New classes of phosphors for emerging lighting applications (invited talk)

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Introduction

During the last decades, numerous inorganic phosphor materials have been developed and optimized, mainly for cathode ray tubes and fluorescent lamps. Mostly oxides were used as hosts in these phosphors, combining a high thermal stability with a good resistance to moisture. In recent years, however, new applications have emerged where these oxide phosphors cannot be applied, typically due to their short excitation wavelength, difficulty in obtaining broad band red emission and high electrical resistivity. Consequently, a lot of research has been devoted to sulfide phosphors for electroluminescent panels (both powders and thin films) and wavelength conversion of LEDs for lighting [1]. While several sulfide phosphors with excellent optical properties were selected, their widespread use has been hampered by difficulties in preparation (often necessitating harmful H₂S gas) and sensitivity to moisture from the ambient atmosphere. In the present overview, we will look at some alternative classes of materials and methods to overcome the typical difficulties associated with sulfides.

Better and cleaner sulfides

A major drawback of sulfide phosphors is the need to use harmful substances at relatively high temperature for their preparation. Already a few years ago, we optimized low temperature solvothermal synthesis as a viable alternative synthesis technique, yielding micron-sized single crystalline CaS:Eu and SrS:Eu luminescent particles [2]. In order to broaden the emission spectrum of the particles for LED applications, double doping of SrS with both Eu and Ce turned out to be unsuccessful due to energy transfer from Ce to Eu. However, the synthesis of core (SrS:Eu) – shell (SrS:Ce) particles allowed to physically separate both types of ions and obtain a close-to-perfect broad emission spectrum [3].

Sulfides also suffer from moisture sensitivity: materials deteriorate under the influence of ambient atmosphere. This problem can be overcome by encapsulating a layer of phosphor particles with an inert and transparent coating [4]. Accelerated aging tests have shown that indeed the useful lifetime of the luminescent material can be extended by orders of magnitude using coating techniques.

Next to the common CaS- and SrS-based sulfide phosphors, a number of 'forgotten' phosphor materials were investigated: these are materials that were briefly studied in the 1970's but are gaining renewed interest, as they are candidates for LED wavelength conversion. Results on a whole class of thiosilicates will be presented [5].

Nitrides and oxynitrides

The quest for efficient and stable phosphors for LEDs has also boosted the research into rare earth doped nitride and oxynitride phosphors. An important property of these materials, mostly left unnoticed, is the persistence of the luminescent emission: it is indeed possible, even without codoping, to obtain a long afterglow (of the order of minutes or even hours) after the excitation has stopped [6-8]. We investigated persistent emission of both nitrides and oxynitrides and studied the depth of trap sites using thermoluminescence measurements as a function of the type of rare earth codopant.

- P.F. Smet, I. Moreels, Z. Hens, D. Poelman, Luminescence in Sulfides: A Rich History... and a Bright Future, Materials 3 2834-2883 (2010)
- [2] J.E. Van Haecke, P.F. Smet, K. De Keyser and D. Poelman, Submicron sized CaS:Eu and SrS:Eu phosphors obtained by solvothermal synthesis, J. Electrochem. Soc., 154, J278-J284 (2007)
- [3] K. Korthout, P.F. Smet, D. Poelman, Rare earth doped core shell particles for lighting applications, this conference
- [4] N. Avci, J. Musschoot, P.F. Smet, K. Korthout, A. Avci, C. Detavernier, D. Poelman, Micro-encapsulation of moisture sensitive CaS:Eu²⁺ particles with aluminium oxide, J. Electrochem. Soc. **156**, J333-J337 (2009)
- [5] A. Parmentier, P.F. Smet, F. Bertram, J. Christen, D. Poelman, Structure and luminescence of Eu-doped (Sr,Ca)₂SiS₄ phosphors, J. Phys. D: Appl. Phys., 43 085401 (2010)
- [6] K. Van den Eeckhout, P.F. Smet, D. Poelman, Persistent luminescence in Eu²⁺-doped compounds: a review, Materials 3 2536-2566 (2010)
- [7] K. Van den Eeckhout, P.F. Smet, D.Poelman, Persistent luminescence in rare-earth codoped Ca₂Si₅N₈:Eu, Journal of Luminescence, **129**, 1140-1143 (2009)
- [8] J. Botterman, K. Van den Eeckhout, P.F. Smet, A.J.J. Bos, E. van der Kolk, P. Dorenbos, D. Poelman, Persistent luminescence in rare earth doped oxynitrides, ICOOPMA2010, Budapest, 16-20/08/2010.