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Time decay of the excited states of Eu^{+2} in europium-doped LMA

E. LURIA and S.R. ROTMAN

Ben-Gurion University of the Negev, Department of Electrical and Computer Engineering, P.O. Box 653, 84105 Beer-Sheva, Israel

Abstract Optical measurements of the luminescence of Eu^{+2} -doped lanthanum magnesium aluminate (LMA or $\text{LaMgAl}_{11}\text{O}_{19}$) after high-temperature annealing in various atmospheres are reported. Changes in the time decay can be related to the reversible conversion of Eu^{+2} into Eu^{+3} .

I. INTRODUCTION

During the last twenty years, a series of compounds of $\text{LnMgAl}_{11}\text{O}_{19}$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$) and $\text{LaMAl}_{11}\text{O}_{19}$ ($\text{M} = \text{Al}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) have been synthesized as large crystals and optically analyzed.^{1,2} In particular LMA ($\text{LaMgAl}_{11}\text{O}_{19}$) has been doped with Eu^{+2} and its absorption, emission and excitation spectra have been measured.^{3,4,5} Considerable discrepancies have been noted between the 450 nm excitation spectra of Eu^{+2} measured in LMA and in related crystals.³⁻⁶

The purpose of this research is to study in more detail the spectroscopic properties of $\text{Eu}:\text{LMA}$, to determine the dependence of the luminescence of the Eu^{+2} ions on the concentration of the dopant ions, and the degree that Eu^{+3} can change the spectroscopic properties of Eu^{+2} . In a previous paper⁷, we examined spectral changes that occur with annealing. In this paper, we wish to consider the changes in the temporal responses of Eu^{+2} as a function of the annealing conditions.

II. EXPERIMENTAL PROCEDURE

Three crystals of LMA were prepared by Airtron Corporation with nominal concentrations of europium equal to 0.1%, 1% and 10%. The crystals were measured in the as-grown state, after annealing at 1100° for 24 hours in oxygen and after a subsequent reannealing at 1300° for 24 hours in hydrogen.

The optical pumping was performed by using a nitrogen laser, which produces approximately 10 nsecs pulses at 337 nm. The emission spectra were recorded using a double PTI monochromator and a Hamamatsu R636 photomultiplier tube connected to a SRS Model 510 lock-in amplifier and PC computer. All excitation spectra were corrected taking into

consideration the monochromator efficiency and the wavelength-dependence intensity of the excitation light.

III. RESULTS

The 450 nm time decay for Eu^{+2} was measured after pumping at 337 nm; the results (Fig. 1) show a time constant of approximately 60 μsecs for the 10% Eu^{+2} -doped crystal. The lightly-doped crystal shows somewhat longer time constants with a definite non-linearity; this is seen in the semi-log plot in Fig. 2 for the 0.1% Eu^{+2} crystal. Moreover, as seen in Fig. 3 the non-linearity is more pronounced for the shorter wavelength emission.

Annealing has a significant, if not drastic, effect on the observed time decay (Fig. 4). The 450 nm decay is observed to shorten under oxidation and to lengthen under reduction.

IV. DISCUSSION:

The emission centered at 450 nm for Eu^{+2} in LMA is caused by an electric dipole permitted ($4f^65d \rightarrow 4f^7$) transition. The excited state can be strongly influenced by the local crystal field. Since it is known that the Eu^{+2} can enter both 2d and 6h sites (with their different crystal field strengths)⁸, we would expect considerably broad Eu^{+2} emission and excitation spectra. The excited 5d level of Eu^{+2} is expected to split into three levels (singlet A', double E', and doublet E'') in lower symmetry crystal fields.

The measurements we've taken of the Eu^{+2} time decay are consistent with the previous spectral measurements we've taken. Spectrally, our previously published excitation spectra showed a shift to longer wavelengths as the europium concentration increased. In addition, oxidation seriously reduced the short-wave excitation peaks. If we now examine our time decay measurements, the picture is consistent. The long-wavelength emission is exponential and shorter than the short-wavelength emission. The oxidizing process which enhances the long wave-length excitation peak also causes a shorter time constant.

It appears, from the non-linearity of the short wavelength emission, that there are at least two types of Eu^{+2} sites in the crystal; since they both emit in broad bands, it is difficult to separate between them. The long-wavelength center can transfer energy to the short-wavelength center causing the observed non-linearity in the short-wavelength emission. Oxidation reduces the short-wavelength emission and causes the characteristic long-wavelength center shortened time-decay to appear; reduction reverses the process. Further research to identify these possible sites is underway.

V. CONCLUSION

Annealing Eu :LMA crystals in reducing or oxidizing atmospheres can significantly change the luminescence properties of the Eu^{+2} ions. Oxygen annealing inhibits the short-wave length excitation peaks and shortens the time-decay of the Eu^{+2} emission; hydrogen annealing reverses this effect

REFERENCES

- 1 A. Kahn, A. M. Lejus, M. Madsca, J. They, D. Vivien, and J. C. Bernier, J. Appl. Phys. **52** (1981) 6864.
- 2 D. Saber and A. M. Lejus, Mater. Res. Bull. **16** (1981), 1365.
- 3 A. L. N. Stevels and A. D. M. Schrama-De Pauw, J. Lumin. **14** (1976), 147.
- 4 A. L. N. Stevels and A. D. M. Schrama-De Pauw, J. Lumin. **14** (1976), 153.
- 5 A. L. N. Stevels and A. D. M. Schrama-De Pauw, J. Electrochem. Soc. **123** (1976), 691.
- 6 A. L. N. Stevels, J. Lumin. **17** (1978), 121.
- 7 H. Luria and S. R. Rotman, "Converting Eu^{+2} to Eu^{+3} in Europium-Doped LMA," to be published in J. Luminescence.
- 8 D. Saber, S. Dexpert-Ghys, P. Cago, A. M. Lejus, D. Vivien, J. Chem. Phys. **82** (1985), 5648.

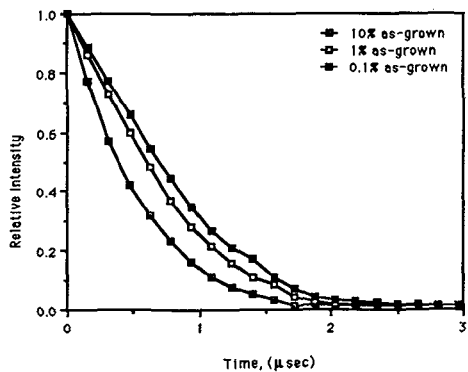


Fig. 1: Time decay of 450 nm Eu^{+2} emission for 0.1%, 1% and 10% Eu-doped LMA crystals.

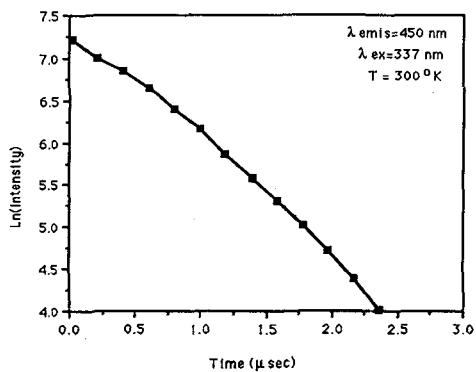


Fig. 2: Semi-log plot of time-decay of 450 nm Eu^{+2} emission for the 0.1% Eu-doped LMA sample.

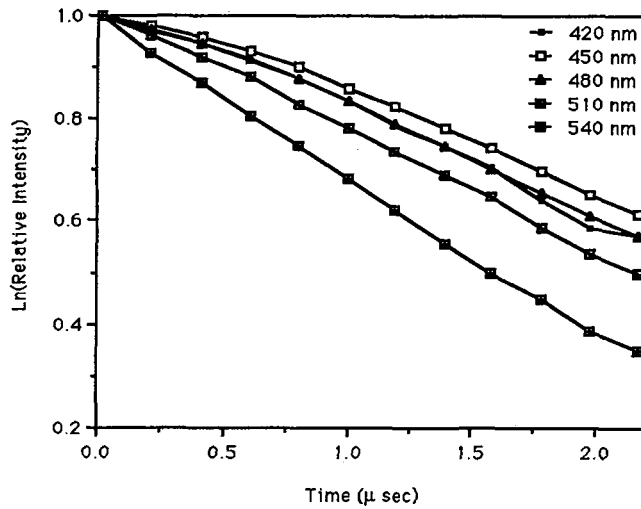


Fig. 3: Semi-log plots of the time-decay of Eu^{2+} emission for the 1% Eu-doped LMA sample for several emission wavelengths.

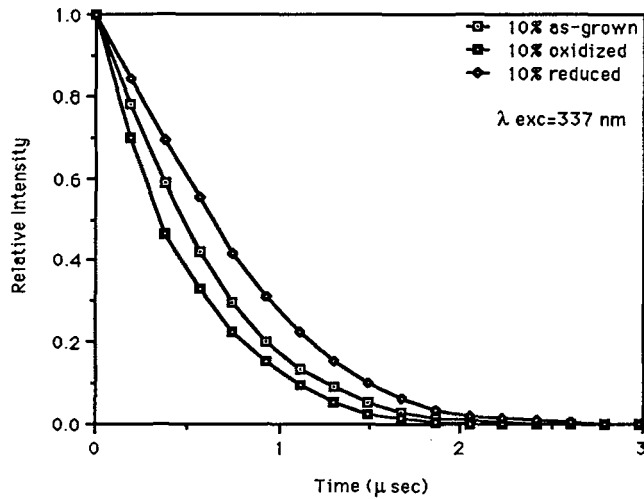


Fig. 4: 450 nm Eu^{2+} emission for as-grown, hydrogen and oxygen-annealed crystals.