Mendeleev Commun., 2018, **28**, 661–662

Mendeleev
Communications

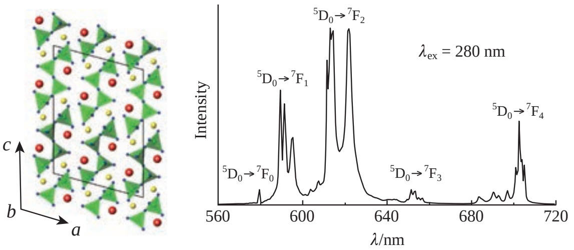
Crystal structure and luminescence properties of the barium europium tetragermanate $Ba_2Eu_2Ge_4O_{13}$

Alexander P. Tyutyunnik, Alexander Yu. Chufarov,
Ludmila L. Surat, Olga A. Lipina* and Vladimir G. Zubkov

Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, 620990 Ekaterinburg, Russian Federation. Fax: +7 343 374 4495; e-mail: LipinaOlgaA@yandex.ru

DOI: 10.1016/j.mencom.2018.11.035

The tetragermanate $Ba_2Eu_2Ge_4O_{13}$ was synthesized for the first time, and its structural and luminescent properties were examined. It crystallizes in a monoclinic system (space group *C*2/*c*, *Z* = 4) and its crystal structure incorporates a unique linear $[Ge_4O_{13}]^{10-}$ anion. The photoluminescence spectrum of the sample (λ_{ex} = 280 nm) contains several intense peaks in the orange-red spectral range corresponding to the 4*f*–4*f* transitions in Eu^{3+} ions.



The germanate $Ba_2Eu_2Ge_4O_{13}$ belongs to a small family of inorganic compounds whose crystal structures contain linear chains $[T_4O_{13}]$ (T = Ge, Si, V, P, Cr and As) continuing the series of isolated units $[TO_4]$–$[T_2O_7]$–$[T_3O_{10}]$.[1–12] The tetra group was first found in the structure of $K_2Cr_4O_{13}$ in 1970.[1] A little later, the crystal structure of $Na_4Sc_2Ge_4O_{13}$,[2] the first member of tetragermanates, was investigated. Currently, tetraphosphates and tetrasilicates are the most extensively studied compounds, while the tetragermanate family includes $Na_4Sc_2Ge_4O_{13}$,[2] $Cu_2Fe_2Ge_4O_{13}$[3–5] and $Cu_2Sc_2(Ge_4O_{13})$.[6]

The $Ba_2Eu_2Ge_4O_{13}$ sample was prepared by a solid-state method[†] according to equation (1).

$$2\,BaCO_3 + Eu_2O_3 + 4\,GeO_2 \rightarrow Ba_2Eu_2Ge_4O_{13} + 2\,CO_2 \qquad (1)$$

According to the X-ray diffraction data, the $Ba_2Eu_2Ge_4O_{13}$ germanate crystallizes in a monoclinic system, space group C_2/c, $Z = 4$.[‡] The compound is isostructural to $Ba_2Gd_2Si_4O_{13}$, and the results published for this tetrasilicate were used as a starting model for the full profile refinement.[8] Experimental, calculated and difference XRD patterns for $Ba_2Eu_2Ge_4O_{13}$ are presented in Figure S1 (Online Supplementary Materials). The atomic coordinates, isotropic thermal parameters, selected bond lengths and bond angles are given in Tables S1 and S2.

The projection of the $Ba_2Eu_2Ge_4O_{13}$ crystal structure on the (010) plane is shown in Figure 1. Four tetrahedra $[GeO_4]$ sequentially combined through the bridging oxygen atoms O(3) and O(4) form the zigzag chains $[Ge_4O_{13}]$. A symmetry axis of the second order passes through the bridging O(3) atom perpendicular to the (010) plane. The tetragermanate groups are located along the [001] direction, and they form two types of layers with different orientations of the germanium–oxygen tetrahedra. The Ge···Ge···Ge angle is 99.4(1)°. In the isostructural $Ba_2Gd_2Si_4O$ tetrasilicate, the angle Si···Si···Si is 99.88(5)°.[8] The geometry of $[Si_4O_{13}]$ was compared[8] with the geometry of tetrasilicate groups in silicates studied previously and concluded that the chain conformation is most similar to that observed in the struc-

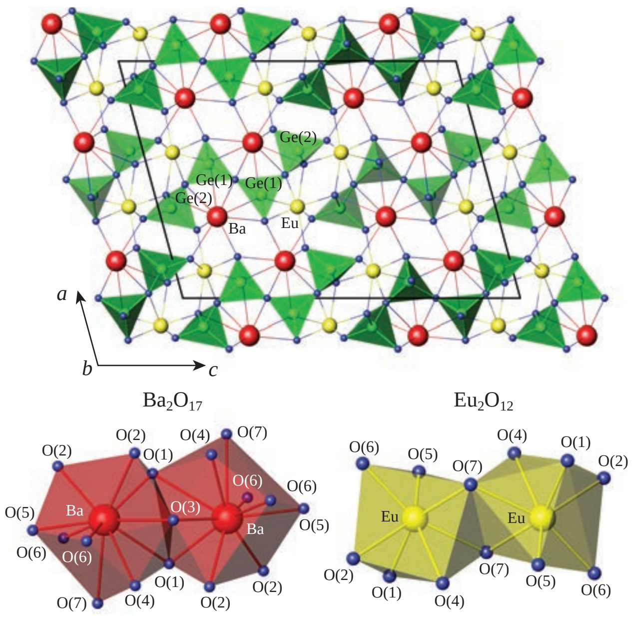


Figure 1 Projection of the $Ba_2Eu_2Ge_4O_{13}$ crystal structure with the GeO_4 tetrahedra (green), barium atoms (red) and europium atoms (yellow) and the coordination environments of the cation sites.

[†] $BaCO_3$, Eu_2O_3 and GeO_2 were used as raw chemicals. The mixtures of the initial components taken in stoichiometric amounts were carefully ground and then heated at 800 °C for 5 h. Afterwards, the samples were pressed into pellets and annealed for 20 h at temperatures of 850, 900, 950, 1000 and 1100 °C with intermediate regrinding.

[‡] *Crystal data for $Ba_2Eu_2Ge_4O_{13}$.* M = 1076.93, monoclinic, space group C_2/c, at 273 K: a = 13.11322(11), b = 5.38012(4) and c = 18.00659(17) Å, β = 105.1833(4)°, V = 1226.034(18) Å^3, Z = 4, d_{calc} = 5.834 g cm^{-3}. The number of measured reflections is 899. R_{wp} = 1.34%, R_p = 1.03%, $R(F^2)$ = 2.45%. All XRD patterns were collected on a STOE STADI–P automated diffractometer equipped with a linear mini-PSD detector using CuKα_1 radiation (5° ⩽ 2θ ⩽ 120° with a step of 0.02°). Polycrystalline silicon [a = 5.43075(5) Å] was used as an external standard. The crystal structure refinements were carried out with the GSAS program suite.[13,14] Further details of the crystal structure investigation can be obtained from FIZ Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808 666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the deposition CSD number: 434546.

tures of $Ag_{10}Si_4O_{13}$ (Si···Si···Si angles of 101.0 and 110.2°) and $K_5Eu_2F(Si_4O_{13})$ (Si···Si···Si angles of 102.8 and 104.7 °).[9,10] The Ge–O interatomic distances vary from 1.725(10) to 1.842(10) Å, which are close to those (1.61–1.83 Å) published for $Na_4Sc_2Ge_4O_{13}$, $Cu_2Fe_2Ge_4O_{13}$ and $Cu_2Sc_2(Ge_4O_{13})$.[2–6] The greatest deviation from the expected value (1.76 Å) is observed for the terminal tetrahedra, $Ge(2)O_4$, while the angular distortions for them are insignificant (see Table S2). The bonds between germanium and bridging oxygen atoms are the longest, as was also noted previously[15–17] for the $[Ge_3O_{10}]$, $[Ge_3O_9]$ and $[Ge_4O_{12}]$ groups.

The central tetrahedra of the tetragermanate groups, $Ge(1)O_4$, are connected through the O(2)–O(4) common edges with distorted EuO_7 polyhedra. The latter are combined through the O(7)–O(7) common edges, forming Eu_2O_{12} dimers (see Figure 1), to cause the cross-linking of layers formed from oppositely oriented $[Ge_4O_{13}]$ units. Barium atoms are located in voids between polyhedra, and they are coordinated by ten oxygen atoms. The calculated Ba–O distances range from 2.706(10) to 3.263(10) Å (see Table S2). The BaO_{10} polyhedra are joined to each other by O(1)–O(3)–O(1) faces (see Figure 1) to form zigzag chains along the [100] direction.

Figure 2 shows the luminescence spectra of the tetragermanate $Ba_2Eu_2Ge_4O_{13}$ and Y_2O_3 : 5% Eu^{3+}.§ The spectra consist of line multiplets in the orange-red spectral range, which correspond to the $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3, 4) transitions in Eu^{3+} ions. The spectrum of $Ba_2Eu_2Ge_4O_{13}$ is similar to that of $Ba_2Gd_2Si_4O_{13}$: Eu^{3+}.[18,19] Since the Eu^{3+} ions occupy sites with the C_1 local symmetry, there is a symmetric line (578–581 nm) originating from the forbidden $^5D_0 \rightarrow {}^7F_0$ transitions in the spectrum. Furthermore, the absence of an inversion center also leads to a high intensity of peaks at 604–640 nm caused by the electric dipole $^5D_0 \rightarrow {}^7F_2$ transitions. The asymmetry ratio of integrated intensities of the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transitions is 3.2. The lines at 645–710 nm assigned to the $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ transitions are also present in the spectrum.

The excitation spectra of the test tetragermanate and Y_2O_3 : 5% Eu^{3+} are presented in Figure 2. The maximum of a charge transfer band (CTB) in the spectrum of $Ba_2Eu_2Ge_4O_{13}$ locates at longer wavelengths compared with that of Y_2O_3 : 5% Eu^{3+}. It is obvious that $Ba_2Eu_2Ge_4O_{13}$ demonstrates higher luminescence intensity than Y_2O_3 : 5% Eu^{3+} under 265–310 nm excitation. This fact suggests that the tetragermanate can be successfully used as a phosphor for LED if the diode chip emits light at this wavelength range (one possible option is a commercially available AlN-based UV-LED chip). The quantum efficiency and light yield of $Ba_2Eu_2Ge_4O_{13}$ may be enhanced by composition optimization by the partial replacament of Eu^{3+} by Y^{3+}, Lu^{3+} or Gd^{3+} ions and by the introduction of sensitizer ions. The optimization of synthesis conditions should also improve the optical performance.

The synthesis of $Ba_2Eu_2Ge_4O_{13}$ is the first step towards creating new optical materials based on $Ba_2RE_2Ge_4O_{13}$ (RE is a rare earth element) tetragermanates emitting in a wide spectral range. The previous luminescence studies carried out for the related compounds $BaRE_2Si_3O_{10}$ have revealed that a number of phosphors $BaY_2Si_3O_{10}$: Ln^{3+} (Ln = Ce, Tb, Eu) showing quantum yields of up to 82% can be successfully synthesized.[20] We expect that, in the case of $Ba_2RE_2Ge_4O_{13}$ tetragermanates, a similar efficiency can be achieved for their application in LEDs, optoelectronic devices, lasers, *etc*.

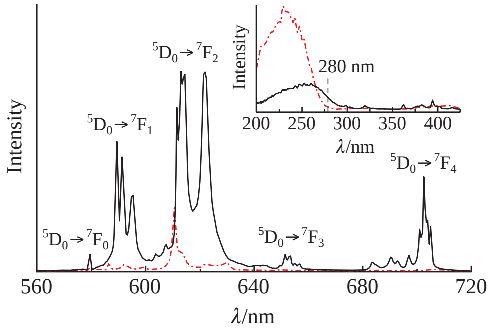


Figure 2 Luminescence spectra (λ_{ex} = 280 nm) of $Ba_2Eu_2Ge_4O_{13}$ (black solid line) and Y_2O_3:5% Eu^{3+} (red dash-dotted line). Inset: the excitation spectra (λ_{em} = 614 or 611 nm).

The work was carried out in accordance with the state assignment for the Institute of Solid State Chemistry of the Ural Branch of Russian Academy of Sciences within the Comprehensive Program of Basic Scientific Research of the Ural Branch of RAS (theme no. 18-10-3-32). The structural studies were carried out at the multiple-access center for X-ray structure analysis at the Institute of Solid State Chemistry, Ural Branch of Russian Academy of Sciences (Ekaterinburg).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.11.035.

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Received: 14th May 2018; Com. 18/5575

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§ The Y_2O_3:5% Eu^{3+} oxide was synthesized to compare the luminescence properties of $Ba_2Eu_2Ge_4O_{13}$ with those of a commercial red emitting phosphor. The photoluminescence spectra were recorded using an MDR-204 LOMO-Photonica monochromator (90° geometry; diffraction grating, 1200 lines mm^{-1}), a photon counter based on PMT R928 (Hamamatsu) and a NLS-UV/40 picosecond pulse generator (InTop) as an external excitation source (λ_{ex} = 280 nm). The photoluminescence excitation spectra of $Ba_2Eu_2Ge_4O_{13}$ and Y_2O_3:5% Eu^{3+} were recorded on a Varian Cary Eclipse fluorescence spectrophotometer by monitoring emission at 614 and 611 nm, respectively. A 75 kW Xenon lamp was used as an excitation source (pulse length τ = 2 μs; pulse frequency ν = 80 Hz).