Luminescence properties and crystal structure features of three new potassium silicates of rare earth elements (REE = Ce, Gd, Eu)

Rassulov, V.A.¹, Aksenov, S.M.²*, Rastsvetaeva, R.K.², Taroev, V.K.³

¹Fedorovsky Institute of Mineral Resources, Moscow, Russia
²Shubnikov Institute of Crystallography RAS, Moscow, Russia
³Vinogradov Institute of Geochemistry Siberian Branch of RAS, Irkutsk, Russia

*e-mail: aks.crys@gmail.com

Microporous, REE-containing alkaline silicates attract the attention essentially owing to its photoluminescent, ion-exchanging, etc., properties. This work is a part of research on the synthesis of rare earth potassium silicates, their crystal structures (Rastsvetaeva et al. 2010) and luminescence properties. Here we report on investigation of three REE-containing phases, where REE=Ce, Gd, Eu.

The crystals of compounds HK₆Eu[Si₁₀O₂₅], K₄Ce₂[Al₂Si₈O₂₄] and K₄Gd₂[Al₂Si₈O₂₄] were synthesized using hydrothermal techniques. Colorless transparent crystals were obtained either of cubic or prismatic faceting with the truncated vertexes and with the edge lengths up to 1.5-2 mm. The synthesis was performed using autoclaves ~200 cm³ in volumes made of stainless steel with nickel containers, which were sealed by argon-arc welding. Making use of nickel containers enables one to keep the oxygen potential at a permanent level, which is particularly important for experiments with europium as this element is characterized by variable valence.

The X-ray structure analysis was performed using single-crystal diffraction data collected in a full sphere of the reciprocal space on Xcalibur Oxford Diffraction CCD-diffractometer. Chemical formulae of the compounds were established from the X-ray analysis.

Monoclinic unit-cell values of the phase HK₆Eu[Si₁₀O₂₅] are: a = 27.6960(3) Å, b = 7.0504(1) Å, c = 14.2190(2) Å, β = 116.306(1)°, space group C2/c. The compound crystallizes in a new structure type that is based on nano-scale tubes of eight-membered rings [Si₈O₂₄] joint by additional Si-tetrahedra. The Eu³⁺ atoms, which are located in a staggered order in the center of symmetry at the origin, form octahedrons with Eu–O distances within 2.300(1)-2.325(1) Å participating in the integration of the nano-scale tubes into a three-dimensional construction. Potassium atoms occupy channels and cavities of the structure.

Monoclinic unit-cell values of the phases K₄Ce₂[Al₂Si₈O₂₄] and K₄Gd₂[Al₂Si₈O₂₄] are:

- a = 26.867(1) Å, b = 7.4150(2) Å, c = 14.910(1) Å, β = 123.52(1)°, and a = 26.6520(2) Å, b = 7.2854(1) Å, c = 14.8182(1) Å, β=123.46(1)°, respectively, space group P21/n. These compounds are isostructural and crystallize in a new structure type that is based on double layers [Al₂Si₈O₂₄]. These layers are linked by column of edge-sharing REE-polyhedra form three-dimensional framework with large porous occupied by potassium atoms. REE³⁺-atoms form seven-vertex polyhedra (pentagonal bipyramids) with average distances <Ce1–O> = 2.474 Å, <Ce2–O> = 2.462 Å and <Gd1–O> = 2.396 Å, <Gd2–O> = 2.396 Å.

A simple picture of splitting of Eu³⁺ luminescence lines is used traditionally as a luminescence probe. It corresponds to ⁵D₀ →⁷F₁ and ⁷F₂ transitions. A splitting of these lines to different number of components in crystal fields with different symmetry allows to determine a symmetry of Eu³⁺ surrounding. Not less effectively to use UV-luminescence of Gd³⁺. A shift of wide lines of transitions from ³D lower level to ³F₁₂- and ³F₃₂-sublevels was described (Dorenbos, 2000). Term ³F of Ce³⁺ is splitted by spin-orbital interaction. Recently created semiconductor UV-sources (SETi, USA) with λexc = 248 nm (UVTOP 240) allowed to study luminescence properties of synthesized REE-crystals.
Fig. 1. Luminescence spectrum of the three phases $K_4Gd_2[Al_2Si_8O_{24}]$, $K_4Ce_2[Al_2Si_8O_{24}]$ and $HK_6Eu[Si_{10}O_{25}]$ excited by UV LEDs radiation with $\lambda_{exc} = 248$ nm, $T=300$ K.

The study of the above-mentioned phases consists in visual evaluation of luminescence color and measurement of spectra of optically active centers (Fig.). The used equipment (microscope-spectrophotometer, UV LED with $\lambda_{exc} = 248$ nm, and registration system on the basis of the personal computer and blocks in CAMAC standard) allowed to record the spectral-characteristics of small objects with sizes $\geq 50$ $\mu$m in the spectral range 220–850 nm.

Narrow luminescence lines even at ambient conditions confirm high order of synthesized crystals. UV-radiation of $Ce^{3+}$ is identical to the condition this luminogen at well-studied feldspars (Moroshkin et al. 2005).

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References: