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UFS·UV
NATURAL AND
AGRICULTURAL SCIENCES
NATUUR- EN
LANDBOUWETENSAPPE

Contribution ID: 87

Type: **Poster Presentations**

Interplay between phase transitions and thermoluminescence in BaAl₂O₄

Wednesday, 6 May 2015 13:30 (1h 30m)

1. Introduction

The Eu²⁺ and R³⁺ doped alkaline earth aluminates (MAl₂O₄; M: Ca, Sr, Ba) are among the best persistent luminescence materials [1]. The most efficient is, however, SrAl₂O₄:Eu²⁺,Dy³⁺ – partly due to its emission in green to which the human eye is sensitive. Also the blue emitting CaAl₂O₄:Eu²⁺,Nd³⁺ is more efficient than the barium one. All three materials should have similar properties since they have the stuffed tridymite (SiO₂) type structure. However, SiO₂ is known for polymorphism and MAl₂O₄ derived from this do not behave dissimilarly. Although CaAl₂O₄ seems to have only one form and SrAl₂O₄ two, for BaAl₂O₄ one knows two hexagonal [2] and one orthorhombic forms. These polymorphs are found at high temperatures quite far from the usual operating range (<200 °C) of persistent luminescent materials. Nevertheless, the role of possible low temperature phase transitions should not be excluded as a reason for the less good persistent luminescence performance of BaAl₂O₄:Eu²⁺,(R³⁺) [3,4]. Further studies were carried out by using the high-temperature X-Ray Powder Diffraction (HT-XPD), Differential Scanning Calorimetry (DSC) and thermoluminescence (TL) methods.

2. Results

The HT-XPD patterns of BaAl₂O₄ (Fig. 1) at room temperature (RT) correspond to the hexagonal P63 form. Additional weak reflections may indicate symmetry decrease to e.g. orthorhombic but this needs further proof. The RT structure is not stable for more than some 50 °C before significant changes occur in the intensity of all reflections. Characteristic to these changes is that they occur over a wide temperature range and smooth changes seem to be the rule rather than the exception. The intensity variation suggests displacement of atoms away from the reflection planes and changes may thus occur just in the space group. The DSC measurements were inconclusive since only a few broad signals and strong background variation were found instead of sharp signals. These features are in agreement with the slow and gradual nature of the changes in the XPD patterns. Both the HT-XPD and DSC results correlate well with the bands observed in the TL glow curves. When compared to the very simple (1 or 2 TL bands) glow curves of CaAl₂O₄:Eu²⁺ or SrAl₂O₄:Eu²⁺ (without R³⁺ co-doping), the five broad TL bands for BaAl₂O₄:Eu²⁺ between 100 and 400 °C (Fig. 2) indicate a more complex trap structure with energies from 0.8 to 1.4 eV. Thus a reason for the inferiority of the BaAl₂O₄ host vs. CaAl₂O₄ and SrAl₂O₄ is clear: the close to continuous distribution of traps does not allow long term storage of input energy but the bleaching of the traps occurs too rapidly. The persistent luminescence is then of short duration.

Are you currently a postgraduate student? (Yes/No)

No

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Session Classification: Poster

Track Classification: SACPM