Temperature Dependence of Phosphors via Photo-and Thermo-Luminescence

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Introduction

Phosphors used in discharge lamps and light emitting diodes, displays, and scintillators, are commonly characterised via photoluminescence spectroscopy. Their light emitting properties are connected to the structure and the interaction of the active ions with the lattice. Moreover, vibrations in the lattice are sensitive to environmental temperature changes. In this note, the temperature dependence of a phosphor widely used in plasma displays, Hg and Xe discharge lamps, is studied via photoluminescence and thermally-activated luminescence or often called thermoluminescence spectroscopy.

Methods and Materials

Luminescence temperature measurements were performed using an FLS980 Photoluminescence Spectrometer equipped with double excitation and emission monochromators in L geometry, a photomultiplier tube detector (PMT-900) and a 450 W Xe lamp. Gratings blazed at 250 nm were used in the excitation and at 400 nm in the emission arm, with higher diffraction orders being filtered by the integrated long wave-pass filters in the FLS980.



FLS980 Photoluminescence Spectrometer

BaMgAl $_{10}$ O $_{7}$: Eu phosphor (General Electric, BAM) was used without further purification treatment. The phosphor was diluted in water and deposited by evaporation on rectangular copper plates. A liquid nitrogen-cooled cryostat (Oxford Instruments, Optistat DN) was used to vary the sample temperature from 100 K to 480 K with accuracy of ± 2 K. Photoluminescence was measured under steady state excitation, while for the thermoluminescence glow curves, the sample was charged with 255 nm light for 30 s prior to the measurement. Then, illumination was blocked and various ramp rates were selected by adjusting the temperature step and stabilisation time in the spectrometer's software, F980.

Results-Discussion

The photoluminescence spectra of BaMgAl $_{10}$ O $_{17}$: Eu between 120 K and 480 K are shown in Figure 1. The band with a peak around 450 nm is assigned to the $4f^6$ 5d 1 excited state to $4f^7$ ground state transition of Eu $^{2+}$. Lower energy photoluminescence was not detected, confirming the divalent state, 5 to $4f^7$ ground state transition of Eu $^{2+}$. Lower energy photoluminescence was not of europium. It can be seen that the intensity decreases monotonically

as the temperature rises, associated with temperature quenching.² A shift of the peak can also be seen as the temperature rises, with a maximum shift of 10 nm. Moreover, with increasing temperature, band broadening of the emission occurs with increased FWHM from approximately 40 nm to 60 nm due to reduced lattice vibrations. This photoluminescence behaviour was linked to the location of Eu ions in Beevers-Ross sites and to electron traps in the lattice.⁶

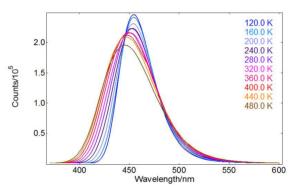


Figure 1: Photoluminescence spectra of BaMgAl $_{10}$ O $_{17}$: Eu upon 255 nm excitation from 120 K to 480 K. The parameters of this measurement were, $\lambda_{\rm exc}$ =255 nm, $\Delta\lambda_{\rm exc}$ =3 nm, $\Delta\lambda_{\rm em}$ =1 nm, step=2 nm, dwell=0.2 s, t $_{\rm exs}$ =60 s.

To investigate further the role of traps in the BaMgAl $_{10}O_{17}$ lattice, the thermoluminescence of BaMgAl $_{10}O_{17}$: Eu was measured. The obtained normalised glow curves are shown in Figure 2. Linear heating rates of 30, 45 and 60 K/min were used for this measurement, without prior thermal cleaning during the heating ramps. A thermal cleaning step can be introduced by cooling the sample without illumination during this process. This way, it is ensured that any energy stored in deep traps from prior charging or environmental factors, is extracted.

A single peak can be seen at approximately 175 K, associated with emission from traps that were not thermally cleaned. The presence of the glow peak indicates the existence of traps below the band gap of BaMgAl₁₀O₁₇.² An apparent shift of the peak to higher temperatures can be seen for faster heating rates, in agreement with previous studies.⁷ Furthermore, a single peak is only detected after charging at 255 nm. A structure of multiple traps is not observed at this excitation energy. On the other hand, a re-convoluted structure could be seen when charged with light above the band gap.^{6,7} This suggests that to resolve this structure, measurements at longer charging periods are required. In addition, the technique can be readily applied to thermoluminescence excitation to confirm the origin of the emission from excited 5d states in luminescent and other phosphors.1

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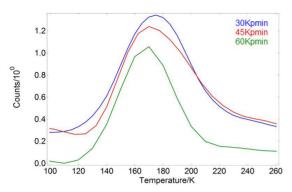


Figure 2: Normalised thermoluminescence glow curve of BaMgAl $_{10}$ O $_{17}$: Eu at various heating rates. Experimental parameters were $\lambda_{\rm exc}$ =255 nm for 30 s, $\lambda_{\rm em}$ =450 nm, $\Delta\lambda_{\rm exc}$ =10 nm, $\Delta\lambda_{\rm em}$ =15 nm, step=5 K, dwell=0.5 s, t $_{\rm stab}$ =10 s.

Conclusion

Photoluminescence and thermoluminescence measurements of BaMgAl $_{10}$ O $_{17}$: Eu were presented in this application note. The temperature dependent photoluminescence was shown by band broadening and lattice relaxation, while information about the trap states were clearly shown in the thermoluminescence curves. This makes these techniques a very versatile tool for the study of photo- and thermoluminescent materials with an FLS980 Photoluminescence Spectrometer equipped with a liquid nitrogen cryostat.

References

- [1] Ueda, J., Dorenbos, P., Bos, A. J. J., Meijerink, A. & Tanabe, S. Insight into the Thermal Quenching Mechanism for Y3Al5O12:Ce3+ through Thermoluminescence Excitation Spectroscopy. J. Phys. Chem. C 119, 25003–25008 (2015).
- [2] Bizarri, G. & Moine, B. On the role of traps in the BaMgAl10O17:Eu2+ fluorescence mechanisms. *J. Lumin.* **115**, 53–61 (2005).
- [3] Bos, A. J. J., van Duijvenvoorde, R. M., van der Kolk, E., Drozdowski, W. & Dorenbos, P. Thermoluminescence excitation spectroscopy: A versatile technique to study persistent luminescence phosphors. *J. Lumin.* 131, 1465– 1471 (2011).
- [4] Ogiegło, J. M. et al. Luminescence and Luminescence Quenching in Gd3(Ga,Al)5O12 Scintillators Doped with Ce3+. J. Phys. Chem. A **117**, 2479–2484 (2013).
- [5] Kim, Y.-I., Kim, K.-B., Jung, M.-J. & Hong, J.-S. Combined Rietveld refinement of BaMgAl10O17:Eu2+ using X-ray and neutron powder diffraction data. J. Lumin. 99, 91–100 (2002).
- [6] Tanno, H., Zhang, S., Shinoda, T. & Kajiyama, H. Characteristics of photoluminescence, thermoluminescence and thermal degradation in Eu-doped BaMgAl10O17 and SrMgAl10O17. J. Lumin. 130, 82–86 (2010).
- [7] Jüstel, T., Lade, H., Mayr, W., Meijerink, A. & Wiechert, D. U. Thermoluminescence spectroscopy of Eu2+ and Mn2+ doped BaMgAl10O17. J. Lumin. 101, 195–210 (2003). Ligand Passivation, ACS Energy Lett. 1, 438–444 (2016)

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