Optically Stimulated Luminescence and Signal Stability of Magnesium Borate doped with Gadolinium-Lithium

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Abstract: This paper explores the effects of codopance with lithium using the gadolinium metal from the lanthanide series. The embodied work include an analysis on a material's ability to capture and hold a 'signal' – or a radio-receptive induced excited state – over time. Recombination centers of optically stimulated luminescence (OSL) and thermoluminescence (TL) will be discussed in some detail when considering the stability of the material. The gadolinium-lithium material is of interest because of its instability; however, its codopant participation with lithium-lanthanide impurities make it a viable candidate for illuminating a strong signal [1]. This investigation will provide a calibration approach to explore and identify the dopant conditions to synthesize an OSL material that is both bright and stable. Stability is used in a variety of different contexts when it comes to OSL and TL measurements. The actual term, however, is attributed to the material's ability to hold and maintain a signal over certain constraints. Since the material has immediate applications in OSL since it is a bright material, the focus of this exploration will be upon the stabilization of the doped material in regards to OSL.

Introduction

In optically stimulated luminescent spectroscopy there exist certain, preferable materials in analyzing radiation dosage. One of these to be explored is a doped form of magnesium borate. Magnesium borate, as an OSL material, is a dim, but stable radio-receptive material. Gadolinium – Lithium dopants in the magnesium borate matrix have been observed to be unstable but quite luminescent, providing a strong OSL signal [1]. The instability is attributed to the probability of electrons inhabiting particular energy bands under certain conditions, but the bands are readily able to transfer the electrons, diminishing the signal as time progresses. Control of the dopants provides control for the energy bands and control of the stability of the material. This investigation focuses on the stability attributed to the OSL signal of magnesium borate doped with gadolinium and lithium. The material that minimizes the variation of the OSL signal over twelve hours will constitute a 'stable' OSL material. An extensive study performed on lanthanide dopants by Millikan et al. provided a foundational approach for trapping center identification [1]. Just specific spectra of infrared radiation can be utilized to identify the unique dipole moments within an aqueous structure, the TL curves – which is also described as 'peaks' or 'lines' – can also be utilized to identify the trapping mechanisms inside of a solid TL material. This investigation was performed in practice of identifying these mechanisms as a result from stabilizing the signal from the material; however, even after the stable compound is identified, the original discrepancy between the TL readings remained as two peaks as the photo-multiplier tube's filters differed.

Material science is a main contributor to dosimetry of any kind. Radiation dosimetry is the study of measurable, dose-dependent properties under select, material conditions. The conditions under observation are both temperature and optical stimulation. Both of these

conditions are a direct contributor to the energy state an electron can occupy. The conditions prior to the capture of radiation are attributed by a variety of mechanisms. Electron-trap/ hole-recombination, or hole-trap/ electron-recombination are the two proposed mechanisms behind the radiation signal absorption [1]. Over time, the signal can be lost as the energy states relax back to their lower energy bands. There exist two energetic bands within the solid material that utilize the mechanisms within the dosimeter. The two bands are known as the conduction and valence band, separated by a forbidden zone. This forbidden zone is energetically penetrated by the use of dopants to supply intermediate electron energy bands in order to cycle between the conduction and valence bands [5].

The material under observation is known as magnesium borate, doped with a fraction of gadolinium and lithium. These combinations of dopants are known for producing a strong, luminescent signal; however, they are not able to hold this signal for very long. The goal of this paper is to apply a systematic approach to stabilizing this material. The selection of the lithium codopant is relevant because it increases the luminescence of the material as doped with the lanthanide series [1]. This strong luminescence counteracts the typical dim nature of magnesium borate.

Methods

The synthesis of magnesium borate doped with gadolinium and lithium relies on a combustion-oxidation reaction with urea. This method is the preferred synthesis of magnesium borate as it readily introduces of dopants [1]. The overall oxidation-combustion reaction is described by B.A. Doull [1]. The reaction begins with heating a boric acid solution in fifty milliliters of deionized water. The excess of boric acid is then mixed with high purity – 99.98%

purity-- magnesium nitrate. The excess of boric acid is necessary for a fuel rich combustion of the reactants [3]. High purity urea – 99.99% purity -- is added to the reaction as ‘fuel’ for the oxidation-reduction reaction. For the sake of preventing the introduction extra impurities into the reaction, the heated solution is then set to a rolling boil until there is more solid in the mixture than water. The appropriate aqueous, lanthanide series metals and lithium nitrate are then introduced as dopants before combusting the reaction at five hundred degrees Celsius for about eight to ten minutes; the final combusted mixture should be void of all steam rising out of the beaker. The combusted samples are then annealed and crushed into a fine powder. The purpose of the annealing the material is to homogenize the lattice within the solid. As determined in this synthesis, the minimum annealing time is about two hours, annealed at nine-hundred degrees Celsius. The material under observation studies the population of electrons over conducting bands of the solid [4]. The solid material, both before and after annealing, should have a bright, foamy-white appearance. Upon heating or optical stimulation, the electron population returns to a lower-level energy band, releasing photons, the measurable signal. The actual measurement of the optical stimulation in regards to dosage involves an integration of dose over time. This is simply done with a Reimann sum of all values over the readout time, with the intensity at arbitrary units. For the OSL measurements, all of the dosage measurements are taken as a reference dosage from the immediate readouts.

The method of experimentation began with a high dopance of lithium in magnesium borate. The percent dopance of gadolinium was varied, taking an OSL measurement over the duration of twelve hours. The initial measurement was considered the base-peak measurement from which all other measurements were normalized. The gadolinium-doped material with the smallest variation in signal will be the ‘selected’ percent dopance for further testing. This method

will be repeated by varying the lithium dopance while maintaining the ‘selected’ percent dopance. The smallest variation in signal over time will then be considered the most stable material. Each doped sample was measured with a photo-multiplier tube. Before each irradiation, the samples are ‘bleached’ with 450 degree Celsius temperature for twenty seconds. Bleaching is essentially a method of applying conditions to a material to void the conduction band of as great of a population as possible, virtually resetting the material’s signal [5].

The samples were irradiated with five seconds of beta radiation. Both OSL and thermoluminescence (TL) measurements were taken for material information data. The actual stability readouts were taken in a similar fashion such that the samples were each bleached at 450 degrees Celsius and then irradiated for five seconds with beta radiation. The actual optically stimulated readout was delayed for six hours. This sequence was repeated with a readout delay of twelve hours. The error was measured between the readouts at six and twelve hours, using the immediate readout as a reference dosage. The lithium percentage was fixed at ten percent. The instrumentation error very clearly increases as the dopance increases; this same trend is seen with the gadolinium dopance.

Within the TL readings of the material, there were two different filter sets used over the photo-multiplier tube. One of which, the U340, is a filter of only visible light. The BG39 is an ultraviolet filter. The OSL also utilizes the U340 filter. The photo-multiplier tube can also utilize an aperture as a measurement accessory. These measurements varied enough so that an aperture was not necessary. The actual size of the samples used in the Risoe rotary was ten milligrams per aliquot. The OSL readings just utilized the U340 filter, using green, LED light to stimulate the luminescence within the material.

Results

When the actual error is normalized to the initial dosage reading, the minimum error appears at the codopance percentage of 0.2% gadolinium and 10% lithium. This same measurement is taken as lithium is taken. Any variation of lithium dopance above or below 10% results in an increase in error, making the dopance ratio of 0.2% gadolinium and 10% lithium the most stable OSL material. The TL readouts require two different filters. One of which allows only the ultraviolet spectrum into the material. For the gadolinium codopant of lithium, these two peaks differ greatly in intensity. Upon synthesis of the final bins of the magnesium borate with varying lithium dopance, there was an instrumentation error in the process of annealing the final magnesium borate samples. Annealing typically has an effect on the trapping centers of TL deep traps [2]. The material analysis of observing the TL peaks in the newly synthesized bins would compensate for the discrepancy as the second readout for the 0.2% gadolinium and 10% lithium still maintained the minimum peak in error. There were differences in the actual measurements in intensity as reflected in **Table 1**.

Currently, it is unclear on the true nature of the gadolinium-lithium codopant trapping mechanisms. In exploration of the stabilization of the magnesium borate material with gadolinium and lithium dopance, it was certainly a task to find a clear, first-order approximation of the true mechanisms behind the luminescence of the material. This task, however, could not be achieved with the methods utilized. It is worth future investigation to analyze the varying dopance with radioluminesence. The measurements utilized in the scope of this investigation still led to a difference in peaks in both filter selections of BG39 and U340, which did not produce a

consistent, characteristic line peak for the material given. It is also worth noting the several TL trends that occurred with the variance in dopance. As seen in **Figure 1**, holding the lithium constant, the TL peak presented a clear, increase in signal as the dopance of gadolinium increases. The prominence of a shoulder is also suppressed with the 0.1% dopance of gadolinium along with a vastly varying peak height between the U340 and the BG39 filters. As the lithium varies, the TL presents a fairly consistent peak height, but the high dopance ratio of 10% lithium keeps the difference in the TL peaks at a minimum (**Figure 2**). All of the samples were heated at a rate of five degrees Celsius per second. The time and temperature in the presented figures are one in the same; however, the temperatures should be considered as approximate.

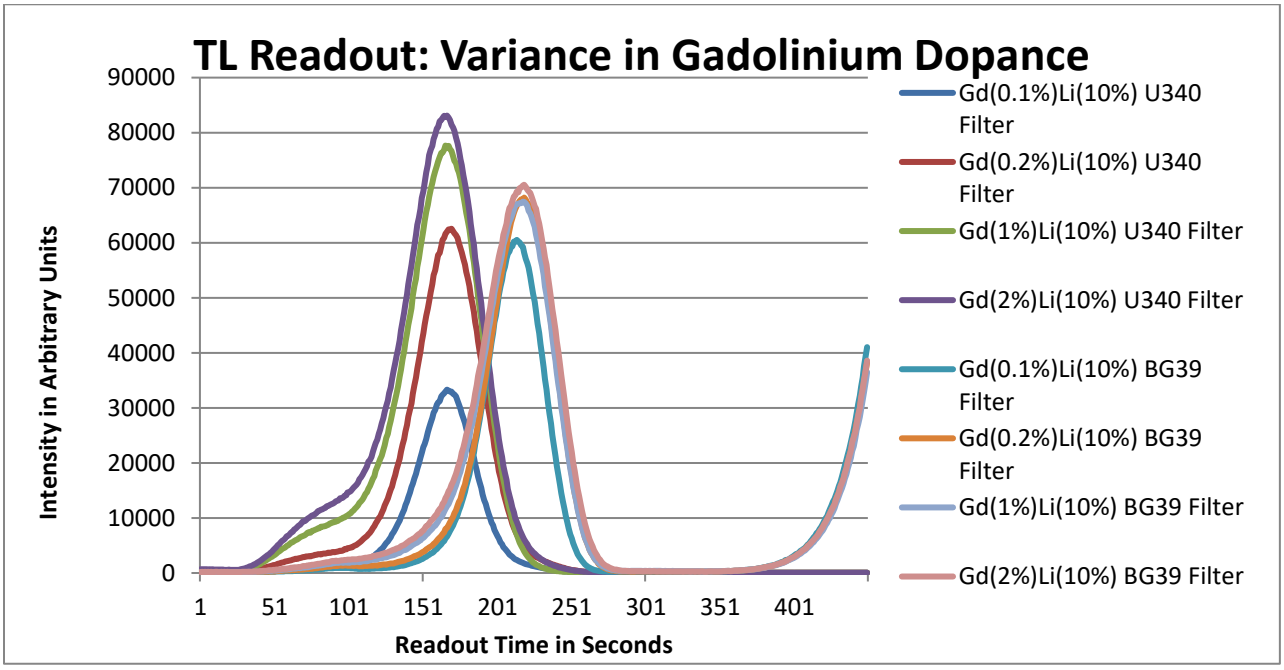

Figure 1. Cross comparison of TL peaks between U340 and BG39 filters with lithium dopance held constant.

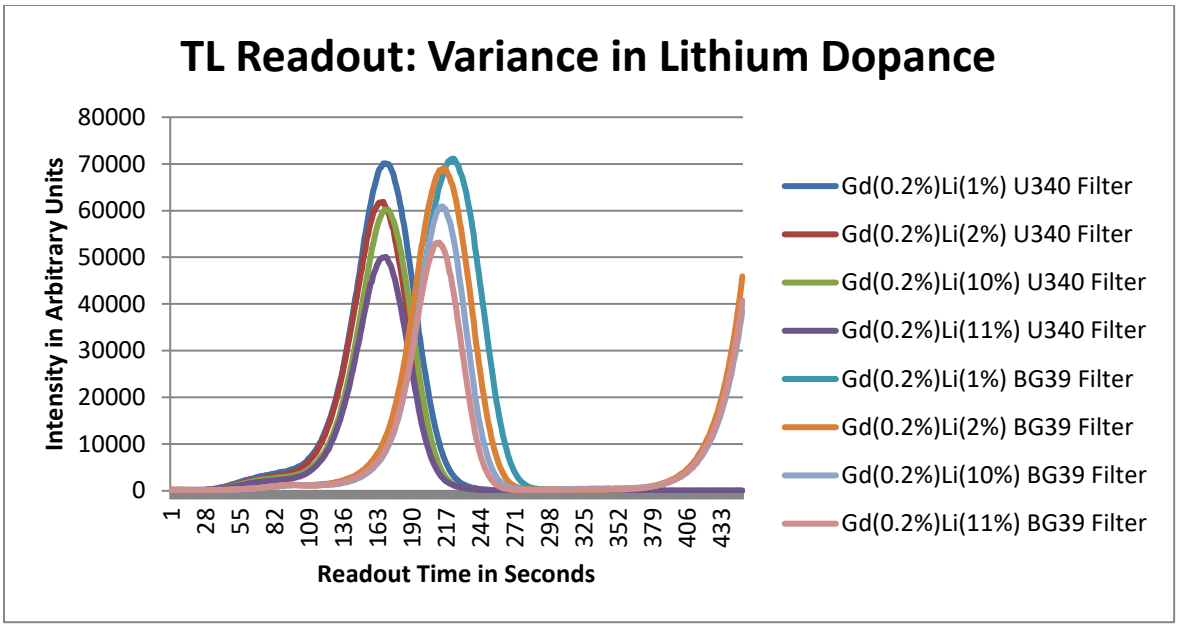

Figure 2. Cross comparison of TL peaks between U340 and BG39 filters with gadolinium dopance held constant.

Stability Analysis taken over Twelve Hours in Six Hour Increments				
Dopant Ratios				
Gd (%)	Li (%)	Average	StDev	Error
0.1	10	0.37	0.04	9.7%
0.2	10	0.30	0.00	0.1%
1	10	0.27	0.01	4.1%
2	10	0.31	0.03	9.4%
0.2	1	0.30	0.01	2.1%
0.2	2	0.26	0.03	11.3%
0.2	10	0.24	0.00	1.8%
0.2	11	0.22	0.01	2.9%

Table 1. Stability readout of gadolinium-lithium dopants. All statistics are presented in a normalized unit of dosage. The highlighted values are the selected, stable material.

Conclusion

The stability of the magnesium borate material doped with gadolinium and lithium is rather inconsistent as the signal is held over time. The error is vastly greater than 1% in most cases of dopant ratios (**Table 1**), except for the case of a high dopance of lithium and a lower

codopance of gadolinium. Ultimately, this is an intuitive result to an essential point elicited by E.G. Millikan: the lithium metal dopant is utilized with a codopance of a lanthanide metal for an increase in signal intensity. The more dopance with the lithium alkali metal, the complimentary effects of signal magnification will be increased with an increase in concentration. The presence of the main lanthanide series dopant, gadolinium, is more liable to broaden the energy bands attributed to the signal loss. This, however, is not the entire description of the error phenomenon seen in **Table 1**. Both variances of the individual dopants have a localized minimal error as the data supplies a positive concavity.

Discussion

The current, proposed mechanism of luminescence is really a dichotomy between hole traps and electron traps [1]. Although the first-order evaluation of gadolinium-lithium made by E.D. Millikan retained the mechanistic discrepancy in TL analysis, a uniquely doped material was able to satisfy an apparent problem with the OSL properties for the magnesium borate material doped with gadolinium and lithium, the problem of maintaining a signal. A further investigation of the deep traps within the magnesium borate material can be analyzed with sensitization measurements – whether or not the same material will lose or accumulate signal after repeated use [2]. Within the measurement procedures, the magnesium borate samples were utilized twice within the TL measurements using both ultraviolet and the visible spectrum. No appreciable discrepancies between the measurements were noticed between the two measurements (**Figure 1** and **2**). This is not to say that multiple measurements will not eventually induce sensitization or desensitization of the magnesium borate material, but two measurements of thermoluminescence will not induce any appreciable change in signal. A further exploration of TL signal stability can also be quantified by light and dark fading of the

material. This can be achieved by irradiating the sample with a known dosage and then exposing the sample to either light or dark conditions for twenty-four hours.

Thermoluminescence, in contrast to optically stimulated luminescence, utilizes temperature-based distribution in order to determine the population of electron energy levels in a given material [4]. Optically stimulated luminescence relies specifically on physical attributions of polarization and photon flux [5]. In the case of the OSL the resulting intensity given by the photonic flux has a direct relation to the electron energy population. The induced energy from the incoming radiation signal excites these electrons to a near-conduction state of energy. For OSL, there are two conduction bands which penetrate the forbidden energies in the given material that work in correspondence with each other [5]. The induction of an excited energy state by a population of electrons induces an electron energy hole – effectively a 'bubble' in which the electron must eventually fill. These corresponding energy levels are known as 'trap' and 'recombination' centers. The recombination centers are defined as the lowest of the correlation energy level. Or, the recombination center is effectively the energy level closest to the conduction band. The energy levels nearest the conduction band are known as trapping centers. Upon energy induction, either electrons or holes, but not both, enter a trapping center [5]. The material is then additionally energized by an external light source, moving the particles from the traps to the conduction band. It is then likely for this population of particles along the conduction band back towards a recombination center, where the energized particle meets its counterpart. This recombination releases energy in the form of light, which is the measurable luminescence interpreted by the photo-multiplier tube. The more energy gained by radiation, the more trapping centers filled; the more trapping centers filled, the more recombination centers are set; the more recombination centers that are set, there exists a higher potential for light to be

released. Thus, the amount of radiation energy induced by the radio-receptive material, in this case magnesium borate with the metallic dopants, is directly related to the intensity of luminescence from the dosimeter.

References

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