

Luminescence of Eu^{2+} doped SrAl_2O_4

R. Job¹⁾, H. Yamada²⁾, C.-N. Xu^{2,3)}

¹⁾ University of Hagen, Department of Electrical Engineering and Information Technology,
P.O. Box 940, D-58084 Hagen, Germany

²⁾ PRESTO, Japan Science and Technology Agency,
4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan

³⁾ National Institute of Advanced Industrial Science and Technology (AIST), Kyushu Shuku 807-1,
Tosu, Saga 841-0052, Japan

A photoluminescence (PL) analysis at temperatures between 80 and 300 K was carried out on Eu^{2+} doped strontium aluminate ($\text{Sr}_{1-x}\text{Al}_2\text{O}_4:\text{Eu}_x$, $x = 0.004 - 0.02$). Samples were prepared with and without the support of flux (B_2O_3). The common feature of various solid state materials, which are doped with Eu^{2+} , is an intense broad band luminescence originating from the transitions between the $^8S_{7/2}$ ($4f^7$) Eu^{2+} ground state and the crystal field components of the $4f^65d^1$ excited state¹⁾. At low temperatures the emission spectrum of Eu^{2+} doped strontium aluminate ($\text{Sr}_{1-x}\text{Al}_2\text{O}_4:\text{Eu}_x$, SAO-E) shows two broad PL bands at ~ 445 and 520 nm wavelength (Fig. 1). At room temperature (RT) only the low energy band notable, since the 445 nm band is nearly quenched.

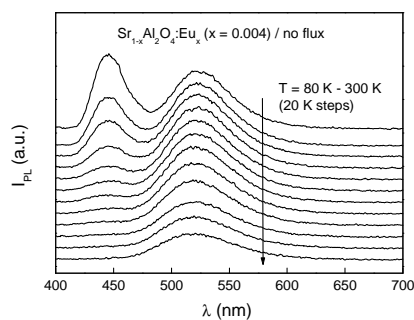


Fig. 1: PL spectra of $\text{Sr}_{1-x}\text{Al}_2\text{O}_4:\text{Eu}_x$ ($x = 0.004$) measured in dependence on the temperature ($T = 80 - 300$ K); the sample was prepared without flux.

At RT the crystallographic stable form of SrAl_2O_4 (SAO) is the stuffed-tridymite structure ($P2_1$ space group). Appropriate sites with sufficient space are provided for the Sr^{2+} cations, which are located in cavities formed by AlO_4 tetrahedrons. Due to x-ray diffraction analysis²⁾, two crystallographic sites are available for the Sr^{2+} ions. They are located along the a-axis, which are not perfectly aligned. The distances between sequential Sr^{2+} ions are alternating by 3.9 and 4.6 Å, respectively. The Sr sites with low symmetry are surrounded by nine oxygen atoms. The distances between Sr^{2+} and the nearest adjacent oxygen atoms are different for the two Sr sites. For the shorter Sr-O distance (Sr-I site) no preferential orientation of d-orbitals occurs, but preferential orientation is possible for the larger Sr-O distance (Sr-II site)³⁾. Eu^{2+} ions substituting the Sr-I site show broad emission at higher energy (at ~ 445 nm), and on the Sr-II site they cause the lower energy band. Both Sr sites occur in equal amounts in the SAO lattice.

If the samples are prepared without B_2O_3 flux the PL spectra of the SAO-E samples exhibit two broad bands show almost equal intensities at low temperatures (Fig. 1). The appearance of two bands can be explained by the fact whether preferential orientation of the d-orbitals occurs (Sr-II site) or not (Sr-I site)³⁾. With increasing temperature the high energy band disappears due to energy transfer. In SAO-E the energy transfer is very effective since the critical transfer distance R_c between inequivalent Eu^{2+} ions is large (~ 14 Å)³⁾. But the situation is even more complicated, as can be seen from detailed PL analysis. Non linear least square fits show that at $T \leq 140$ K each of the two broad bands can be described by two Gauss lines (Fig. 2). For $T \geq 160$ K the high energy band can be described by a single Gauss line, i.e. the line at smaller wavelength is quenched, since energy transfer occurs also

between the two lines of the high energy band. Two Gauss lines are always needed for the profiling of the low energy band up to RT; no significant energy transfer between these two lines was found. The appearance of a fine structure (represented by the fitted Gauss lines) of the two broad luminescence bands can be explained by the fact that in addition to the negative charges of the adjacent anions the Eu^{2+} ions also ‘feel’ the cationic Eu^{2+} neighbours.

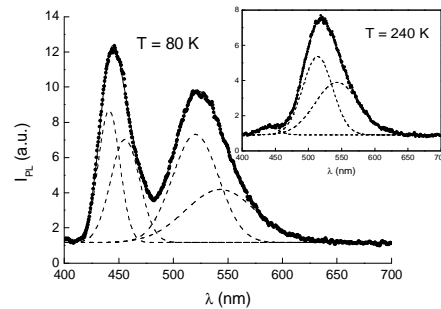


Fig. 2: Deconvolution of the PL spectrum at $T = 80$ K / 240 K by four / three Gaussian profiles (spectra from Fig. 1).

Similar results as shown in Fig. 1 and 2 ($x = 0.004$) can be obtained for higher Eu^{2+} concentrations ($x = 0.01, 0.02$), if the sample are prepared without flux. The situation is changed, if Eu^{2+} doped samples are prepared with flux. In this case the intensity of the high energy band is significantly lower than the one of the low energy band; and the higher the Eu^{2+} concentration the lower the intensity of the high energy band. This can be especially seen very well for the case of the 2 % Eu^{2+} concentration (Fig. 3); even at lower temperatures the intensity of the high energy band can be nearly neglected in comparison to the one of the low energy band.

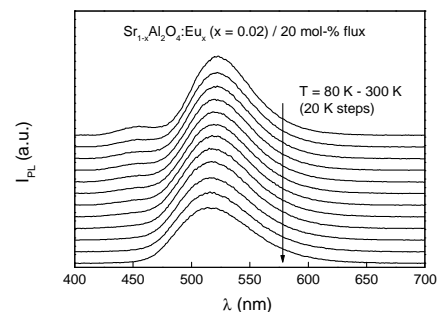


Fig. 3: PL spectra of $\text{Sr}_{1-x}\text{Al}_2\text{O}_4:\text{Eu}_x$ ($x = 0.02$) measured in dependence on the temperature ($T = 80 - 300$ K); the sample was prepared with flux.

One can conclude that by numerical analysis of the fine structure of SAO-E PL spectra detailed information about the energy transfer not only between the high and the low energy PL bands but also with these bands can be observed. The character of the spectra is significantly altered if the SAO-E samples are prepared with or without flux. By this the PL colour can be tuned.

¹⁾ G. Blasse, B. C. Grabmeier, *Luminescent Materials*, Springer, Berlin (1994).

²⁾ A.-R. Schulze, Hk. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **475**, 205 (1981).

³⁾ S. H. M. Poort, W. P. Bokpoel, G. Blasse, *Chem. Mater.* **4**, 1547 (1995).