

SYNCHROTRON RADIATION STUDIES OF PERSISTENT LUMINESCENCE MATERIALS

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The persistent luminescence is obtained continuously from materials for even tens of hours after ceasing the irradiation – either with the UV radiation or, preferably, with the visible light [1]. This requires extensive storage of the exciting radiation for a very long but not for too a long time. The energy stored is required to be released from the traps without an input of artificial energy, so the temperature should do the job. This means that the traps must be rather shallow, of the order of less than 1 eV. At first, this seems totally incompatible with the high energies used in the synchrotron radiation studies of materials, but more and more frequently the phenomena dealing with the band structure of the host lattice are studied – and this is done most easily with the synchrotron radiation UV-VUV excitation spectroscopy [2]. Moreover, with the trapping and release of the charge carriers – either electrons or holes (or both), the question whether a change – a real or a virtual one – in the valence state of the dopant takes place becomes a critical question. In this context, the synchrotron radiation methods as EXAFS and XANES become interesting in probing the valence of the species present in the persistent luminescence materials.

The persistent luminescence materials with very good performance are usually oxidic compounds as alkaline earth aluminates (MAl_2O_4) or disilicates ($\text{M}_2\text{MgSi}_2\text{O}_7$) which are doped with divalent europium (Eu^{2+}). The broad band $4f^65d^1 \rightarrow 4f^7$ emission from this dopant ensures efficient conversion of the energy stored into visible – usually blue or green – light. In order to make these materials even more efficient, these are customarily co-doped with trivalent lanthanides (R^{3+}). The presence of at least one ($\text{Eu}^{2+}/\text{Eu}^{3+}$) but maybe a second ($\text{R}^{2+}/\text{R}^{3+}/\text{R}^{\text{IV}}$) set of ions, too, capable of undertaking redox reactions – real or virtual, no importance at the moment – has intrigued the minds of the researchers from the very beginning of the modern persistent luminescence era – that means from the mid 1990s.

In this work, the synchrotron radiation source of HASYLAB (Hamburg, Germany) with the SUPERLUMI beamline was used to study the band gap energies of the aluminate and disilicate persistent luminescence materials. In addition, the $\text{Eu}^{2+} 4f^7 \rightarrow 4f^65d^1$ excitation

band structure was monitored as a function of the temperature from 10 K to ambient. The band gap energy of ca. 7 eV together with the Eu^{3+} charge transfer band energy of ca. 5 eV leaves no doubt about the concept that the persistent luminescence mechanism is based on the electron transfer from the Eu^{2+} dopants to the traps via the conduction band. The holes – if present – thus play only a minor role. Even if the exciton structure was not observed for the Eu^{2+} doped materials – probably due to the too high Eu^{2+} concentration – the defect luminescence of the non-doped materials indicates the presence of defects in these materials.

The XANES measurements carried out in the MAX-lab (Lund, Sweden) with the beamline I811 for the $\text{Eu}^{2+},\text{R}^{3+}$ co-doped SrAl_2O_4 and $\text{Sr}_2\text{MgSi}_2\text{O}_7$ materials indicated the presence of both the Eu^{3+} and Eu^{2+} ions in all materials. For the $\text{Sr}_2\text{MgSi}_2\text{O}_7$ host, the relative amount of Eu^{3+} was observed to increase upon increasing exposure to X-rays, whereas for SrAl_2O_4 there was very little or no change. For the Dy and Yb co-dopants, only trivalent species were observed. On the other hand, traces of tetravalent cerium were present in the Eu,Ce co-doped materials. Nevertheless, the redox behaviour of the dopant and the co-dopants seem to be rather complicated, and thus the present XANES results are so far inconclusive and more work is needed to elaborate the persistent luminescence materials.

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References

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