in good agreement with the experimental arguments of Butler (7) concerning the statistical variation in the composition of a unit volume of a powder mixture and its relation to luminescence efficiency. The firing temperature which gives the optimum TL signal is reported to be in the 900-950°C range, with a firing time of 4.5 h. Several reports confirm that Dy is the most efficient activator, with Tm providing a strong emission also. There is conflicting evidence concerning the activating efficiency of Ce, Sm, and Mn. The use of argon gas during cooling is reported to enhance the TL emission. Sensitivity has also been improved by sintering. The most sensitive samples reported to date employ an undisclosed dopant to improve the emission.
III. Experimental Procedure

A. MgB\textsubscript{4}O\textsubscript{7} Powder Preparation

Following the results of Kazanskaya et al (15), magnesium carbonate (basic) and boric acid powders were mixed in proportions to achieve a mole ratio of 2.5 B\textsubscript{2}O\textsubscript{3} to 1 MgO. Lanthanide activators were introduced as oxides, while lithium was added as a carbonate. The starting materials were mixed under acetone with a glass mortar and pestle, until the acetone evaporated and the mixture had set. After mixing the residual acetone was allowed to evaporate. The dried mixture was then calcined at 400°C for 24 h to decompose the starting materials to their oxides. The calcined mixture was again ground under acetone, allowed to dry, then fired in a box furnace. The resulting sintered mass was dry ground in an alumina mortar and screened through a 200 mesh sieve. X-ray diffraction data from the sieved powder was compared with the results of Morris et al (19) to determine the phases present.

Samples were fired at a variety of temperatures, with the optimum temperature being determined by evaluation of the XRD data and an examination of the TL emission. XRD data were examined for indications of the presence of additional phases, or of glass, which would be a sign of melting. The TL emission was examined by exposing the samples to the primary beam of an x-ray diffractometer with a copper-anode tube source for fifteen minutes, followed by heating on a hot plate. The emission
intensities were compared visually. An optimum firing time was selected in similar fashion.

B. MgB$_4$O$_7$ Wafer Preparation

To avoid the difficulties of testing the TL emission of powders, wafers were prepared. The sub-200 mesh powder was mixed with an amount of methyl cellulose binder equal to three weight percent of the base powder and subjected to 5000 psi in a hydraulic press. The resulting rectangular bar was sintered by firing at 900°C for 1 h. Sintering was preceded by a heat treatment of 400°C for 2 h to burn off the binder. The sintered bar was sliced into wafers 0.25 mm thick using a low speed wafering saw with a diamond-edged blade. The wafers were trimmed to the dimensions of the heating planchet of the TL reader using the same saw. The wafers were then fired at 600°C for 2 h to remove cutting fluid residue. After rinsing in acetone, the wafers were weighed and packaged in preparation for TL evaluation.

C. Evaluation of TL sensitivity

Sensitivity was evaluated by exposing samples to a uniform radiation dose and measuring the total intensity of the TL emission during a uniform readout cycle. Along with a measurement of the sample weight, this allows calculation of sensitivity. To reduce the effects of experimental error, five wafers prepared under identical conditions were evaluated and an
average sensitivity was calculated. The glow curve from each readout was recorded to provide a check on the uniformity of the TL response from a given group of samples.

Samples were weighed to an accuracy of 0.0005 g using a Sartorious model 1872MP8 electronic analytical balance. Following this, they were packaged in tin storage boxes painted black on the inside. The boxes served to protect the wafers during shipment and also to shield them from light between dosage and readout.

In order to eliminate the effects of any charge trapped during processing and shipping, the wafers were run through the readout cycle repeatedly until no signal was detected. Radiation dosage was applied using a $^{137}$Cs source located at the Naval Surface Warfare Center in White Oak, MD. The wafers were exposed for one minute each, equal to a dose of 31.25 rad. Immediately after readout the wafers were inserted in a Harshaw model TLD 4000 TL reader and read out. When not in the sample boxes or in an instrument chamber, the wafers were handled in the dark.

The TLD 4000 is equipped with a bulk sample drawer which houses a platinum heating planchet. It is also equipped with plumbing to allow the use of nitrogen gas during readout, but a nitrogen flux was not used in this work. The wafers were heated from room temperature to 400°C at 2°C/sec. No annealing procedure was employed. The total charge delivered by the photomultiplier tube to the amplifying circuitry, a measurement
displayed by the instrument, was recorded as a measurement of the TL signal. This quantity is representative of the area under the entire glow curve and is thus an accurate expression of the total light output of the wafer during the readout cycle.

D. Sensitized UV Photoluminescence

Two samples were prepared one co-doped with Eu and Dy, the other with Sm and Dy, in an attempt to sensitize a UV stimulated emission from Dy. All dopants were at 0.8 mol% concentration. Samples were evaluated by exposing them to a 254 nm emission mercury lamp.

E. TL emission spectra

Emission spectra were recorded with a device incorporating an EG+G PARC optical multichannel analyzer and a hot plate. Located at the NSWC in White Oak, MD, it has been described in a previous publication (8).

Samples used for the spectral work were 200 mesh powders and were irradiated for periods of two to three days to achieve a strong signal.
IV. Experimental Results

A. Firing time and temperature

A firing temperature of 900°C resulted in an x-ray diffraction pattern matching the results of Morris et al., with no evidence of a second phase or of melting, and a TL emission intensity higher than samples fired at lower temperatures. A firing time of 4 h produced an emission stronger than one of 2 h. Samples fired at longer times were not noticeably brighter.

B. Activator concentration

Plots of TL sensitivity versus activator concentration appear in figs. 2-5 for Dy and Tm dopants. The smaller symbols represent the TL sensitivity relative to the applied radiation dose for a given wafer at the indicated activator concentration. The larger symbol represents the average sensitivity for all samples of a given activator concentration. This illustrates the variance within a certain set of samples.

Fig. 2 represents the results from the initial Dy concentration series. Clearly, in some samples the variance was low, resulting in a distribution of points close to the mean. In others, the variance was quite high, and the sensitivity values are scattered. This figure has the appearance of a concentration quenching curve, with maximum emission at a Dy concentration of 0.8 mol %. To supplement this data, two further
Fig. 2 Plot of TL sensitivity vs Dy concentration for first five samples. Small symbols represent data points, large symbols are the average of points at the indicated concentration.

Fig. 3 Full Dy concentration curve. Note the wide variance in the point at 0.6 mol%.
groups were prepared, at 0.6 and 1.0 mol%. The full data set is illustrated in fig. 3. One group showed high variance (90% of the mean value). The other, while displaying low variance, had an unexpectedly low mean sensitivity.

The Tm concentration curve appears in fig. 4, and has a different form than the Dy data. Again the variance in the data is different for different samples. Because of the unexpectedly high average sensitivity values and the high variance, samples at 0.61 mol% and 4.04 mol% were reassessed. The result appears in fig. 5, with the remeasured values overlaid on the original curve. The mean sensitivity dropped by 24.8% in the lower concentration sample, and increased by 21.0% in the one with high concentration. The variance increased from 11.4 to 31.0% and 13.0 to 26.7% of the mean value, respectively.

C. TL Glow Curves

Various glow curves recorded for MgB\textsubscript{4}O\textsubscript{7} samples appear in figs. 6-8.

Fig. 6 represents a typical glow curve for the material. Fig. 6A is plotted on a vertical scale which is 2.5 times higher than fig. 6B. It is evident that the scale has a marked effect on the appearance of the curve features such as the sharpness of the maximum. Thus the typical features of the MgB\textsubscript{4}O\textsubscript{7} glow curve will be understood to mean the large glow peak centered at approximately 200°C, and the smaller peak at a somewhat higher
Fig. 4 Data from Tm concentration series after all samples had been run once.

Fig. 5 Tm concentration curve, with data for run #2 of 0.61 and 4.04 mol% samples overlaid. Note shift in mean sensitivity for these samples.
Fig. 6A "Typical" glow curve for MgB$_2$ plotted with y-scale output of 500 nA.

Fig. 6B "Typical" glow curve plotted with vertical output scale of 200 nA.
temperature. Several of the recorded glow curves deviated from the typical pattern.

Figs. 7–8 illustrate the deviations. In all cases, a glow curve which did not display the typical pattern would, upon re-irradiation and readout, conform to the typical pattern. Irregular features included greater intensity at the high temperature peak, double maxima in the main peak, or shoulders in the main peak. Of special note in fig. 8B where the glow curves from the entire sample group are displayed, is that these do not match well.

D. Sensitized UV photoluminescence

No UV-stimulated emission was observed from either the Eu/Dy or the Sm/Dy sample.

E. TL Emission Spectra

Emission spectra were recorded for only two samples, one doped with Dy and Li at 0.8 mol % each, the other doped with 0.8 mol % Li alone. The results appear in fig 9. In each case, the emission lines match well with the three most intense characteristic lines of Dy as reported by Crosswhite and Dieke (9). However, as illustrated, the signal from the co-doped sample was an order of magnitude more intense than that of the sample doped with Li alone.
Fig. 7a-f Irregular glow curves and their subsequent return to the typical pattern. The curves on the left hand side are the curves recorded on first readout, those on the right were recorded for the same wafers upon subsequent re-irradiation and readout.
Fig. 8A Irregular glow curve recorded on initial readout of sample.

Fig. 8B Glow curves recorded upon second readout for all samples in group which included 8A. Note that while all curves have the "typical" features, and all have identical activator concentration, the glow curves do not display a uniform $T_m$ or uniform sensitivity.
Fig. 9A TL emission spectrum for a Dy/Li doped sample.

Fig. 9B TL emission spectrum for Li doped sample.
V. DISCUSSION

The experimental results presented above are in good agreement with those previously published. Optimum powder preparation conditions and activator concentration results are confirmed, however, a more precise value of the activator concentration is yet to be established. The results concerning the effect of co-doping of a preliminary nature, and it is clear that this is an area requiring further investigation.

A. Powder preparation conditions

A firing temperature of 900–950°C is by now well-established. This is interesting, in that it approaches the incongruent melting point at approximately 1000°C. The cooling rate from this temperature is almost certain to have an effect on the number and type of point defects in the final material. As it is known that the point defects govern the TL emission, it is likely that the cooling rate has an effect on the TL sensitivity as well. Samples prepared with a uniform firing temperature but cooled at unequal rates might show variations in sensitivity.

A firing time of approximately 4 h is less easily understood. All that may be said is that after such time the solid state reaction is largely complete, and further firing would therefore have very little effect.

One aspect of firing conditions which was not investigated
quantitatively in this study might also benefit from further scrutiny, namely the sintering conditions of the wafers. It is well known in ceramics that both powder synthesis and consolidation procedures affect the final properties. In light of this, investigation of the effect of sintering conditions would seem appropriate.

B. Activator concentration

Results from the literature indicate that the optimum activator concentration is in the order of 0.1 to 1.0 mol%. The results for Dy and Tm displayed in figs. 2-5 are in agreement with this, but a lack of precision in the data prevents a more exact determination of the optimum concentration at this time. The differences in variance between sample groups and the irregularities in the glow curves provide clues as to how the precision may be improved.

The fact that the variance for some sample groups is low clearly indicates that precise measurement is possible. The high variance in others indicates that some effect is preventing it. Several possibilities for the source of the variance, and each should be examined and either eliminated as a possibility or corrected in order to achieve the necessary precision.

The extensive discussion of the need for and difficulties with adequate temperature control made by McKeever (18) highlight this aspect of the measurement. Techniques he discusses, such as
welding the thermocouple to the planchet and the use of a high thermal conductivity medium between sample and planchet might be employed. The adequacy of the control might then be verified by employing the heating rate plot he discusses.

The irregular nature of the glow curves in fig. 7 suggest a second likely explanation. The disappearance of the irregularities on succeeding readouts might mean that the source of the irregular signal is an artifact left over from processing, and that the reader anneal trap cleaning procedure is inadequate. Charge accumulated in deeper traps would be liberated by irradiation and retrapped at more shallow levels, and appear as signal during the readout procedure. If this is the case, pre-irradiation annealing at higher temperatures would be recommended. However, the samples used were subjected to a 600°C heat treatment before shipping, implying either that deep-trapped charge accumulates during shipping, annealing would be ineffective, or that this explanation is not a likely one.

A third possibility is that the output signal was measured over the entire glow curve, rather than a single glow peak. This would tend to magnify any noise elements of the signal which might change from readout to readout. A slight change in background level due to, for example, a change in room lighting, would be amplified by the fact that the measurement corresponds to the area under the glow curve. Isolating the main peak and employing it for the sensitivity measurement would also improve
precision.

Further possibilities, such as an uneven distribution of the trapping species within the sintered bar, are more speculative. If the measures discussed do not improve the precision of the sensitivity measurement, a more comprehensive review of the possible sources of error would be called for.

C. Effect of co-doping

The results of the various experiments with co-doped samples are of a preliminary nature.

The samples co-doped with Sm and Eu, while not photoluminescent themselves, do not eliminate the possibility of achieving such a response with other dopants, or even with Eu or Sm. Varying the concentration of the co-dopant may achieve more satisfactory results.

The sample co-doped with Li and Dy was not evaluated for sensitivity, so the effect of the Li additive remains undetermined. However, the spectra of the co-doped sample compared with that doped with Li alone indicates that Li is not as efficient an activator as might be supposed from the results of Paun et al (24).

The spectrum of both samples matches the Dy emission spectrum as reported by Crosswhite and Dieke (9). This indicates that the
Li-doped sample is contaminated with Dy. This is likely, in that the same labware was used for their preparation. However, the signal from the sample is so weak as to indicate that the contamination level is low. Indeed, weak enough to indicate that only the Dy contaminant is emitting, and that Li has no effect.
VI. CONCLUSIONS

Thermoluminescent magnesium tetraborate can be synthesized in the form of sintered wafers 0.25mm thick, appropriate for dosimetry. When the powder is prepared by solid state reaction, a firing temperature and time of 900–950°C for 4 h will produce the optimum signal. The optimum activator concentration for Tm or Dy activators is in the range 0.1 mol% to 1.0 mol%.

When measuring the TL response of the wafers, care must be taken to insure accurate measurement and control of the sample temperature. Also, steps must be taken to eliminate spurious signals.

Europium and samarium co-dopants at equal concentration to dysprosium do not sensitize a photoluminescent emission from Dy. Lithium at 0.8 mol% is not an efficient activator. The effect of Li as a co-dopant with Dy is not yet clearly determined.
SUMMARY

MgB$_4$O$_7$:Dy and MgB$_4$O$_7$:Tm have been synthesized as sintered wafers 0.25mm thick, a form suitable for use in thermoluminescent dosimetry. Previous results concerning firing temperature and time were confirmed. The optimum activator concentration was found to be in the range 0.1–1.0 mol%, but further effort is required to make a more exact determination. MgB$_4$O$_7$:Li was found to have a weak TL signal compared to RE-doped samples, in contrast to an earlier report (24). An unsuccessful attempt was made to sensitize a photoluminescent emission from Dy using Eu and Sm.
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