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Investigations of MgO:Li,Gd thermally and optically stimulated luminescence

L.C. Oliveira, B.A. Doull, E.G. Yukihara *

Physics Department, Oklahoma State University, Stillwater, OK 74078, USA

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ABSTRACT

The purpose of this work is to investigate the thermoluminescence (TL) and optically stimulated luminescence (OSL) properties of MgO:Li,Gd synthesized by solution combustion synthesis as a function of different synthesis parameters. In addition to TL and OSL, characterization techniques include x-ray diffraction (XRD) and radioluminescence (RL). We also investigated undoped and singly-doped samples for comparison. We show that MgO:Li,Gd may serve as the basis for a new OSL material with intensity comparable to commercial Al_2O_3:C and narrow emission at 315 nm associated with Gd^{3+}. Li co-doping has increased the OSL signal by several orders of magnitude when compared to MgO undoped or MgO:Gd. However, elimination of shallow trapping centers (associated with TL peaks <100–150 °C) is necessary to reduce OSL signal fading at room temperature.

1. Introduction

In spite of the advantages and widespread use of the Optically Stimulated Luminescence (OSL) technique in personal dosimetry, as well as increased interest in medical dosimetry, only two materials are commercially used in OSL dosimetry: Al_2O_3:C and BeO [1,2]. This has been pointed out as a disadvantage of the OSL technique in comparison to the thermoluminescence (TL) technique [3], for which a wider range of materials are available (e.g., LiF:Mg,Ti, LiF:Mg,Cu,P, CaF_2:Mn, CaF_2:Dy, CaF_2:Tm, $CaSO_4$:Dy, MgB_4O_7:Dy, etc.) [4]. OSL applications lacking suitable materials include neutron dosimetry and 2D dosimetry [5].

MgO has long been recognized as a material of interest for luminescence dosimetry, mostly for use with the TL technique [4]. Early interests were in the areas of UV and neutron dosimetry [4,6,7]. Nevertheless, the material failed to gain acceptance probably due to the high variability in TL properties with "sample source, pre-exposure treatments, and radiation and thermal histories" [4].

Bos and colleagues raised interest in MgO for OSL dosimetry with their investigation of MgO:Tb [8]. Although OSL from MgO has been reported before [9], Bos et al. describe the OSL properties of a MgO:Tb sample characterized by bright TL emission associated with Tb^{3+} and OSL signal potentially comparable to Al_2O_3:C. The main problems noted by the authors were fading of the OSL signal (43% after 36 h) and the low OSL signal compared to the TL signal. The latter is due to the fact that Tb^{3+} emission is characterized by lines ranging from ~380 nm to 650 nm, most of which are blocked by the optical filters required for OSL measurements when using green or blue stimulation. In other words, the choice of Tb^{3+} doping is not ideal for OSL measurements when using visible optical stimulation.

Whereas early work on luminescence of MgO focused on color centers such as F centers (540 nm/2.3 eV emission) and F^+ centers (~388 nm/3.2 eV emission) introduced by neutron irradiation or "thermochemical reduction" [10–14], there are several reports of MgO doped with lanthanides, including Ce [15], Eu [16,17], Tb [18], and Dy [19,20]. TL emission spectra of MgO doped with transition metals (Mn, Cr, Ni, Fe, Co, Cu) are also reported by Sathyamoorthy and Luthra [21], but only Mn^{2+} (~600 nm emission) and Ni^{2+} (~490 nm emission) introduced new emission bands in comparison with undoped MgO. Other emissions commonly observed are Fe^{2+} emission at 700–750 nm, Fe^{3+} emission at 388 nm, and Cr^{3+} emission at 698 nm, although some of these attributions are speculative [4]. Emission bands in MgO are reviewed extensively by Las and Stoebe [22].

Based on these initial results, we initiated a systematic investigation of MgO doped with different lanthanides to fill the material gap in OSL dosimetry [5,23,24]. MgO was chosen as one of the host materials investigated because of its relatively low effective atomic number ($Z_{eff}=10.8$), the fact that promising OSL properties have been reported [8], and the variety of TL properties and defects that have been reported in the literature. We chose lanthanides as dopants because of their well-known luminescence characteristics and lifetimes.

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* Corresponding author at: 145 Physical Sciences II, Stillwater, OK 74078, USA. Tel.: +1 405 744 5051; fax: +1 405 744 6811.
E-mail address: eduardo.yukihara@okstate.edu (E.G. Yukihara).

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We showed that MgO with TL intensity comparable to LiF:Mg,Ti, a TL material which is well-known and commercially available [4], could be obtained by a combination of lanthanide and Li co-doping [23]. Li co-doping increased considerably the radioluminescence (RL) and TL of lanthanide-doped MgO; a variety of TL curves were observed, depending on the dopants. Oliveira et al. [24] described the properties of MgO:Nd,Li, which had OSL intensity ~1 order of magnitude lower than Al_2O_3:C and short luminescence lifetime ($<30\ \mu s$), for application in 2D dosimetry. The main problem identified was the presence of shallow traps contributing to the OSL signal, which causes the signal to fade ~30% in the first day, although after that the signal was stable in the period investigated (~2 weeks). Nd^{3+} emission consists of several lines ranging from ~380 nm to 550 nm, most of which are blocked by the optical filters used in the OSL measurements (e.g. Hoya U-340 filters, transmission between 290 and 390 nm).

The purpose of this work is to investigate the luminescence properties of MgO:Li,Gd as a function of different synthesis parameters using solution combustion synthesis (SCS). The interest in Gd stems from the narrow emission band at ~315 nm associated with the $^6P_{7/2} \rightarrow {}^8S$ Gd^{3+} transition [25,26], therefore more suitable for an OSL material because of the anti-Stoke shift and large separation between stimulation (>470 nm) and emission. SCS is an efficient method for the synthesis of doped oxides [27–30], allowing a more homogeneous dopant mixing and MgO production without high temperatures (<1200 °C). Characterization techniques include x-ray diffraction (XRD), radioluminescence (RL), TL and OSL. We investigated the influence of dopant concentration, purity of starting reagents, and annealing temperature on TL, RL and OSL signals. In addition, we measured the OSL and TL emission spectra and the thermal quenching of the OSL signal for readout temperatures ranging from 40 to 160 °C. We also investigated the thermal stability of the OSL signal for different pre-heating temperatures and for different storage periods at room temperature.

2. Methodology

2.1. Material synthesis

MgO samples were synthesized by mixing 13.08 g of magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$, ACS, 98.0–102.0%, Alfa-Aesar) and 5.1 g of urea ($CO(NH_2)_2$, ACS, 98%, Alfa-Aesar) in 50 ml of purified water (Type I, Milli-Q, Millipore Corporation, Billerica, MA, USA), except when mentioned otherwise. The beaker with the solution was placed on a hot plate and stirred using magnetic bars for about 30 min at 400 rpm inside a fume hood. After stirring, the magnetic bar was removed and the solution was allowed to dry on a hot plate at 200 °C for ~1.5 h, after which the temperature was raised to 500 °C until combustion took place (~8 min after the increase in temperature). Once the reaction was exhausted, the remaining inorganic powder was allowed to cool to room temperature, collected, ground using an agate mortar and pestle, and placed in alumina crucibles for annealing. For doped samples, a solution of lithium nitrate ($LiNO_3$, Alfa-Aesar) or gadolinium nitrate hexahydrate ($(GdNO_3)_3 \cdot 6H_2O$, ACS grade, 99.9%, Alfa-Aesar), or both, were added to the initial solution.

Annealing was carried out in air in a muffle furnace (Marshall model 1123, ThermCraft Inc.) by heating the powder from room temperature to a pre-defined temperature (900 °C, except when mentioned otherwise) and holding at this temperature for 2 h, after which it was allowed to cool to room temperature inside the oven. The annealed powder was then removed from the crucible and ground again using an agate mortar and pestle.

Doped and undoped MgO were also prepared using reagents of higher purity (12.82 g of $Mg(NO_3)_2 \cdot xH_2O$, Puratronic ®, 99.999, Alfa-Aesar; 5.04 g of urea, $CO(NH_2)_2$, ACS, 99.3+%, Alfa-Aesar) using the same procedure described above.

The dopant concentrations refer to the molar percent of dopant (with respect to Mg) added to the solution. It does not necessarily reflect the concentration incorporated into the host matrix, as dopants can be lost during annealing or segregated as a secondary phase.

Commercial TL and OSL materials were used for comparison. The TL material was LiF:Mg,Ti powder (TLD-100, Thermo Fisher Scientific Inc.) and the OSL material was Al_2O_3:C powder (Landauer Stillwater Crystal Growth Division, Landauer Inc.).

2.2. Characterization techniques

X-ray diffraction (XRD) patterns were acquired using a Bruker AXS D8 Advance X-Ray Diffractometer with Cu Kα radiation by scanning the 2θ in 0.0204° step size. A 0.02 mm Ni filter was used in front of the detector to reduce the diffraction peaks due to Cu Kβ radiation. For matching of diffractograms, the International Center for Diffraction Data (ICDD) PDF-2 Release 2011 Database version 2.1102 was used; the matching powder diffraction files (PDF) are indicated in the figure caption.

TL and OSL measurements were carried out using a Risø TL/OSL-DA-15 reader (Risø National Laboratory, Røskilde, Denmark), equipped with a $^{90}Sr/^{90}Y$ beta source for irradiation and a photomultiplier tube (PMT) for light detection (model 9235QB, Electron Tubes, Inc., Middlesex, UK) [31]. TL measurements were performed at 5 °C/s in nitrogen atmosphere and using Hoya U-340 for detection (7.5 mm total thickness, transmission between 270 and 380 nm, Hoya Corporation). The OSL readouts were carried out using blue light-emitting diodes (peak emission at 470 nm and irradiance of ~30 mW cm^{-2} at the sample position), except when mentioned otherwise. All TL and OSL measurements were carried out using ~10 mg of powder deposited in stainless steel sample carriers.

RL measurements were performed by exciting the samples using a 40 kV/100 μA X-ray tube (Magnum™, Ag transmission target, Moxtek Inc.) delivering a dose of ~150 mGy/s to the sample. The RL signal is detected using an optical fiber spectrometer (USB-2000, Ocean Optics Inc.) configured for detection of low intensity signal in the 200–850 nm region with low resolution (200 μm slit, resolution of ~7.6 nm, grating with groove density of 600 mm^{-1} and 300 nm blaze wavelength) and containing an order-sorting detector filter. The light was collected using an *f*/2 fused silica lens (model 74-UV, Ocean Optics Inc.) coupled to a 1 mm diameter optical fiber of high OH content (model P1000-2-UV/VIS, Ocean Optics Inc.). The data reported here is the average of multiple spectra over a specific temperature range. The spectra were not corrected for the relative detection efficiency of the entire system, which peaks at 500 nm [23].

TL emission spectra were obtained using the optical fiber spectrometer described above mounted on the Risø TL/OSL-DA-15 reader [23].

The OSL emission spectra were measured at room temperature using a Fluorolog-3 spectrofluorometer (model FL3-22, Horiba Jobin Yvon Inc.) equipped with a 450 W xenon lamp (XBO 450W/2 OFR, OSRAM AG, Munich, Germany) for stimulation and a photomultiplier tube (R928P, Hamamatsu Corporation) for detection. The irradiated samples were stimulated with 500 nm light while scanning the detection monochromator from 240 nm to 440 nm in 1 nm steps and 0.1 s integration time. A longpass filter (GG-475 filter, 3 mm thickness, Schott AG) was used in front of the stimulation