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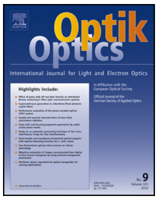

Original research article

# Some investigations on $Tb^{3+}$ and $Eu^{3+}$ doped $Na_2SiO_3$ as a material for LED application

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## ABSTRACT

Terbium and europium single doped and co-doped $Na_2SiO_3$ samples are prepared by solid state synthesis. The samples display the same patterns as in the PDF file for pure $Na_2SiO_3$ compound. For comparison additionally glass and single crystal samples are prepared with concentration of dopants 0.5 at.% $Tb^{3+}$ and 0.1 at.% $Eu^{3+}$. The excitation and the emission spectra of $Tb^{3+}$ and $Eu^{3+}$ doped $Na_2SiO_3$ samples show the characteristic transitions for these two ions. The comparison between the spectra of glass, powder and single crystal samples in the case of $Tb^{3+}$ doping shows difference in the single crystal sample spectrum, where the peaks in the region 400–530 nm are intensive and overlapping and the strongest emission peak from $^5D_4 \rightarrow {}^7F_5$ transition is weaker. In the case of $Eu^{3+}$ doping there is no a large difference in the spectra of glass, powder and single crystal samples. The spectra of co-doped samples show the characteristic peaks of $Tb^{3+}$ and $Eu^{3+}$ ions. The main emission peak of $Tb^{3+}$ ion is rather low and the europium part of the spectra is more intensive. The obtained results suggest that as prepared terbium and europium doped and co-doped $Na_2SiO_3$ samples could be used as phosphors emitting different colors.

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## 1. Introduction

Light emitting diodes (LEDs) are of special interest because they are energy and nature saving devises. Phosphors have to be chemical stable, with strong absorption in the UV region and high conversion efficiency [1,2]. The commercial phosphors are realized by combining of blue, green and red light emitting phosphors and thus the obtained color can be controlled. Unfortunately this method displays different drawbacks [1,3]. As the rare earth ions possess different emission colors, it is expected that multicolor emission could be generated by multiple ions co-doping in a single host. Therefore many co-doped single phase phosphors are investigated. The luminescence of the rare earth activated phosphors depends on the composition of the host, concentration of the activator and methods of preparation [3]. $Tb^{3+}$ doped phosphor materials have a strong excitation band in the near UV region (around 380 nm) and show green emission due to $^5D_4 \rightarrow {}^7F_5$ (545 nm) transition, but it also has blue emission from the higher levels. The emissions from high excited states $^5D_3 - {}^7F_J$ are dependant on the concentration of $Tb^{3+}$ ion and the cross-relaxation. $Eu^{3+}$ doped phosphor materials have excitation band in the near UV light (around 400 nm) and show orange-red emission corresponding to $^5D_0 \rightarrow {}^7F_1$ (around 590 nm) or $^5D_0 \rightarrow {}^7F_2$ (around 610 nm) transitions. Its photoluminescence emission strongly depends on the symmetry of the crystal structure of the host. If the $Eu^{3+}$ ions occupy the sites with inversion symmetry, the emission is in the range 590–600 nm. The emission at approximately

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610 nm dominate if the $Eu^{3+}$ ion occupys the site without inversion symmetry [3,4]. The co-doping with these two ions in a single host could give different colors depending on the dopants concentration and ratio. Such experiments for tunable luminescent materials have been published in the literature: $Eu^{3+}$ and $Tb^{3+}$ co-doped tungstates [5,6], molybdates [7,8], phosphates [9,10], aluminates [11,12], borates [13], germanates [14], cerates [15], silicates [16]. Silicates are one of the most suitable materials because of their high chemical, thermal and mechanical stability, low cost, good optical properties and various crystal structures [2]. Silicate doped by rare earth ions are used for optical fibers, wave guides and color displays.

Our previous investigations on preparation of the $Tb^{3+}$ and $Eu^{3+}$ doped $NaAlSiO_4$ glass-ceramics from the system $Na_2O$-$Al_2O_3$-$SiO_2$-$B_2O_3$ show that the obtained glass-ceramics could be used as green and orange-red phosphors when they are single doped [17] and for emitting of different colors when they are co-doped [18]. Emission depends not only on the dopants concentrations and ratio, but also on the thermal treatment conditions. We found that after thermal treatment of the glasses at 650 °C except $NaAlSiO_4$, $Na_2SiO_3$ crystallizes as a second phase into the glass-ceramic. The ratio between these two phases is almost 70:30. The only exception is the glass-ceramic sample with dopants ratio $Tb^{3+}$:$Eu^{3+}$ = 0.33:0.033 at% treated 24 h, where the ratio $NaAlSiO_4$: $Na_2SiO_3$ is 45:55. The latter glass-ceramic sample possesses CIE coordinates very close to white light (0.33, 0.31). The presence of $Na_2SiO_3$ in a larger amount provoke our interest to investigate the optical characteristics of $Na_2SiO_3$ itself.

To our knowledge this kind of investigations are not published to this moment.

## 2. Experimental

Powder samples were synthesized by conventional solid state method. $Na_2CO_3$ (p.a), $Al_2O_3$ (p.a), $SiO_2$ (p.a.), $Tb_4O_7$ (p.a) and $Eu_2O_3$ (p.a.) was used as row materials. The samples were heated in a resistive furnace with Kantal heating wire permitted maximum working temperature of 1200 °C. The temperature was controlled with Pt/Pt–10%Rh thermocouple and Eurotherm controller. Powder samples were heated in platinum crucibles at 950 °C during 3 h with intermediate grinding in agate mortar. Glassy samples were prepared by melting of the solid state synthesized samples at 1180 °C and rapidly cooling down to room temperature. Single crystals were grown from the melt by slow cooling technique. Structural characterization was carried out by powder X-ray diffraction using a Bruker D8 Advance powder diffractometer with Cu Ka radiation and SolX detector. X-ray diffractograms were recorded at room temperature and identified using the Diffractplus EVA program. The emission and excitation spectra where measured on Horiba Fluorolog 3–22 TCS spectrophotometer equipped with a 450 W Xenon Lamp as the excitation source. All spectra were established at room temperature.

## 3. Results and discussion

The crystal structure of sodium metasilicate $Na_2SiO_3$ was determined by Grund and Pizy and additionally refined by McDonald and Cruickshank [19,20]. This compound crystallizes in orthorhombic space group $Cmc2_1$ with unit cell parameters $a$ = 10.48 Å, $b$ = 6.07 Å, $c$ = 4.82 Å and $Z$ = 4 (PDF 16 0818). The structure consists of infinite corner sharing $[SiO_4]^{4-}$ tetrahedra chains running along the $c$ direction with $[Si_2O_6]^{4-}$ as a repeat unit. The chains are linked together through sodium atoms coordinated by five oxygen atoms, thus forming distorted trigonal bipyramids. The crystal structure of sodium metasilicate shows pseudo-hexagonal symmetry, closely related with that of ZnS (Wurtzite). This relation can be described as mixed substitution in zinc position with sodium and silicon atoms, thus lowering the crystal symmetry to orthorhombic space group [20] (Fig. 1).

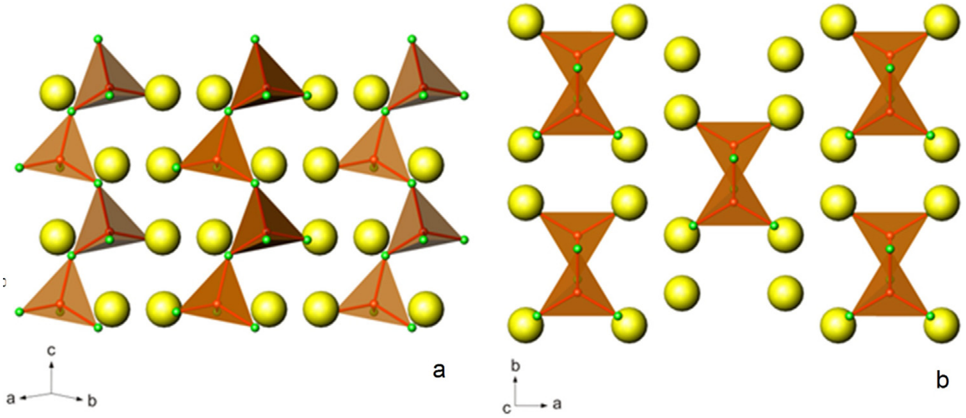

**Fig. 1.** a) Polyhedral representation of $Na_2SiO_3$ crystal structure along [111] direction. Large yellow spheres represent sodium atoms; b) Projection of $Na_2SiO_3$ crystal structure along [001] direction (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

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