Title: Thermoluminescent Properties of Lithium Borate, Magnesium Borate and Calcium Sulfate Developed for Temperature Sensing

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Thermoluminescent Properties of Lithium Borate, Magnesium Borate and Calcium Sulfate

Developed for Temperature Sensing

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Abstract

The objective of this work is to characterize three thermoluminescent (TL) materials synthesized in our laboratory and identified as having properties suitable for temperature sensing, including bright TL emission, low fading at room temperature and low light-induced fading (bleaching) of the TL signal. They are lithium borate doped with copper and silver, Li$_2$B$_4$O$_7$·Cu,Ag (LBO), magnesium borate doped with dysprosium and lithium, MgB$_4$O$_7$·Dy,Li (MBO), and calcium sulfate doped with cerium and terbium, CaSO$_4$·Ce,Th (CSO). We present their synthesis, powder X-ray diffractograms, TL emission spectra, dose response, and sensitivity to ionizing radiation (compared to commercial LiF:Mg,Ti TL material). Important characteristics for temperature sensing applications, such as fading and bleaching, are presented and discussed. LBO and MBO presented in this work have TL emissions in separate regions of the spectrum, meaning that they can be used simultaneously for temperature measurements, their TL signal being separated in the laboratory using appropriate optical filters. The data presented in this paper provides the supporting basic information required to use these materials in temperature sensing experiments.

Keywords: thermoluminescence; lithium borate; magnesium borate; calcium sulfate; temperature sensors
1 INTRODUCTION

Thermoluminescence is a technique widely used in dosimetry of ionizing radiation, luminescence dating, and as a tool for the investigation of defects in insulating crystalline materials [1-4]. Exposure to ionizing radiation creates free electrons and holes that can become trapped at energy levels introduced by defects within the material’s bandgap. These trapped charges can be released upon heating, giving rise to thermoluminescence (TL) as a result of the electron-hole recombination process. The curve of TL intensity versus temperature for a controlled heating (usually linear), the so-called TL curve, typically exhibits several peaks associated with the concentration of charges trapped at different defect energy levels (trapping centers). The TL peak intensity is related to the trapping centers’ population, and the TL peak position (in temperature) is related to the trapping centers’ thermal stability (depth of defect energy levels). In radiation dosimetry and luminescence dating one is interested in the concentration of trapped charges, i.e., in the TL intensity, which gives information on the absorbed dose of radiation in the material.

It has been proposed, however, that the decrease in the concentration of trapped charges with temperature in an irradiated sample can be useful for thermometry in geological and archaeological applications [5-7], research on fire-damaged concrete [8], and research on explosions [9, 10]. Since each trapping center has a different thermal stability, if an irradiated sample is exposed to a temperature profile, the trapped charge concentration will be altered. This change can be detected by recording the TL curve after the sample has been exposed to a temperature profile (temperature versus time), and comparing it with the TL curve of a control sample, which has not been exposed to the temperature profile.
Temperature sensing using TL can be applied in situations in which one is interested in determining the temperature experienced by small particles suspended in air, such as studies on the energy release process and dynamics of energetic materials for “bio-agent defeat” [11]. Application of conventional contact (e.g. thermocouple) and non-contact (e.g., pyrometric, atomic emission spectroscopy) temperature measurement techniques to explosions is challenging, particularly inside an opaque explosion fireball [12-15]. They are limited to measurements at a fixed position or within a specific line of sight and cannot track the temperature experienced by the small particles as they flow during the explosion.

TL is one of several techniques being investigated to address this challenge [9, 10, 16-21]. Irradiated TL powder can be dispersed or mixed with bio-agent simulants and exposed to a temperature profile (e.g. inside an explosion fireball). The TL particles can then be collected and analyzed by recording the resultant TL curve, from which one can, in principle, obtain information about the temperature profile to which the particles have been exposed. If the temperature was high, all trapping centers will be empty and no peak will be observed in the TL curve. If the temperature was low, the trapping centers will not be affected and the TL peaks should be identical to those of the control sample (not exposed to the temperature profile). For intermediate temperatures, low temperature TL peaks will appear with decreased intensity whereas high temperature peaks will appear unaffected [10].

The requirements for TL materials to be used in temperature sensing applications differ from those intended for radiation dosimetry applications [22]. Major requirements for temperature sensing are: (a) high light output (i.e., high sensitivity to ionizing radiation) to allow the detection of the TL signal from small quantities of samples (even a few grains); (b) multiple TL peaks, which can capture information over a wider temperature range than a material containing
a single TL peak; (c) insensitivity to light, to allow sample handling in room light; (d) short-term room temperature stability, i.e., a signal that does not fade between irradiation and readout (for example, humidity has been one of the factors responsible for a decrease in sensitivity [23]; it could also potentially affect the TL signal after irradiation); and (e) simple TL kinetics (e.g., first-order kinetics), to allow for the TL curve analysis according to simple TL models and the superposition principle of TL peaks. Dosimetry requirements such as tissue equivalency [24] are not relevant for temperature sensing applications. Furthermore, in dosimetry there is often an attempt to modify the synthesis procedure and dopants to obtain materials with simple TL curves, preferably with a single, dominant TL peak [25, 26], whereas for temperature sensing multiple TL peaks are desirable.

Li$_2$B$_4$O$_7$, MgB$_4$O$_7$ and CaSO$_4$ with different dopants have been extensively studied in luminescence dosimetry [23], but their suitability for temperature sensing applications has not been explored. The objective of this work is to demonstrate that Li$_2$B$_4$O$_7$:Cu,Ag (LBO), MgB$_4$O$_7$:Dy,Li (MBO) and CaSO$_4$:Ce,Tb (CSO), synthesized as described here, have TL properties suitable for temperature sensing applications. Their crystalline structure was confirmed using powder X-ray diffraction and their sensitivity to ionizing radiation was compared to that of a commercial TL material (LiF:Mg,Ti). We also characterized their dose response, investigated their short-term fading and light-induced fading (bleaching), and performed step-annealing experiments to obtain more information about the nature of the trapping centers associated with the TL peaks. In addition, we present other characteristics that are important for practical applications, such as the TL emission spectrum and grain sizes as determined by scanning electron microscopy. Material synthesis was performed by chemical
routes [27-32], instead of crystal growth, due to the simplicity and rapid production of samples with different dopants in powder form suitable for temperature sensing applications.

2 METHODOLOGY

2.1 Samples

Samples with nominal composition Li$_2$B$_4$O$_7$:Cu$_{0.3\%}$,Ag$_{0.3\%}$ (LBO) and MgB$_4$O$_7$:Dy$_{0.1\%}$,Li$_{1\%}$ (MBO) were synthesized by Solution Combustion Synthesis [27-30]. For MBO, an excess of boric acid was used to achieve the correct crystalline phase. Samples with nominal composition CaSO$_4$:Ce$_{0.2\%}$,Tb$_{0.2\%}$ (CSO) were prepared by the method described by Lakshmanan [31]. The reagents are listed in Table 1. Li was used in the MBO synthesis because it increased the TL and RL intensity by a factor of ~2, which indicates better incorporation of the Dy$^{3+}$ ions probably due to charge compensation.

LBO and MBO synthesis involved the dissolution of metal nitrate, fuel and dopants in purified water (Type I, Milli-Q, Millipore Corp., Billerica, MA, USA). The fuel quantity used in the synthesis was chosen to maintain an elemental stoichiometric coefficient $\phi = 1$ [33]. The mixture was heated on a hot plate at 300°C until the water evaporated. The temperature was then raised to 450-500°C until combustion occurred. The obtained precursor was crushed and placed in alumina crucibles for annealing.

CSO was synthesized by dissolving CaCO$_3$ and the dopants in deionized water. Sulfuric acid was diluted in a separated beaker (3.75 M) and poured into a separatory funnel placed above the beaker containing the CaCO$_3$ solution. The separatory funnel valve was adjusted to allow the sulfuric acid solution to drop into the CaCO$_3$ solution slowly, while the solution was kept under stirring. Once all the sulfuric acid was poured into the CaCO$_3$ solution, the resultant solution was
dried on the hot plate at 170 °C. After complete water evaporation, the hot plate temperature was raised to 350 °C for the evaporation of unreacted sulfuric acid. The resultant precursor was placed in an alumina crucible for annealing.

The samples were annealed using a muffle furnace (model LMF-3550, Omegalux) at the temperatures indicated in Table 1. LBO samples were placed in a preheated muffle furnace for the indicated time, after which they were cooled outside the oven in contact with a metal plate. MBO samples were placed in the muffle furnace at room temperature and the temperature was raised at 5°C/min until the annealing temperature. After the indicated time, the furnace was turned off and the sample was allowed to cool naturally inside the furnace. The annealing regimes are chosen based on our experience with these materials, but a systematic investigation has not been performed yet; preliminary results for LBO were presented by Doull et al. [34].

Commercial LiF:Mg,Ti (TLD-100, Thermo Electron Corporation) in powder form was used for comparison.

2.2 Characterization techniques

2.2.1 XRD

The samples’ phase and crystalline structure were confirmed by powder X-ray Diffraction (XRD) using a Bruker D8 Advance diffractometer equipped with a LYNXEYE detector (D8-25 ADVANCE Bruker AXS GmbH). The diffractograms were obtained with CuKα radiation filtered by a 0.02 mm Ni foil to suppress the Kβ lines, scanning in 2θ with step size 0.02 degrees and 0.5 s per step. The operation voltage and current are 40 kV and 40 mA. The samples were placed in PMMA specimen holders for back-loading (sample reception 25 mm diameter by 0.6 mm depth). Phase identification was performed by matching the diffractograms with patterns.
from the International Centre for Diffraction Data (ICDD) PDF 2 Release 2011 Database version 2.1102.

2.2.2 **SEM**

The morphology of samples was determined by using FEI Quanta 600 field-emission Scanning Electron Microscope (SEM) with magnification around 5000, acceleration voltage of 20 kV. The SEM samples were prepared by suspending the particles in ethanol by ultrasonification and drying a drop of the suspension on an aluminum stub and then coating with gold palladium.

2.2.3 **TL**

TL measurements were carried out using a Risø TL/OSL-DA-15 reader (Risø National Laboratory, Røskilde, Denmark). The TL was detected using a bialkali photomultiplier tube (PMT) (model 9235QB, Electron Tubes, Inc., Middlesex, UK), typically using ~10 mg of material deposited in stainless steel cups and heating rate of 1 °C/s in the presence of high-purity N₂. For high doses we either decreased the amount of material in the cups or used apertures to reduce the TL intensity, avoiding PMT saturation. Optical filters used in front of the PMT included Hoya U-330 (5 mm thickness, transmission in the 240-400 nm range, Hoya Corp., Tokyo, Japan), Hoya U-340 (7.5 mm thickness, transmission in the 290-390 nm range, Hoya Corp., Tokyo, Japan), or Schott BG-39 (6 mm thickness, transmission in the 340-610 nm range, Schott AG, Mainz, Germany).

TL emission spectra was measured replacing the TL reader’s PMT with an optical fiber connected to an Ocean Optics USB-2000 fiber spectrometer (Ocean Optics, Inc., Dunedin, FL, USA). The data was not corrected for the systems’ spectral sensitivity, which is discussed elsewhere along other details of the system [35].
Irradiations were carried out using \(^{90}\text{Sr}/^{90}\text{Y}\) beta sources delivering a dose rate of ~0.1 Gy/s.

3 RESULTS AND DISCUSSION

3.1 Crystal structure and morphology

The crystalline structures of LBO, MBO and CSO were confirmed by XRD, as shown in Figure 1, with no evidence of a secondary phase. The matching PDF cards, crystal systems and space groups are indicated in the figure caption. The relative intensities of the CSO diffraction peaks differ from those in the PDF card due to preferential orientation of the crystallites in the compacted powder sample. This was confirmed by obtaining new XRD data with a small amount of powder deposited without compacting on a layer of silicon grease; in this case the diffraction peak relative intensities were more similar to the corresponding PDF card (data not shown).

The grain sizes can also be important for temperature sensing. For some applications, it may be necessary to use small grain sizes to guarantee a fast response time of the material to a short heating pulse. For this reason, we investigated the grain sizes of the samples synthesized in this study using SEM. First, the powder was sieved with the smallest mesh sizes that we could use to select powder just by shaking. Then the powder obtained was prepared for SEM as described in Section 2.2.2. The micrographs obtained (Figure 2) indicate that grain sizes <20-30 \(\mu\)m can be obtained if necessary. CSO (anhydrite) tends to crystallize in thick tabular or prismatic shape [36, 37], as seen in Figure 2c, which explains the preferential orientation of the compacted powder observed in the XRD data.
3.2 TL emission spectrum

Basic TL characteristics of the samples can be seen in the TL emission spectrum, presented as intensity versus temperature and wavelength contour plots in Figure 3; to increase the TL intensity, the samples were heated at 5 °C/s. Because of the fast heating rate, the TL peak temperatures are shifted towards high temperatures in comparison with data obtained with 1 °C/s. Furthermore, because of possible thermal lag and lack of synchronization between the heating and the detection systems, the temperatures in the TL emission spectra are not accurate and should be used only as a general indication of the TL peak.

In these conditions, the main TL peak from LBO appears at ~210 °C and is characterized by emission at ~370 nm (Figure 3a), which can be attributed to Cu\(^{+}\) emission [38-40]. Ag\(^{+}\) emission in Li\(_2\)B\(_4\)O\(_7\) is reported at ~272 nm [40], which is difficult to detect with our instrument because of its decreasing sensitivity for short wavelengths [35]. The main TL peak of MBO also appears at ~210 °C, with a secondary peak at ~350 °C; both TL peaks are characterized by emission at 480 nm and 574 nm (Figure 3b), which can be attributed to the 4f-4f transitions from Dy\(^{3+}\) (\(^{4}F_{9/2}-^{6}H_{15/2}\) and \(^{4}F_{9/2}-^{6}H_{13/2}\), respectively) [41-43]. The main TL peak from CSO:Ce,Tb appears at ~350 °C, but there are several secondary TL peaks; the TL emission occurring at ~306 nm and 324 nm (Figure 3c) can be attributed to double-band Ce\(^{3+}\) emission (5d-4f transition, with the ground level split into two energy states due to spin-orbit coupling), whereas the other TL emission lines correspond to Tb\(^{3+}\) emission (\(^{5}D_{4}-^{7}F_{J}\) transitions) [41, 44, 45].

3.3 TL curves and sensitivity

The TL peak temperatures can be observed more accurately in Figure 4, which compares the TL curves for the same amount of material measured in the same conditions (except for the optical filters) irradiated with the same dose of ~0.5 Gy and recorded at 1 °C/s. The filters were
chosen to select the main emission of each material, i.e., Hoya U-330 to select the Cu$^+$ in LBO (Figure 4a), Schott BG-39 to select the Dy$^{3+}$ lines in MBO (Figure 4b), and Hoya U-340 to select the Ce$^{3+}$ emission in CSO (Figure 4c). CSO can also be read using Schott BG-39 lines to monitor the Tb emission lines, but here we focus on Ce$^{3+}$ emission because of our interest in high temperature peaks for temperature sensing applications. When monitoring peaks in the visible range of the spectrum, the blackbody radiation introduces a large background for temperature >450 – 500 °C, therefore limiting the range of TL peaks that can be observed. The TL curve of LiF:Mg,Ti (TLD-100) powder, measured in the same condition using optical filter suitable for this material (Schott BG-39), is also presented for comparison.

Figure 4 reveals a variety of TL curves, with emission ranging from <100 °C up to 500 °C. TL peaks below 100-150 °C are typically not of interest for temperature sensing applications, because they will decay at room temperature in a matter of minutes or days. However, they may become relevant if one is interested in measuring relatively low temperatures. In that case, one would need to shorten the time between sample irradiation and readout.

For LBO, a variety of TL curves is observed depending on the dopants and preparation method [40, 46-49]; in dosimetry the most popular dopants are Cu and Mn, probably because of the presence of a single dominant peak at ~200 °C [23, 38, 39, 50-53]. There are few studies on LBO:Cu,Ag [46, 48] and LBO:Cu,Ag,P [54-57]. The TL curves from LBO:Cu,Ag produced here are similar to those presented by Patra et al. [46] and Pekpak et al. [48]. In agreement with their results, co-doping with Cu and Ag leads to a TL curve consisting of two main peaks, which appear here at ~170 °C and ~285 °C (at a heating rate of 1 °C/s) and are associated with emission from Cu$^+$ at ~370 nm, plus a low temperature peak (~75 °C). The sensitivity of LBO:Cu,Ag
obtained by SCS in this study is lower than LiF:Mg,Ti measured in the same conditions, whereas
the sensitivity of LBO:Cu,Ag single crystals has been reported to be higher than that of
LiF:Mg,Ti [46], and LBO:Cu has been reported to be five times more sensitive than LiF:Mg,Ti
[58]. This indicates the potential for improving the TL sensitivity of LBO:Cu,Ag with further
investigations on the influence of synthesis parameters.

The reported temperature of the TL peaks from MBO:Dy vary considerably in the
literature [23, 43, 59, 60]. Nevertheless, the double peak structure of MBO:Dy,Li of the sample
described here (Figure 4) is similar to that observed in MBO:Dy [23]. The sensitivity of
MBO:Dy has been reported to be ~6-15 times that of LiF:Mg,Ti [61], whereas the samples
presented here have a peak TL intensity only three times that of LiF:Mg,Ti. Again, this points
out to the possibility of further material improvement through optimization of the synthesis
parameters.

Finally, the TL curves of CSO also vary a lot according to the dopant and synthesis
method [23, 45]; dosimetric studies have mostly focused on CSO:Dy and CSO:Tm, which have a
dominant peak around 200-300 ºC [23, 62]. The curves we obtained for CSO:Ce,Tb monitoring
the Ce$^{3+}$ emission (i.e., using Hoya U-340 filters) are considerably different than those reported
in the literature, even in comparison to CaSO$_4$:Ce [63], and are characterized by a dominant TL
peak at ~325 ºC with a shoulder at 430 ºC. This material is of particular interest to us because of
the possibility of extending the temperature range of the TL technique for temperature sensing
applications towards higher temperatures. Since we can record the TL using UV transmitting
filter (Hoya U-340), the blackbody radiation in this temperature range is minimum. Also, this
sample has stronger TL emission at higher temperatures (~400 ºC) than LBO:Cu,Ag or
MBO:Dy,Li. The sensitivity is only ~twice that of LiF:Mg,Ti, whereas CSO:Dy, CSO:Mg and
CSO:Tm are reported to have sensitivities 30-60 times that of LiF:Mg,Ti [1]. One should remember, however, that in this work we are focusing on the Ce\(^{3+}\) emission, which for this material is in the UV range, not on the main Tb\(^{3+}\) emission in the visible range.

### 3.4 Dose response

The comparison of the dose response of the TL materials at relatively low doses (<1 Gy) is not relevant for temperature sensing applications, since the materials will be irradiated with high doses before exposure to a temperature profile. Therefore, it is important to investigate their TL responses with dose.

The dose response from the materials is presented in Figure 5, where one can see that at ~500 Gy the signals from LBO, MBO and CSO are still increasing, whereas the signal from LiF:Mg,Ti is already saturated. Therefore, for LBO, MBO and CSO higher TL signals can be obtained by increasing the doses, whereas this is not possible using LiF:Mg,Ti.

The shape of the TL curves varies slightly with dose (Figure 6). The main peaks in LBO and MBO show only a small shift in maximum temperature towards lower temperatures, whereas CSO shows a small shift towards higher temperatures. This indicates that the TL kinetics is close to one (first-order kinetics), otherwise the peak position would present large shifts with dose [1].

There is also a relative change in the intensity of the TL peaks, such as those comprising the high temperature TL of LBO (225 - 300°C). The changes in the relative intensity of the high temperature peaks of MBO and CSO may indicate some degree of sensitization, since we have also observed it when the samples are repeatedly irradiated with the same dose (results not shown here). We have yet to investigate the mechanism responsible for this phenomenon.
Combined, these results on the dose dependence of the TL curves point to the importance of comparing curves obtained after irradiation with the same dose when trying to determine how the TL curves were affected by a temperature profile.

3.5 Step-annealing data

Step-annealing experiments [1] were performed to determine how the curve shape changes with different preheat temperatures and to gain an insight into the more complex peak structures which may be present. The materials were irradiated, preheated to a given temperature \( T_{\text{stop}} \) (at 1 \( ^\circ \text{C/s} \)) and immediately cooled back to room temperature. The entire TL curve was then recorded from room temperature up to a maximum readout temperature at 1 \( ^\circ \text{C/s} \). This sequence was repeated with increasing value of the pre-heating temperature \( T_{\text{stop}} \).

The step-annealing data (Figure 7) shows that the TL peaks are sequentially emptied with increasing \( T_{\text{stop}} \), as expected. Moreover, the peak shifts indicates the possible existence of a distribution of energy states which are sequentially emptied. Although this shift could also be an indication of TL processes characterized by non-first-order kinetics, caused for example by retrapping of the released charges [4], for the most part this hypothesis is not supported by the TL curves obtained at various doses. If the peak shift were caused by non-first-order kinetics, i.e., by the dependence of the temperature on peak trap occupancy, the same shift should be observed when the trapping centers are filled (dose response data) or emptied (step-annealing data). TL peak shifts observed with increasing doses (Figure 6), however, are not as extreme as those observed in the step-annealing data Figure 7. Combined, these results suggest that the TL curves are more likely governed by a superposition of TL peaks caused by trapping centers closely distributed in energy, each following approximately first-order kinetics.
In fact, the complexity of the TL curves has been noted by other authors, who pointed out that the TL peaks are generally interpreted as a distribution of closely overlapping components (LBO and MBO) [23] or as several overlapping peaks over a wide temperature range [45]. The mechanism is certainly more complex than this first approximation, since the relative intensity of the TL peaks change with dose, possibly indicating saturation of the TL peaks at different doses and sensitization processes. Nevertheless, a more in-depth investigation of each material separately would be necessary to answer some of these questions.

3.6 Fading and bleaching

Figure 8 shows representative results on storage fading and bleaching. To perform the bleaching experiments, each sample was irradiated and exposed to room light (about 0.4 mW cm$^{-2}$) for ~3 h, after which the TL signal was read. The sample was then irradiated and the TL read again, providing the TL signal immediately after irradiation used in the comparisons; this has the advantage of avoiding variations due to handling of the sample or due to changes in the system sensitivity. Unirradiated samples were also exposed to room light conditions for 3 h to determine if a light induced signal occurred, but none was observed. The same protocol was followed to determine the fading, except that the samples were stored in the dark for 24 h or one week instead of exposed to light.

The data (Figure 8) show no appreciable fading over the period of 24 h investigated, indicating that the TL peaks are mostly stable at room temperature, except of course for the low temperature TL peaks associated with shallow traps. The cause for the one week increase in LBO is not clear, but it does not affect significantly the shape of the TL curve. In practice fading
should be monitored using control samples, particularly if there will be a delay of months between the temperature exposure and the TL readout.

MBO, however, showed a decrease in TL of almost 40% with 3 h of room light exposure. Although this does not prevent the use of this material for temperature sensing, it does indicate that exposure of the samples to light should be minimized. The samples should be protected from light until the time of the experiment, and immediately protected from light as soon as the samples are collected.

3.7 Signal separation

One advantage of the materials developed in the current work, particularly LBO and MBO, is that their TL emissions are well separated in wavelength. This opens the possibility of using a mixture of materials in a detonation test, using optical filters in laboratory to select only the TL from LBO or MBO. No optical separation of MBO and LBO was attempted with CSO, because CSO has emission in wavelength regions overlapping with both LBO and MBO.

To test this idea, optical separation of LBO and MBO was investigated by selecting optical filters based on the TL emission wavelengths of the samples: Hoya U-330 filters for LBO (emission at ~370 nm), and a combination of Schott BG-39 and Schott GG-435 nm for MBO (emission at 480 and 574 nm). The Schott GG-435 is a long pass filter used to cut the Cu\(^{+}\) emission of LBO.

Figure 9a shows the TL curves for LBO and MBO recorded with Hoya U-330 filter, showing multiple orders of magnitude difference for the detected signal between the two materials. The TL recorded for MBO is nearly identical to the background, whereas the TL from LBO is more than two orders of magnitude more intense.
The opposite situation is observed in Figure 9b, which shows the TL curves for LBO and MBO recorded with the Schott BG-39 + GG-435 combination. In this case, the MBO intensity is orders of magnitude more intense than the LBO intensity.

Therefore, these results demonstrate that, using these optical filters, it is possible to select the TL emission from either material, allowing both powders to be used in a single detonation test, for example to obtain two independent measurements of the temperature.

4 CONCLUSIONS

This work demonstrates that Li$_2$B$_4$O$_7$:Cu,Ag, MgB$_4$O$_7$:Dy,Li, and CaSO$_4$:Ce,Tb can be obtained with TL properties suitable for temperature sensing applications. The TL intensity is comparable or superior to the TL intensity from a commercial TL material (LiF:Mg,Ti) at low doses, but these materials have the advantage of saturating at higher doses than LiF:Mg,Ti. For temperature sensing applications, they can be prepared with high doses of ionizing radiation, guaranteeing sufficient TL intensity in case of only a small amount of TL material is recovered. In addition, the materials did not show evidence of fading in the short-term (24 h), and showed minimum or small (40%) bleaching (light-induced fading) over a 3 h exposure to room light. The TL curves are likely associated with trapping centers having a distribution of activation energies and behavior close to first-order kinetics. If necessary, grain sizes <20-30 μm can be obtained and two materials (LBO and MBO) can be used simultaneously in the same temperature measurement experiment, since their TL emissions are sufficiently separated to be resolved in laboratory using optical filters.

The materials presented here are currently being tested under realistic conditions, including detonation tests at the Naval Surface Warfare Center, Indian Head Division, and the University of Illinois, Urbana-Champaign. We are also currently developing TL models, which
will be used in conjunction with a mathematical algorithm also under development to extract the
temperature profiles to which these materials have been exposed to. Further material
development is also possible, since the position of the TL peaks can be controlled to a certain
degree using different dopants.

In this sense, the results presented here represent a first step towards the development of TL for temperature measurements, providing an initial basis on which further material and methodological development can be achieved.

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FIGURE CAPTIONS

Figure 1. XRD for (a) Li₂B₄O₇:Cu,Ag (PDF 00-018-0717, tetragonal, space group I41cd), (b) MgB₄O₇:Dy,Li (PDF 00-031-0787, orthorhombic, space group Pbca), and CaSO₄:Ce,Tb (PDF 00-037-1496, orthorhombic, space group Bmmb).

Figure 2. SEM from (a) Li₂B₄O₇:Cu,Ag sieved with mesh size between 10 – 20 µm, (b) MgB₄O₇:Dy,Li sieved with mesh size between 20 – 32 µm and (c) CaSO₄:Ce,Tb sieved with mesh size between 20 – 32 µm.

Figure 3. TL emission spectra of (a) Li₂B₄O₇:Cu,Ag (~100 Gy) and (b) MgB₄O₇:Dy,Li (~100 Gy), and (c) CaSO₄:Ce,Tb (~300 Gy). The heating rate was 5 °C/s.

Figure 4. Comparison between TL curves of Li₂B₄O₇:Cu,Ag (Hoya U-330), MgB₄O₇:Dy,Li (Schott BG-39), CaSO₄:Ce,Tb (Hoya U-340), and LiF:Mg,Ti (Schott BG-39) following a dose of ~0.5 Gy using optical filters optimized to select the emission of interest from each material. For MgB₄O₇:Li,Di and LiF:Mg,Ti, which were recorded using Schott BG-39 filters, the increasing emission for temperature higher than 400 °C is due to blackbody radiation.

Figure 5. Dose response of Li₂B₄O₇:Cu,Ag, MgB₄O₇:Dy,Li, and CaSO₄:Ce,Tb compared with TLD-100 from ~0.5 Gy to 500 Gy. Lines indicate linearity behavior through the 10 Gy data points.
Figure 6. Normalized TL curves from the dose response of (a) Li$_2$B$_4$O$_7$:Cu,Ag, (b) MgB$_4$O$_7$:Dy,Li, and (c) CaSO$_4$:Ce,Tb in the dose range of about 0.5 Gy to 500 Gy. All curves are presented for completeness, but the trend with increasing doses is indicated.

Figure 7. Step-annealing data for (a) Li$_2$B$_4$O$_7$:Cu,Ag (~100 Gy, U-330 filter), (b) MgB$_4$O$_7$:Dy,Li (~20 Gy, BG-39 filter), and (c) CaSO$_4$:Ce,Tb (~100 Gy, U-340 filter). In (a) the step-annealing was performed increasing the pre-heating temperature in 10 °C steps; all curves are presented for completeness, but the pre-heating temperature for some of them are indicated. The heating rate for both pre-heating and TL readout was 1 °C/s.

Figure 8. Short-term fading and bleaching for (a) Li$_2$B$_4$O$_7$:Cu,Ag, (b) MgB$_4$O$_7$:Dy,Li, and (c) CaSO$_4$:Ce,Tb indicating minimal storage fading and bleaching over the expected time periods for use in thermal sensing. Light exposure was under fluorescent room light (~0.4 mW cm$^{-2}$ at sample location). Each material was exposed to ~100 Gy. Each curve is the average of three aliquots; the standard deviation of the peak intensity was 2.9% for Li$_2$B$_4$O$_7$:Cu,Ag, 2.0% for MgB$_4$O$_7$:Dy,Li, and 1.5% for CaSO$_4$:Ce,Tb.

Figure 9. TL signals from Li$_2$B$_4$O$_7$:Cu,Ag and MgB$_4$O$_7$:Dy,Li using optical filters selected based on obtained TL emission spectra (Figure 3): (a) Hoya U-330 filters to select the Li$_2$B$_4$O$_7$:Cu,Ag emission; and (b) a combination of Schott BG39 and GG435 to select the MgB$_4$O$_7$:Dy,Li emission. Each curve is the average of three readouts; the standard deviation of the peak intensity was 1.9% for Li$_2$B$_4$O$_7$:Cu,Ag and 0.4% for MgB$_4$O$_7$:Dy,Li.
Table 1. Typical reagents and reagent quantities used for the synthesis of LBO, MBO and CSO.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reagent</th>
<th>Quantity</th>
<th>Annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$B$<em>4$O$<em>7$:Cu$</em>{0.3%}$,Li$</em>{0.3%}$</td>
<td>LiNO$_3$, anhydrous, 99% (Alfa-Aesar, 13405)</td>
<td>4.22 g</td>
<td>875 °C/1 h Fast cooling</td>
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<td></td>
<td>Boric acid, 99.99% (metals basis) (Alfa-Aesar, 36771)</td>
<td>7.42 g</td>
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<td></td>
<td>Glycine, ReagentPlus®, ≥99% (TLC, Sigma-Aldrich, G7126)</td>
<td>2.50 g</td>
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<tr>
<td></td>
<td>CuCl$_2$•2H$_2$O, 99% (Alfa-Aesar, 12458)</td>
<td>1.8 ml (0.05 M)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AgNO$_3$ (EMD Chemicals, SX02053)</td>
<td>1.8 ml (0.05 M)</td>
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<tr>
<td>MgB$<em>4$O$<em>7$: Dy$</em>{0.1%}$,Li$</em>{1%}$</td>
<td>Mg(NO$_3$)$_2$•6H$_2$O, ACS, 98.0-102.0% (Alfa-Aesar, 11564)</td>
<td>10.1 g</td>
<td>900 °C/2 h Slow cooling</td>
</tr>
<tr>
<td></td>
<td>Boric acid, 99.99% (metals basis) (Alfa-Aesar, 36771)</td>
<td>12.4 g (25% excess)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Urea, 98+% (Alfa-Aesar, A12360)</td>
<td>4.00 g</td>
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</tr>
<tr>
<td></td>
<td>LiNO$_3$, anhydrous, 99% (Alfa-Aesar, 13405)</td>
<td>10 ml (0.04 M),</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dy(NO$_3$)$_3$•5H$_2$O, 99.9% (REO) (Alfa-Aesar, 12922)</td>
<td>1 ml (0.04 M),</td>
<td></td>
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<tr>
<td>CaSO$<em>4$:Ce$</em>{0.2%}$,Tb$_{0.2%}$</td>
<td>CaCO$_3$, BioXtra, ≥99.0% (Sigma-Aldrich, C4830-100G)</td>
<td>8.012 g</td>
<td>700 °C/2 h Slow cooling</td>
</tr>
<tr>
<td></td>
<td>Sulfuric Acid, ACS, 95.0-98.0% (Alfa-Aesar, 33273-A1)</td>
<td>16 ml</td>
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<tr>
<td></td>
<td>Ce(NO$_3$)$_3$•6H$_2$O, Reacton®, 99.5% (REO) (Alfa-Aesar, 11329)</td>
<td>4 ml (0.04 M)</td>
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<tr>
<td></td>
<td>Tb(NO$_3$)$_3$•xH$_2$O, 99.9% (REO) (Alfa-Aesar, 74103)</td>
<td>4 ml (0.04 M)</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1

(a) Li$_2$B$_4$O$_7$:Cu,Ag

(b) MgB$_4$O$_7$:Dy,Li

(c) CaSO$_4$:Ce,Tb
Figure 4

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Figure 5

TL intensity (cps)

CaSO₄:Ce,Tb

LiF:Mg,Ti

MgB₄O₇:Dy,Li

Li₂B₄O₇:Cu,Ag

Dose (Gy)
Figure 6

(a) Li$_2$B$_4$O$_7$:Cu,Ag

(b) MgB$_4$O$_7$:Li,Dy

(c) CaSO$_4$:Ce,Tb
(a) $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu,Ag}$

(b) $\text{MgB}_4\text{O}_7:\text{Dy,Li}$

(c) $\text{CaSO}_4:\text{Ce,Tb}$
Figure 9

(a) U-330

Li$_2$B$_4$O$_7$:Cu,Ag

MgB$_4$O$_7$:Dy,Li

(b) BG39+GG435

MgB$_4$O$_7$:Dy,Li

Li$_2$B$_4$O$_7$:Cu,Ag

background