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## THE EFFECT OF SYNTHESIS PARAMETERS ON LUMINESCENCE PROPERTIES OF Ca- $\alpha$ -Sialon:Eu<sup>2+</sup>

### WPLYW PARAMETRÓW SYNTEZY WYSOKOTEMPERATUROWEJ NA WŁAŚCIWOŚCI OPTYCZNE PROSZKÓW Ca- $\alpha$ -Sialon:Eu<sup>2+</sup>

The goal of this study was to investigate influence of the synthesis parameters on the luminescence properties of Ca- $\alpha$ -Sialon doped with Eu<sup>2+</sup>. The compound of Eu<sub>0.07</sub>Ca<sub>0.73</sub>Si<sub>9.6</sub>Al<sub>2.4</sub>O<sub>0.8</sub>N<sub>15.2</sub> was prepared by the solid state reaction method from the mixture of the relevant oxides, Si<sub>3</sub>N<sub>4</sub> and CaCO<sub>3</sub>. Synthesis was carried out in the temperature range of 1600-1700°C for 2-8 h in a reduction atmosphere (N<sub>2</sub>+CO). The structure and morphology of obtained powders were analyzed by XRD and SEM/EDS methods, respectively. Content of nitrogen/oxygen was also measured. Optical properties were investigated by excitation, emission and reflection spectra. Obtained results show strong influence of synthesis temperature on the phase composition and intensity of emission of Ca- $\alpha$ -Sialon:Eu<sup>2+</sup> powder compound.

*Keywords:* phosphor, oxynitride, sialon, WLED

Celem badań było przeanalizowanie wpływu parametrów syntezy wysokotemperaturowej na właściwości ceramicznego proszku Ca- $\alpha$ -sialon domieszkowanego europem. Związek o stechiometrycznym wzorze Eu<sub>0.07</sub>Ca<sub>0.73</sub>Si<sub>9.6</sub>Al<sub>2.4</sub>O<sub>0.8</sub>N<sub>15.2</sub> został przygotowany metodą reakcji w fazie stałej z odpowiednich tlenków, Si<sub>3</sub>N<sub>4</sub> oraz CaCO<sub>3</sub>. Reakcje wysokotemperaturowe prowadzono w zakresie temperatur 1600-1700°C przez 2-8h w atmosferze redukcyjnej (N<sub>2</sub>+CO). Morfologię oraz skład chemiczny proszków zbadano przy użyciu skaningowego mikroskopu elektronowego z przystawką do mikroanalizy rentgenowskiej (SEM/EDS). Skład fazowy analizowano przy pomocy metod dyfrakcji rentgenowskiej (XRD). Określono stosunek tlen/azot w otrzymanych związkach. Scharakteryzowano zmiany właściwości optycznych na podstawie widm wzbudzenia, emisji oraz odbicia dyfuzyjnego (PL). Otrzymane wyniki prezentują wpływ temperatury syntezy na skład fazowy oraz intensywność emisji luminoforu Ca- $\alpha$ -Sialon:Eu<sup>2+</sup>.

### 1. Introduction

Development of new phosphors in white LEDs and ways of their preparation fall in the hottest topics of nowadays materials engineering. Since desired phosphors should show the efficient absorption bands in the blue region (= 420-480 nm) or NUV region (= 365-410 nm) the 4f-5d transition of some RE ions could meet those requirements. Owing to the exposure of the d orbital to the crystal coordination environment, the 4f-5d transition of RE ions is strongly affected by crystal field splitting and the nephelauxetic effect as a result of a high degree of SiN<sub>4</sub> tetrahedra crosslinking in the structure of silicon-based oxynitrides and nitrides [1-2]. Similar effect was observed by the authors elsewhere [3] in case of nitrogen/silicon doping the YAG:Ce host lattice. Thus silicon-based oxynitrides and nitrides with the relevant rare-earth elements have received considerable attention in the last few years as potential materials for the efficient downconversion in white LEDs and substitution of YAG:Ce phosphors.

The most suitable candidate for novel yellow phosphors is Eu<sup>2+</sup>-doped Ca- $\alpha$ -sialon phosphor as it shows a broad-band emission spectrum extending from 500 to 750 nm [4].

The significantly longer emission wavelength in comparison to that of YAG:Ce (550-570 nm) provides warmer white light after downconversion of blue light. Moreover, it has been shown that the yellow emission of Ca- $\alpha$ -sialon:Eu<sup>2+</sup> can be tuned by tailoring the solid solution of Ca- $\alpha$ -sialon (Ca<sub>0.5m</sub>Si<sub>12-(m+n)</sub>Al<sub>m+n</sub>O<sub>n</sub>N<sub>16-n</sub>) or by substituting Ca<sup>2+</sup> with other cations [5-6]. As demonstrated by R.-J. Xie [7] Ca- $\alpha$ -sialon:Eu<sup>2+</sup> shows considerably lower thermal quenching if compared to the YAG:Ce phosphor.

All those above-mentioned features triggered the burst of research on the methods of the Ca- $\alpha$ -sialon phosphor manufacturing: gas-reduction nitridation [8], gas-pressure sintering of nitrides [9], carbothermal-nitridation [10] of oxides or precipitated precursor [9] as initial materials. However, the most recent results show several drawbacks of the applied methods: multiphase composition, large particle size over 1  $\mu$ m after gas-reduction nitridation or larger from other methods, contamination etc. Multiphase compositions lead to scattering of absorbed light and result in decrease of emission intensity of  $\alpha$  phosphor.

Application of carbon black to the solid-state synthesis of  $\alpha$ -sialon from nanopowders of silicon nitride and relevant ox-

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ides in nitrogen atmosphere is a new way to obtain a designed solid solution in that oxynitride system. In this article, authors focused on the influence of the synthesis parameters (time and temperature) on the phase composition and luminescence properties of Ca- $\alpha$ -sialon with a given composition ( $m=1.6$   $n=0.8$ ) doped by  $\text{Eu}^{2+}$  (8.75 wt%).

## 2. Experimental

The samples with the general formula of  $\text{Eu}_{0.07}\text{Ca}_{0.73}\text{Si}_{9.6}\text{Al}_{2.4}\text{O}_{0.8}\text{N}_{15.2}$  were prepared by a solid-state reaction using high purity commercial powders of:  $\eta$ - $\text{Al}_2\text{O}_3$  (Sasol, 99.96%),  $\alpha$ - $\text{Si}_3\text{N}_4$  (UBE, SN-E10, >98%),  $\text{CaCO}_3$  (POCH, >99%) and  $\text{Eu}_2\text{O}_3$  (Treibacher, 99.99%) as the optical activation ions. Carbon black (POCH, 99%) was added to the mixture of initial powders in order to reduce excess of oxygen and to compensate stoichiometric O/N ratio according to the above-mentioned formula of Ca- $\alpha$ -sialon.  $\eta$ - $\text{Al}_2\text{O}_3$  powder was chosen because of its high chemical activity and the high specific surface area (40  $\text{m}^2/\text{g}$ ).  $\text{CaCO}_3$  as a source of Ca decomposes to CaO at 900°C and produces highly defective and reactive CaO.

The stoichiometric amount of raw powders was grinded and mixed in an agate mortar with acetone, dried at room temperature for 2 hours and at 60°C for 6 hours. Initial powders were heat-treated for 2-8 hours in an  $\text{N}_2/\text{CO}$  atmosphere in a graphite furnace (Thermal Technology) at temperatures varied from 1450 to 1700°C.

An Rigaku MiniFlex II diffractometer was used for taking the powder diffraction patterns. The XRD patterns were collected in the  $2\theta$  range of 10-80° with a step of 0.02° and a scanning speed of 10° per minute using Cu  $K\alpha 1$  radiation with  $\lambda = 1.5406 \text{ \AA}$  with a nickel filter. Calculation of the phase weight fraction was done with the help of the Maud v2.22 software. The grain size and morphologies of the samples were observed by a Hitachi 3400N scanning electron microscope (SEM) operated at 15 kV with energy-dispersive X-ray spectrometer (EDS). Oxygen and nitrogen content were measured by the combustion method (ELTRA-ON). Measurement of the optical properties of the resultant powders was performed on the grounded powders. Excitation and emission spectra were taken with an Optron DongWoo monochromators with 750 mm focal length and detected by Hamamatsu R-955 photomultiplier. Emission spectra were recorded in the regions of 460-700 nm, excited at 384 nm. All measurements were carried out at room temperature.

## 3. Results and Discussion

XRD patterns of the samples, which reacted for two hours at various temperature are shown in Fig. 1 together with the reference one of Ca- $\alpha$ -Sialon (ICSD #201683). It clearly demonstrates that more than 95 wt% of a designed Ca- $\alpha$ -sialon was present in all tested specimens. At the lowest synthesis temperature (1600°C) about 2 wt% of initial  $\alpha$ - $\text{Si}_3\text{N}_4$  remained non-reacted. On the other hand, increase of synthesis temperature up to 1700°C resulted in formation of 3 wt% AlN apart from Ca- $\alpha$ -sialon. Powder from synthesis at 1650°C

showed the composition very close to the designed one and only traces of AlN were present. Thus the most suitable synthesis temperature seems to be 1650°C.

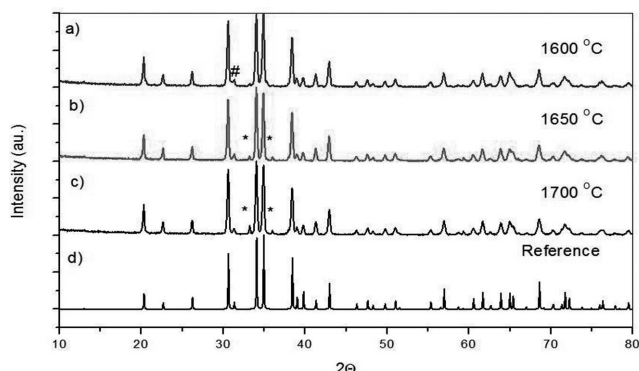


Fig. 1. XRD patterns of specimens reacted at 1600-1700°C for 2 hrs and reference pattern of  $\text{Ca}_{0.67}\text{Si}_{10}\text{Al}_2\text{O}_{0.7}\text{N}_{15.3}$  – ICSD #201683 (d). # –  $\alpha$ - $\text{Si}_3\text{N}_4$  – ICSD #92156, \* – AlN – ICSD #44107

Cation fractions of the specimen synthesized at 1650°C were measured by the EDS technique and compared to a designed composition. Table 1 shows small deviation of aluminum and silicon concentration in comparison to a designed composition and higher calcium content. One possible reason of these difference could be the rough particle surface. This kind of surface has influence on scattering of X-ray radiation and it could change the intensity of the element characteristic emission. In the case of a very small element concentration, as it occurs in the case of europium, the observed alteration could be caused by nonhomogeneous distribution of that element in the micro-scale. Other possible explanation of those deviations could be related to various equilibrium partial pressures of the cation related species. Calcium excess could indicate that part of silicon and aluminum was lost during synthesis. That assumption is confirmed by formation of a deposit on the surface of the specimen itself and on the crucible walls. Their microstructure is shown in Fig. 2 and chemical composition is given in Table 2.

Careful examination of the deposits show their various morphology (Fig. 2) and chemical composition relative to the place of origin. Those on the crucible top contain mostly silicon with some aluminium while those inside the crucible consist mostly of AlN. The last finding is in a good accordance with XRD data.

TABLE 1  
Chemical analysis of the sample synthesized at 1650°C for 2 hrs as obtained by EDS and O/N analysis

at%	Cation analysis by EDS				O/N analysis		Al/Si ratio
	Al	Si	Ca	Eu	O	N	
Specimen	17.6	74.8	7.4	0.3	2.83	53.39	0.24
<b>According to a designed formula</b>	<b>18.75</b>	<b>75</b>	<b>5.7</b>	<b>0.55</b>	<b>2.78</b>	<b>52.78</b>	<b>0.25</b>

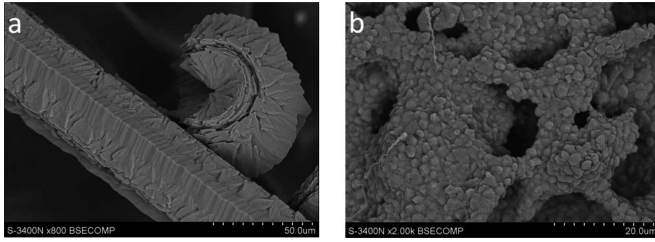
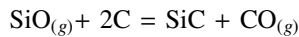
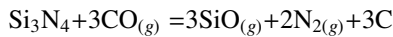


Fig. 2. Deposits observed on the top of crucibles (a) and on the specimen's surface (b)

Decomposition of  $\text{Si}_3\text{N}_4$  above  $1400^\circ\text{C}$  in a reducing atmosphere is a well known process. Several heterogeneous reactions can take place:



Those reactions strongly depend on the partial pressure of all gas species and can alter direction of the reactions. We can assume that if  $\text{SiO}_{(g)}$  escapes from the crucible then it condensates on the top of the alumina crucible and it forms aluminosilicates or silicon carbide. Remained aluminium inside crucible forms AlN.

TABLE 2

Chemical composition of deposits after synthesis at  $1650^\circ\text{C}$  (EDS and O/N analysis)

at%	EDS analysis				O/N analysis	
	Al	Si	Ca	Eu	O	N
Deposit on the crucible top (needles)	22.90	74.50	-	-		
Deposit on the crucible wall	65.20	-	-	-	0.15	42.65
Deposit on the surface of samples	67.20	-	-	-	0.53	42.89

Thus we can conclude that AlN presence in the Ca- $\alpha$ -sialon powder shows a deviation from the designed reaction and it confirms some silicon losses.

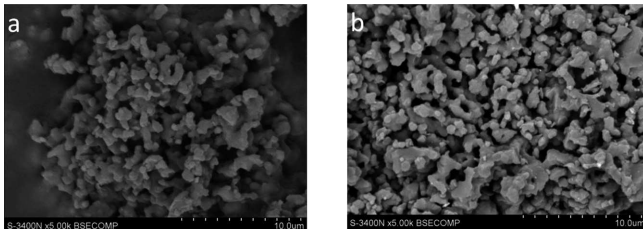


Fig. 3. Morphology of powders after reaction at temperature of  $1450^\circ\text{C}$  for 2 hrs (a) and at  $1650^\circ\text{C}$  for 4 hrs (b) (SEM, backscattered mode)

Morphology of specimens after synthesis at various temperature is presented in Fig. 3. The average particle size of Ca- $\alpha$ -sialon:Eu powder is about  $1\mu\text{m}$ . However, a higher reaction temperature and a longer reaction time leads to sintering

process and subsequent crushing of specimens is necessary to obtain the fine powder. Areas with different chemical compositions on the BSE pictures were not observed.

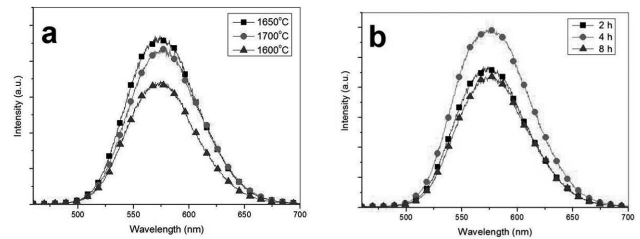


Fig. 4. The effect of the reaction temperature in the range of  $1600$ - $1700^\circ\text{C}$  (a) and the reaction time in the range of 2-8 h (b) on the emission spectra of specimens

Fig. 4 shows photoluminescence (PL) spectra of specimens versus the time and temperature of the reaction. We can see a broad emission band in the range of 500-670 nm and a peak located at 574 nm for a sample reacted at  $1650^\circ\text{C}$ . The emission spectra of specimens after 2 hrs synthesis at different temperature show the highest intensity of emission in the specimen synthesized at  $1650^\circ\text{C}$ . Slight red shifting of the wavelength maximum with increase of synthesis temperature was also observed (1nm per  $50^\circ\text{C}$ ). Relation between the reaction time at that temperature and emission intensity shows the best result for 4 hours reaction time.

Photoluminescence properties and XRD data of tested specimens are closely related to each other thus they illustrate a direct link between the phase composition and optical activity in the resultant material. Presence of non-reacted  $\alpha$ - $\text{Si}_3\text{N}_4$  in specimens heat treated at  $1600^\circ\text{C}$  clearly indicates that formation of  $\alpha$ -sialon was not completed thus some amount of europium remain outside the structure of  $\alpha$ -sialon. On the other hand, occurrence of AlN after synthesis at higher temperature suggests decomposition of already formed  $\alpha$ -sialon. If a total amount of europium entered the structure of  $\alpha$ -sialon then its breakdown must lead to europium precipitation in the form of oxide or nitride where its excitement and emission is significantly lower.

## 4. Conclusions

Formation of Ca- $\alpha$ -sialon:Eu by the solid state reaction in a reducing atmosphere was efficient if initial nanopowders were applied with appropriate amount of carbon black. It has been shown that the reaction was the most effective if it was carried out at  $1650^\circ\text{C}$ , however some decomposition of  $\text{Si}_3\text{N}_4$  or  $\alpha$ -sialon was observed during the prolonged reaction time and/or at higher reaction temperature. The highest PL spectra of the resultant phosphor were measured for the powders synthesized at  $1650^\circ\text{C}$  for 4 hours.

## Acknowledgements

The financial support by NCN under the project No: 2011/01/B/ST8/07480 is gratefully acknowledged.

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*Received: 20 September 2013.*