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

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Abstract

Optical measurements of the luminescence of Eu$^{+2}$-doped lanthanum magnesium aluminate (LMA or LaMgAl$_{11}$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 LnMgAl$_{11}$O$_{19}$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd) and LaMAl$_{11}$O$_{19}$ (M = Al, Mn, Fe, Co, Ni) have been synthesized as large crystals and optically analyzed. In particular LMA (LaMgAl$_{11}$O$_{19}$) has been doped with Eu$^{+2}$ and its absorption, emission and excitation spectra have been measured.

Considerable discrepancies have been noted between the 450 nm excitation spectra of Eu$^{+}$ measured in LMA and in related crystals.

The purpose of this research is to study in more detail the spectroscopic properties of Eu: 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 paper, 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$^\circ$C for 24 hours in oxygen and after a subsequent reannealing at 1300$^\circ$C 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

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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 $\mu$secs 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$^5$5d $\rightarrow$ 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), 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', doublet 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


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.