UV Thermoluminescence and Phosphorescence Properties of Mg$^{2+}$ and Nd$^{3+}$ Doped Nanostructured Al$_2$O$_3$

J F S Bitencourt$^1$, K A Gonçalves$^1$, S H Tatumi$^{2,4}$, P J B Marcos$^3$

$^1$Escola Politécnica da Universidade de São Paulo, Depto. de Engenharia de Sistemas Eletrônicos, av. Luciano Gualberto, 380, 05508-970, São Paulo, SP, Brazil.
$^2$Faculdade de Tecnologia de São Paulo, Depto. de Ensino Geral, pça. Cel. Fernando Prestes, 30, 01124-060, São Paulo, Brazil.
$^3$Faculdade de Tecnologia de São Paulo, Depto. de Mecânica de Precisão, pça. Cel. Fernando Prestes, 30, 01124-060, São Paulo, Brazil.

e-mail: tatumi@fatecsp.br

Abstract. Mg$^{2+}$ and Nd$^{3+}$ doped aluminium oxide samples were produced by polymer calcination method. Mg$^{2+}$ doped samples did not exhibited significant fluorescence emission, using IR (LED, emission centered at 862nm) or green (Xe-lamp plus optical filter, emission centered at 520 nm) sources. Nonetheless, high thermostimulated luminescence was detected, with high emission peak at 190°C. A nanoscopic layer (about 50 nm width) of magnesium spinel was observed by Transmission Electronic Microscopy (TEM) for 2.61mol% doped sample; this layer can be the responsible for TL enhancement. Nd$^{3+}$ doped sample exhibited low phosphorescence emission in the UV (Schott U-340) using IR source. TL peaks were detected at 185 and 265°C; the intermediary peak showed the highest emission. Occurrence of NdAl and NdAl$_2$ structures were detected in 5 mol% doped sample and NdAl$_2$ and NdAl$_4$ structures in 10 mol% doped sample.

1. Introduction

Since the 50’s, aluminium oxide have been used as radiation detection and dosimetric material [1] using Thermoluminescence (TL) technique. Early samples exhibited high luminescent sensitivity but also high intensity fading, which prevent its use in a practical way. However, a lot of doped samples appeared in the last 25 years, presenting several new characteristics and improvements; the better example being the carbon doped alumina [2, 3, 4]. Although most of those materials did not exhibited such sensibility as carbon doped alumina, other characteristics can be obtained, such as high saturation point or low energy dependence.

Ceramic dosemeters, such as Al$_2$O$_3$, LiF and phosphate glasses, show advantages in comparison with polymeric films. Reproducibility, multi-readability [5], high-dose saturation point and low energy dependence are some of them.

Magnesium doped alumina is a well know material for dosimetry and radiation detection purposes; nonetheless, structural studies in order to explain luminescence enhancement had not been done. The

$^4$ To whom any correspondence should be addressed. tatumi@fatecsp.br
knowledge of the mechanisms of luminescence production will help the development of new materials and procedures.

Papin et al [6] studied Mg$^{2+}$ doped alumina and found out TL peaks at, approximately, 190 and 350°C. He tried to explain the lower peak by the occurrence of oxygen vacancies. However, the emission intensity decreased for increasing dopant concentration and no explanation was given for high temperature peak.

Neodymium doped alumina is a novel material which application purposes are still in research. This dopant is easily found in photonic glasses, used in waveguides and optical fibres.

Thus, the objectives of the present work are to obtain characteristics TL curves from Mg$^{2+}$ and Nd$^{3+}$ gamma-irradiated samples, so as their OSL (Optically Stimulated Luminescence), in order to verify their use for radiation dosimetry and radiation detection. TEM (Transmission Electron Microscopy) images were obtained, trying to explain the change in luminescence properties from different compositions of samples.

2. Experimental Procedure

Magnesium and neodymium doped samples were produced using polymer calcination method (a variation from Pechini method). Four samples of neodymium doped material were produced (0.5, 2, 5 and 10 mol% of Nd$_2$O$_3$) and five ones doped with magnesium were obtained (0.47, 0.88, 1.33, 2.61 and 3.36mol%). Magnesium concentrations were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP – AES).

Grain size study and crystals morphology were discussed previously at Bitencourt and Tatumi, 2009, achieving an average dimension of 8 µm for grain diameter.

The samples were irradiated using a $^{60}$Co gamma radiation source (doses of 1, 2, 3, 4 and 5 Gy), which Kerma in air was 33.2 Gy.h$^{-1}$ at 40 cm from the source.

TL and OSL measurements were taken in a 1100-series model from Daybreak Medical and Nuclear Systems Inc. coupled with Schott U-340 optical filter (267-377.5 nm, 2 mm thickness) in the entrance of the photomultiplier tube (EMI 9235QA). Measured aliquot mass of magnesium doped samples was around 1.8 mg and 5.4 mg for neodymium doped samples. Heating rate was kept at 5°C.s$^{-1}$ from RT to 300°C.

OSL measurements were carried out using two different sources of light: infrared (862 nm), provided by a LED, and green light from a xenon lamp coupled with one Schott VG-6 optical filter (transmission band centered at 520 nm). OSL decays were measured for the first 100 seconds under continuous excitation.

TEM images and Electron Diffraction (ED) were obtained using model CM200 from Philips Inc.

3. Results and Discussion

Figure 1 shows the average TL emission response variation for five different concentrations of magnesium (0.47, 0.88, 1.33, 2.61 and 3.36 mol%); in this case, the samples were irradiated with 3 Gy of gamma-radiation and the intensities values were calculated using the mean term of three TL maximum peaks intensities. It is possible to verify that the standard deviations from all the samples were kept low and the 2.61 mol% composition exhibited the greater sensibility to radiation exposure.

The luminescence decay observed for 3.36mol% composition is due to phase transition from alumina to magnesium spinel, which could be observed in TEM images and electron diffraction results, showed later in this section. Apparently, doping alumina with 3.36 mol% of magnesium converts most of the crystals into magnesium spinel, which TL response is not as high as alumina itself. Probably, the remaining emission is due to non-transformed crystals.

For Nd$^{3+}$ doped samples (Figure 2), the data was obtained in the same way as the previous sample. The most sensitive sample was the 0.5 mol% Nd$_2$O$_3$ doped composition.

TL glow curves obtained from the best of magnesium and neodymium doped samples indicated above are shown, respectively, in Figure 3 and Figure 4.
Magnesium doped sample produced high intensity TL peak at 190°C and its intensity is proportional to the absorbed radiation dose. The already mentioned work by Bitencourt and Tatumi showed the formation of higher temperature peaks, at 280, 360 and 432°C. The trapping centres responsible for these emissions are filled only when the material is exposed to even higher doses of radiation (above 100 Gy). For low doses, the emission of these centres is hidden behind the background.

Nd$^{3+}$ doped samples, in the other hand, exhibited two TL peaks at 185 and 265°C for low radiation doses. Considering that the 190°C peak found for Mg$^{2+}$ doped sample and 185°C peak detected in Nd$^{3+}$ sample are produced by the same trapping and recombination centres, it can be said that the presence of neodymium atoms change significantly the concentration of such centres. Meanwhile, electronic transitions that produce luminescence at 265°C became proportionally significant. These two peaks were not visualised in Mg$^{2+}$ doped sample, but it does not mean that they do not exist. TL intensity growth of 185°C TL peak from this sample was also proportional to the absorbed radiation dose.

Osvay and Deme [7], working with high-dose irradiated magnesium and yttrium co-doped alumina samples, found two TL peaks, one at 250 and another at 400°C. These peaks do not seem to be related to the presented results, despite of the similarity of both materials.

Unlike the first sample, Nd$^{3+}$ doped material did exhibit OSL decay. The measurements were taken using ninety-nine channels of one second each. Due to low sensitivity or mismatch of the optical
filter used, the decay was not abrupt and the signal was low. Nonetheless, it is possible to distinguish among the five different radiation doses applied to the samples. These decay curves are almost linear, allowing to be taken several times before a significant decrease of the luminescent intensity; that is the concept of multi-readability found in many commercial dosemeters, discussed in the first section.

![Graph showing decay curves for different absorbed doses.]

**Figure 5.** OSL from Nd\(^{3+}\) doped sample using IR stimulation source and detection in UV band.

![TEM image and Electron Diffraction from Mg\(^{2+}\) doped alumina.]

**Figure 6.** TEM image and Electron Diffraction from Mg\(^{2+}\) doped alumina. Superficial structure composed by magnesium spinel was generated on alumina clusters.
TEM imaging and ED from Mg\textsuperscript{2+} doped sample detected a superficial structure composed by magnesium spinel (Figure 6). Such structure only appears in doped material and can be closely related to luminescence enhancement described previously. Also, the images showed a certain number of nanopores, i.e., nanometric pores, but they seem not to be linked to the luminescence properties of the material, for their dimensions do not change significantly when magnesium concentration is increased.

Probably, the spinel layer was created due to magnesium atoms diffusion to clusters surface, where its concentration was high enough to create another material composed by magnesium, aluminium and, of course, oxygen.

Alumina clusters are formed due to the coalescence among several nanometric single-crystals at high temperatures (above 1000°C). This means that the temperature is not enough to melt the substance, but only its surface, creating chemical bonds to nearby single-crystals.

The luminescence results from these samples are different from those published by Yoshimura & Yukihara, 2006 [8] and Lorincz et al., 1982 [9], that dealt with magnesium spinel. So, the luminescence properties must be originated by the junction, or interface, produced between spinel and alpha-alumina.

From Nd\textsuperscript{3+} doped alumina TEM images (Figure 7), it is not possible to discriminate the present phases, or how they interfere in luminescence behaviour. If neodymium atoms are changing places with aluminium in alumina molecules, just like what is occurring with magnesium doped samples, the local charge is not changed, once aluminium and neodymium have the same valence value (3+). Nonetheless, the atomic mass of neodymium (144.24 a.m.u.) is bigger than the mass of aluminium (26.98 amu); so, it is not expected that substitution of Al atoms by Nd atoms really occurs.

Furthermore, it was observed the formation of nanostructures composed by Nd and Al atoms; for 5 mol% doped samples, NdAl\textsubscript{1} and NdAl\textsubscript{2} were observed and, for a higher dopant concentration sample, NdAl\textsubscript{3} nanoparticles, located at the surface of alumina clusters. Our results suggest that complex cluster of Nd and Al does not contribute at all to the luminescence efficiency of the sample.

4. Conclusions
TL measurements of irradiated Mg-doped samples indicate the presence of a high sensitive luminescent centre, producing a UV TL peak at 190°C. This emission is proportional to the
magnesium concentration in the material. However, if the addition of magnesium surpasses the limit, alumina crystals turn into magnesium spinel crystals. So, the best composition found in this work is 2.61mol% magnesium doped alumina.

For Nd-doped alumina, the highest sensitivity was obtained with 0.5mol% Nd$_2$O$_3$ doped sample; two TL peaks were observed: 185 and 265°C. OSL measurement produced proportional emission intensity to the absorbed radiation dose, but a slow decay luminescence was observed.

Both samples exhibited proportional TL emission intensity growth within the radiation dose range, from 1 to 5 Gy, and no saturation point was reached in this dose interval.

Spinel nanolayer was observed on the surface of alumina aggregates in TEM images. This layer is highly probable to be the responsible for the luminescence enhancement observed in TL glow curves, because it is expected that the greatest concentration of luminescence defects or, in other words, anionic defects or F-centres, is located in the interface between the two compounds.

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