

Towards the structure of rare earth luminescence centres – terbium doped aluminium nitride as an example system

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Abstract. Sputter deposited terbium doped aluminium nitride layers were investigated with respect to the distribution and surroundings of the terbium luminescence ions. Semi-empirical calculations indicate that terbium forms complexes consisting of one aluminium vacancy surrounded by three oxygen ions on nitrogen lattice positions and one nitrogen ion that is bound to a terbium ion on a distorted aluminium lattice position. The crystal field splitting of the terbium ions indicate their surroundings to be not tetrahedral but, as anticipated from the determined complex, C_{3v} . Complementary electron microscopic investigations show a random distribution of these complexes within the layer volume. The terbium ions cause a shape of the $Tb M_{5,4}$ edge similar to the shapes in other ionic compounds like Tb_2O_3 .

1. Introduction

Rare earth doped semiconductors exhibit unique optical properties such as very narrow emission lines. Possible applications include data transfer [1], biological sensing [2] or light emission in electroluminescent devices [3].

The wavelengths of the emission lines are hardly influenced by the matrix material since the luminescence arises from inner-lying 4f orbitals, which are effectively shielded from the matrix by outer-lying orbitals [4]. Further experimental results suggest that the energy transfer between the rare earth ions is insensitive against the matrix material [5]. Thus one could be tempted to describe the influence of the matrix on a rare earth ion by the dielectric properties and the bandgap of the matrix only and consider this rare earth ion as kind of an independent system in an isotropic medium. This fact holds essentially for the farther surrounding of the ions, say from the next-nearest neighbour shell on outwards. The next-nearest neighbour surroundings, however, and the microstructural position of the rare earth ion with reference to this shell play a mostly beneficial role in rare earth ion luminescence. Firstly, the shell's symmetry influences the excitation of the rare earth ion by matrix excitations and, secondly, it creates a so-called (local) crystal field that breaks the conditions of luminescence transitions, which are in a free ion quantum mechanically forbidden. This contribution presents an attempt to approach these two roles by clarifying the microscopic structure of the centres.

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2. Experimental procedure

The used terbium doped aluminium nitride samples were produced by reactive DC magnetron sputtering. Two aluminium targets and one terbium target were used in order to adjust the terbium concentration to approximately 1-2 at.-%. A mixture of argon and nitrogen was used as deposition atmosphere. After deposition the samples were annealed at 1000°C under 1 bar pure nitrogen atmosphere for 30 min. This step is necessary for activating the luminescence centres (gain in luminescence intensity approximately 25 times).

Photoluminescence experiments were carried out using a 450 W xenon lamp as excitation source. A first monochromator was used for selecting the desired excitation wavelength, a second one was used for spectral recording the emission using a photomultiplier tube. The intensity of the excitation light was recorded with a silicon photodiode. For these experiments room temperature was used. Additional cathodoluminescence (CL) measurements were recorded at a temperature of 4 K.

Transmission electron microscopic investigations were performed using a JEOL 2010F FEG-TEM microscope operated at 197kV and equipped with scan unit, Gatan Imaging Filter (GIF2000), and X-ray spectrometer (Si:Li, ATW, Oxford Instruments, ISIS300).

3. Simulation of the centre structure

The semi-empirical programme MOPAC2012 [6] together with the appropriate expansion SPARKLE [7] was used for a preliminary investigation of the rare earth centre nature. The PM6 algorithm [8] was used for all calculations. First, an aluminium nitride super-cell consisting of 18 unit cells (72 atoms) was built and optimised. Periodic boundary conditions were used. The obtained lattice constants match with X-ray diffraction experiments. Subsequently, a terbium ion, an aluminium vacancy, and up to three oxygen ions were introduced into the simulation volume. (There are indications that vacancies and oxygen take part in optically active centres in AlN, see *e.g.* refs. [9,10].) Different atomic arrangements were used in order to work towards the energetically lowest configuration. As a result, a configuration is obtained that has the lowest energy of all calculated configurations of approximately 5 eV below a random arrangement of these atoms. It consists of one aluminium vacancy surrounded by the three oxygen ions and one nitrogen ion that itself is bound to the terbium ion. The terbium (1.4 at.-%) and oxygen impurity concentrations (4 at.-%) of our measured samples approximately match the 1:3 relation between terbium and oxygen. Figure 1 shows this complex embedded in the aluminium nitride super-cell. The same result was always obtained for different initial arrangements and different positions in the simulation volume.

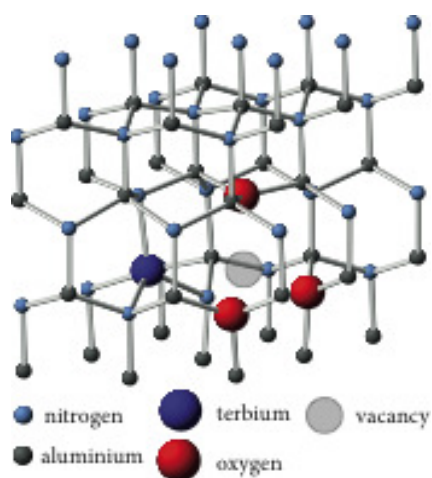


Figure 1. Obtained lowest energetic complex ($E \approx -5$ eV), consisting of an aluminium vacancy surrounded by three oxygen ions and one nitrogen that is itself bound to a terbium ion.

It is remarkable that the local symmetry at the position of the terbium ion in this complex is C_{3v} instead of T_d , the point group for a perfect tetrahedron.

4. Experimental results and discussion

The local symmetry at the position of the rare earth ion influences the number of sublevels into which a state with a certain total angular momentum is split (crystal field splitting). For the state 7F_5 of the trivalent terbium ions a splitting into seven states is anticipated for the C_{3v} point group, for T_d four sublevels are expected [11]. The CL spectrum recorded at 4 K (*cf.* Figure 2) shows the emission due to the transition $^5D_4 \rightarrow ^7F_5$. At such a low temperature it can be expected that the transition occurs from the lowest sublevel of 5D_4 only. Therefore the observed splitting is solely due to the splitting of the ground state 7F_5 . The spectrum shown in Figure 2 confirms the assumption that the local symmetry is lower than T_d , *e.g.* C_{3v} as expected from the simulation shown above.

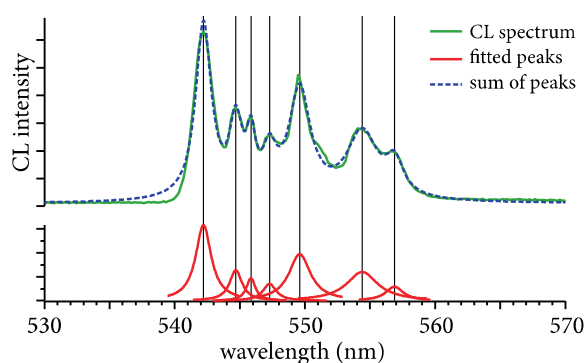


Figure 2. CL spectrum recorded at 4 K of transition $^5D_4 \rightarrow ^7F_5$: peak split into seven sub-peaks due to crystal field.

Figure 3 shows a bright field image of the investigated layer together with STEM X-ray maps for the elements Si, Al and Tb. The layer has a columnar grain structure with a grain diameter of approximately 20 nm. The X-ray maps indicate that the terbium ions do not occupy specific positions in the microstructure (*e.g.* the grain boundaries, the layer surface, *etc.*). In fact it rather appears that the ions are randomly distributed, although clustering at an atomic scale might occur and not be observable.

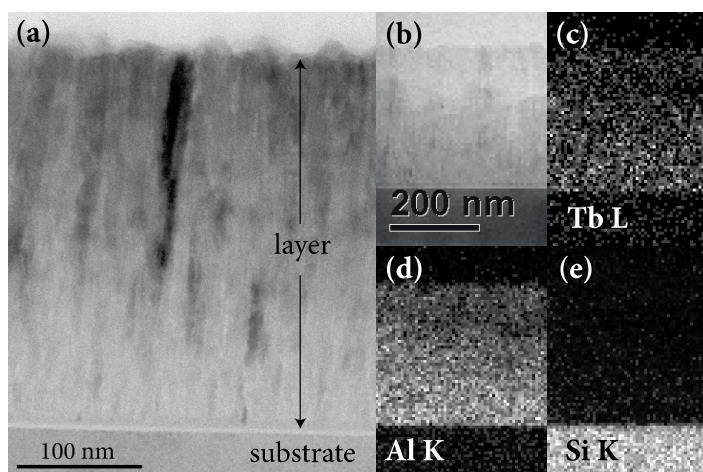


Figure 3. Electron microscopy study of a cross-section in bright field (BF) (a), STEM BF (b) with corresponding X-ray maps of Tb L (c), Al K (d) and Si K (e) at a sampling of 6.4nm/pixel. The sample thickness of the foil tapers off towards the top of the layer, leading to a corresponding contrast gradient.

Additionally, the layer was investigated by electron energy-loss spectroscopy (EELS), see Figure 4. The Tb $M_{5,4}$ edges can be seen at 1240 eV (Tb M_5) and 1259 eV / 1271 eV (Tb M_4). The shapes of the edges are similar to those observed for other ionic terbium compounds like Tb_2O_3 (observed by EELS) [12] or $TbMnO_3$ (observed by XANES) [13], underlining the ionic character of terbium incorporated into AlN.

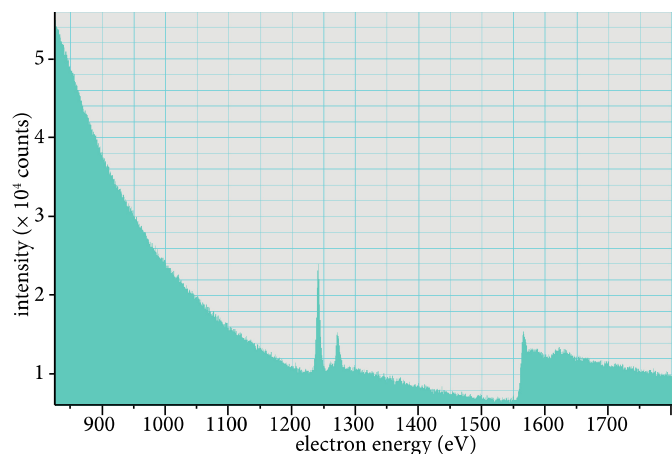


Figure 4. EELS spectrum of AlN:Tb, recorded with an energy offset of 800 eV with 1 eV / channel dispersion and an integration time of 100 s.

5. Conclusion

Both experimental and theoretical results indicate that terbium ions in aluminium nitride form complexes containing one aluminium vacancy, three oxygen ions, and one terbium ion connected to the vacancy through a nitrogen ion. STEM results indicate that the terbium ions are randomly distributed in the microstructure through the whole layer. Furthermore, the EELS spectrum of terbium ions doped into aluminium nitride is presented. The Tb $M_{5,4}$ edge shows discrete peaks at 1240 eV (strong), 1259 eV (weak), and 1271 eV (strong), which is similar to spectra reported for other ionic terbium compounds.

References

- [1] J K R Weber, J J Felten, B Cho, and P C Nordine, *Nature* **393**, 769 (1998).
- [2] H Jeong, S Lee, G Y Sung, and J Shin, *IEEE Photon. Technol. Lett.* **23**, 88 (2011).
- [3] A Nishikawa, T Kawasaki, N Furukawa, Y Terai, and Y Fujiwara, *Appl. Phys. Express* **2**, 071004 (2009).
- [4] T Kano in *Phosphor Handbook*, 2nd edition, edited by W M Yen, S Shionoya, and H Yamamoto (CRC Press, Boca Raton, Florida, USA, 2006).
- [5] F Benz, J A Guerra, Y Weng, A R Zanatta, R Weingärtner, and H P Strunk, *J. Lumin.* **137**, 73 (2013).
- [6] J J Steward (Steward Computational Chemistry), MOPAC2012, <http://openmopac.net> (2012).
- [7] R O Freire and A M Simas, *J. Chem. Theory Comput.* **6**, 2019 (2010).
- [8] J J P Steward, *J. Mol. Model.* **13**, 1173 (2007).
- [9] R A Youngman and J H Harris, *J. Am. Ceram. Soc.* **73**, 3238 (1990).
- [10] B Bastek, F Bertram, J Christen, T Hempel, A Dadgar, and A Krost, *Appl. Phys. Lett.* **95**, 032106 (2009).
- [11] B Henderson and R H Bartram, *Crystal-Field Engineering of Solid-State Laser Materials* 1st edition (Cambridge University Press, Cambridge, 2000).
- [12] C C Ahn and O L Krivanek, *EELS Atlas* (Gatan Inc. and ASU HREM Facility, 1983).
- [13] T R Forrest, *et al.*, *J. Phys.: Condens. Matter* **20**, 422205 (2008).