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Synthesis and crystal structure of the rare earth borogermanate $EuGeBO_5$

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Abstract: The synthesis and crystal structure of the rare earth borogermanate $EuGeBO_5$ are reported. It is synthesized by high-temperature solid-state reaction and crystallizes in the monoclinic space group $P2_1/c$ (no. 14) with the unit cell parameters $a = 4.8860(5)$, $b = 7.5229(8)$, $c = 9.9587(10)$ Å, and $\beta = 91.709(3)°$. Its crystal structure features a polyanion-type layer $(GeBO_5)^{3-}$ constructed by BO_4 and GeO_4 tetrahedra connected alternatingly. Eu^{3+} ions are located in cavities and are coordinated by eight O atoms. Various structures of the related compounds $REMM'O_5$ (RE = rare earth metal; M = Si, Ge, and Sn; M' = B, Al, and Ga) are also discussed.

Keywords: crystal structure; rare earth borogermanate; $REMM'O_5$ compounds; solid state reaction.

1 Introduction

Rare earth borogermanates demonstrate various types of structures and rich physical properties, the latter includes magnetic, luminescent, second-order nonlinear optical and ferroelectric properties [1–3]. For the former, several series of compounds have been reported, these include, but are not limited to, $REGeBO_5$ [4–6], $RE_2GeB_2O_8$ [7], $RE_6Ge_9B_2O_{30}$ [8], $RE_{14}Ge_2B_6O_{34}$ (RE = rare earth metal) [9], and several series of their derivatives, including $REMM'O_5$ [10, 11], $RE_3Si_2BO_{10}$ [12], $RE_3Ge_5AlO_{16}$ [13], $RE_3MGa_5O_{14}$ [13], and $REGe_2M'O_7$ (M = Si, Ge, and Sn; M' = Al, Ga, and In) [14].

Pushed by the versatile structures and physical performance of rare earth borogermanates, we recently started to explore new compounds with wide potential applications [15]. In the present work, $EuGeBO_5$, a rare earth borogermanate was obtained using high-temperature solid-state methods. It crystallizes in the monoclinic space group $P2_1/c$. It has to be mentioned that monoclinic $EuGeBO_5$ was first described by Rulmont and Tarte as early as in 1988 [16]. Herein, we report its synthesis and single-crystal structure determination, and discuss the rich structural chemistry of the $REMM'O_5$ compounds.

2 Experimental section

2.1 Synthesis and analyses

All starting materials were used as-received without further purification. A powdery sample of the title compound was obtained by a high-temperature solid-state reaction with KI as a flux. The employment of KI can help reduce reactive temperature and make the reaction happened more uniformly because of its low melting point and reactive inertness in such system. The starting materials were H_3BO_3 (99.9%, Aladdin, China), GeO_2 (99.9%, Aladdin, China), and EuO (99.9%, Aladdin, China). The sample had a total mass of 500 mg with an addition of 400 mg KI (99%, Aladdin, China), and the molar ratios of Eu : Ge : B were 1 : 1 : 1. The mixture of starting materials was ground into a fine powder in an agate mortar and pressed into a pellet, followed by loading into a corundum crucible. The sample was placed into a muffle furnace, slowly heated to 1223 K in 24 h, and maintained for 7 days, finally cooled down to 573 K at a speed of 5 K h^{-1} and powered off. The colorless single crystals of the title compound were stable in moisture and air. They were washed using ethanol and water under ultrasound irradiation, and the purity was confirmed by powder X-ray diffraction (PXRD). The PXRD pattern was collected with a Bruker D8 advance diffractometer (Germany) at 40 kV and 100 mA with Cu$K\alpha$ radiation ($\lambda = 1.5406$ Å) with a scan speed of 5° min^{-1} at room temperature. The simulated pattern was produced from single-crystal data with the program Mercury (v2.3) provided by the Cambridge Crystallographic Data Center. The PXRD pattern (Fig. 1) corresponds well with the simulated one, indicating a single phase sample. A semiquantitative microscopic elemental analysis on the as-prepared single crystals was performed

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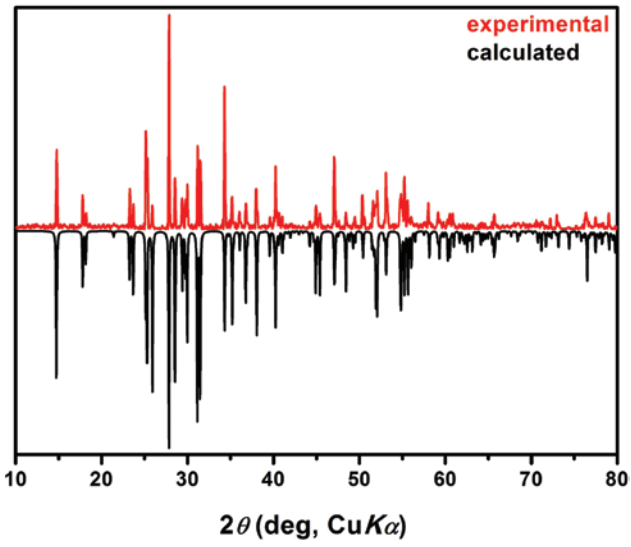

Fig. 1: PXRD pattern of $EuGeBO_5$. The red and black patterns are the experimental and simulated ones, respectively.

on a field-emission scanning electron microscope (Zeiss Supra 55, Germany) equipped with an energy-dispersive X-ray spectroscope (Bruker Quantax, Germany), which confirmed the presence of Eu, Ge, and O with the approximate ratios of 1 : 1 : 5, and no other elements were detected (boron could not be detected using energy-dispersive X-ray spectroscope because it is too light).

2.2 Structure determination

The intensity data set of $EuGeBO_5$ was collected on Bruker D8 QUEST X-ray diffractometer with graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). Its structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 with anisotropic displacement parameters for all atoms. All the calculations were performed with the SHELXTL-97 crystallographic software package [17]. The final refinement included a secondary extinction correction. It has to be mentioned that atoms B1, O4, and O5 were nonpositive definite in the first refinement, so the command ISOR was applied to restrict them altogether with 18 restraints. The crystallographic data, atomic coordinates, equivalent isotropic displacement parameters, and bond lengths are listed in Tables 1–3, respectively.

Further details of the crystal structure investigation may be obtained from FIZ Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de) on quoting the deposition number CSD-430764.

Table 1: Crystal data and structure refinement parameters for $EuGeBO_5$.

Chemical formula	$EuGeBO_5$
M_r	315.36
T/K	296(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	4.8860(5)
b/Å	7.5229(8)
c/Å	9.9587(10)
β/deg	91.709(3)
V/Å^3	365.89(7)
Z	4
$\rho_{calcd.}$/g cm^{-3}	5.73
μ/mm^{-1}	25.1
$F(000)/e$	560
Crystal size/cm^3	0.02 × 0.02 × 0.02
Radiation; λ/Å	Mo$K\alpha$, 0.71073
θ range/deg	3.39 to 27.54
Limiting indices hkl	$-6 \le h \le 5$, $-9 \le k \le 9$, $-12 \le l \le 12$
Absorption correction	Semiempirical from equivalents
Measd. reflns	3169
Indep. reflns; R_{int}	833; 0.0442
Obs. reflns ($I > 2\sigma(I)$)	2978
$R1$; $wR2$ ($I > 2\sigma(I)$)	0.0284; 0.0782
$R1$; $wR2$ (all data)	0.0289; 0.0785
GOF (F^2)	1.084
$\Delta\rho_{max}$; $\Delta\rho_{min}/e$ Å^{-3}	1.27; −1.94

Table 2: Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (U_{eq}[a], Å^2×10^3) for $EuGeBO_5$.

Atom	Wyckoff site	x	y	z	U_{eq} (Å^2)
Eu1	4e	57(1)	3921(1)	1785(1)	3(1)
Ge1	4e	5264(2)	2323(1)	4243(1)	8(1)
B1	4e	4542(18)	934(11)	1693(8)	3(2)
O1	4e	2237(12)	5876(7)	276(6)	7(1)
O2	4e	2595(12)	6032(7)	3104(6)	6(1)
O3	4e	2949(11)	1598(7)	2979(5)	5(1)
O4	4e	3352(11)	1598(7)	2979(5)	5(1)
O5	4e	6714(11)	4175(7)	3507(6)	6(1)

[a]U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

3 Results and discussion

3.1 Synthesis

The title compound was synthesized in a corundum crucible, not in a platinum crucible as used for the synthesis of many other *REMM*′O_5 compounds [1–14]. First, a powdered sample of $EuGeBO_5$ was obtained through the reaction $EuO + 2GeO_2 + 2H_3BO_3$ targeting to synthesize

Table 3: Bond lengths (Å) for $EuGeBO_5$.[a]

Bond	Dist./Å	Bond	Dist./Å
Eu(1)–O(1)	2.378(6)	Ge(1)–O(1)#7	1.694(6)
Eu(1)–O(1)#1	2.313(6)	Ge(1)–O(3)	1.753(5)
Eu(1)–O(2)	2.386(6)	Ge(1)–O(4)#8	1.740(5)
Eu(1)–O(2)#4	2.534(6)	Ge(1)–O(5)	1.735(6)
Eu(1)–O(3)	2.523(6)	B(1)–O(2)#7	1.409(10)
Eu(1)–O(3)#3	2.508(5)	B(1)–O(3)	1.599(10)
Eu(1)–O(4)	2.410(5)	B(1)–O(4)	1.498(10)
Eu(1)–O(5)#2	2.411(6)	B(1)–O(5)#7	1.470(10)

[a]Symmetry transformations used to generate equivalent atoms: #1 $-x, -y+1, -z$; #2 $x-1, y, z$; #3 $-x, y+1/2, -z+1/2$; #4 $-x, y-1/2, -z+1/2$; #5 $x-1, -y+1/2, z-1/2$; #6 $-x+1, y+1/2, -z+1/2$; #7 $-x+1, y-1/2, -z+1/2$; #8 $x, -y+1/2, z+1/2$; #9 $x+1, -y+1/2, z+1/2$; #10 $x+1, y, z$; #11 $x, -y+1/2, z-1/2$.

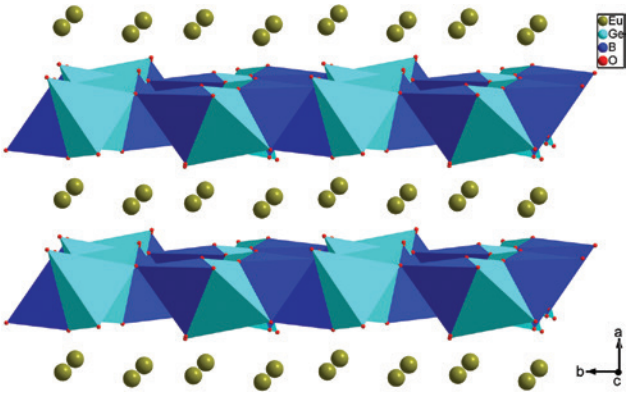

Fig. 3: Crystal structure of $EuGeBO_5$. For the sake of clarity, Eu–O bonds were omitted. Dark and light blue polyhedra represent $(BO_3)^{3-}$ and $(GeO_4)^{4-}$ units, respectively.

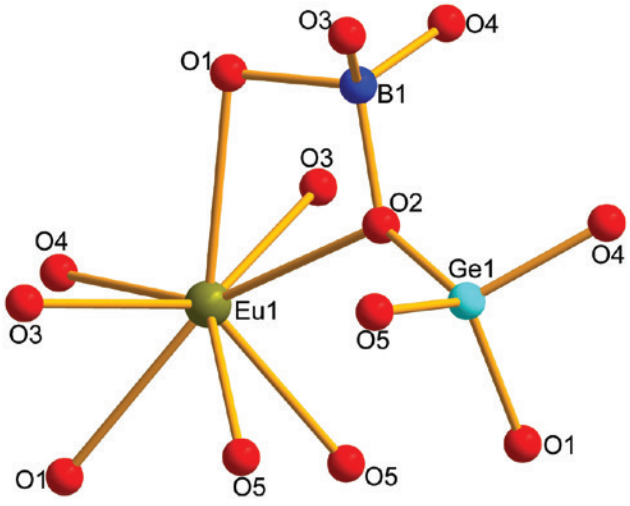

Fig. 2: Coordination geometry of $EuGeBO_5$.

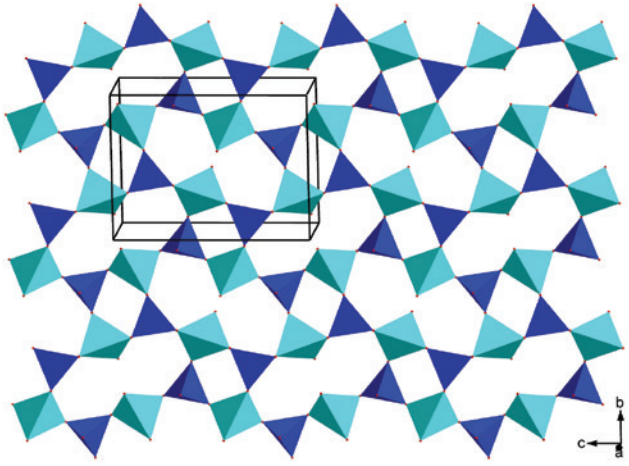

Fig. 4: $(GeBO_5)^{3-}$ polyanion layer in the *ab* plane constructed by $(BO_4)^{5-}$ and $(GeO_4)^{4-}$ polyhedra. Dark and light blue polyhedra represent $(BO_4)^{5-}$ and $(GeO_4)^{4-}$ units, respectively.

$EuGe_2B_2O_8$. No single crystal could be picked up in this synthesis to collect the single-crystal data. Fortunately, the main product of the reaction was the monoclinic phase $EuGeBO_5$ as the PXRD pattern is very similar to that of $NdGeBO_5$. Until now, only powder data for $EuGeBO_5$ had been available [16]. We made efforts to prepare single crystals of $EuGeBO_5$ to obtain its structural data in more detail. As described in the Experimental section, the single crystals of $EuGeBO_5$ were finally obtained using KI as a flux and reducing the reactive temperature to 1223 K, where the flux KI could be washed away easily with water. Here, it has to be mentioned that the oxidation state change of Eu from divalent to trivalent was probably induced by oxygen in the air as the reactive system was exposed to air. Our synthetic method is different from that used for the syntheses of the other *REMM'*O_5 compounds. The method should also be advantageous for the synthesis of other *REMM'*O_5 compounds with the monoclinic structure type.

3.2 Crystal structure

$EuGeBO_5$ crystallizes in the monoclinic space group $P2_1/c$, isotypic with the monoclinic phase of $NdGeBO_5$ [18]. Rulmont and Tarte reported its unit cell parameters by indexing the PXRD data and refinement using a least-squares program. They reported the values $a=9.9960(10)$, $b=7.5260(14)$, $c=4.8874(9)$ Å, and $\beta=91.65(1)°$ [16]. By comparison, our parameters obtained from single-crystal diffraction are $a=4.8860(5)$, $b=7.5229(8)$, $c=9.9587(10)$ Å, and $\beta=91.709(3)°$. The reinvestigation of monoclinic $EuGeBO_5$ using single-crystal data resulted in a more precise structure determination.

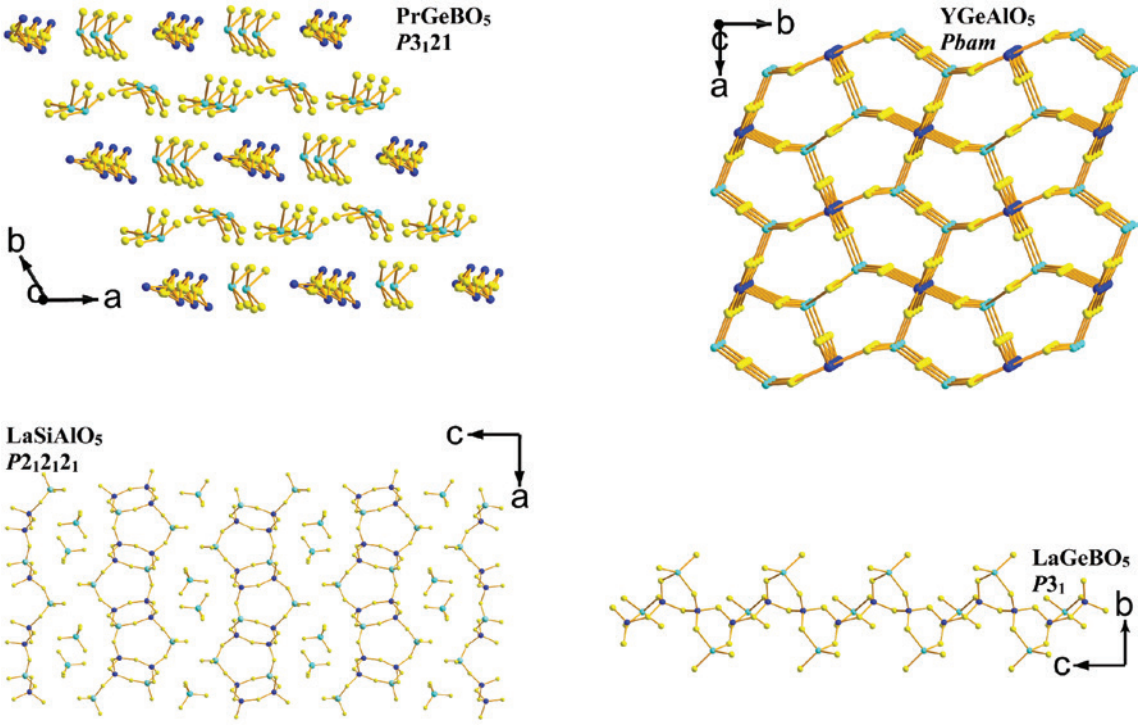

Fig. 5: $(MM'O_5)^{3-}$ (M = Si, Ge; M' = B, Al) polyanions in the structures of $REMM'O_5$ compounds. M, M', and O atoms are represented as turquoise, blue, and yellow spheres, respectively.

There are one Eu, one Ge, one B, and five O atoms in the asymmetric unit of the $EuGeBO_5$ structure. Ge and B atoms are coordinated with four O atoms to form GeO_4 and BO_4 tetrahedra, respectively, and each Eu atom has eight neighboring O atoms (Fig. 2). All three BO_4, GeO_4, and EuO_8 units share corners with each other.

The structure of $EuGeBO_5$ can be considered as a pseudo-layer structure, where the layers are constructed from BO_4 and GeO_4 tetrahedra, and Eu ions occupy the cavities between the layers (Fig. 3). From Fig. 4, it can be observed that the layers extend parallel to the *ab* plane. There are no GeO_4 tetrahedra or BO_4 tetrahedra interconnected with themselves, but GeO_4 and BO_4 tetrahedra alternate to form a layer that can be regarded as polyanionic group $(GeBO_5)^{3-}$.

The Ge–O and B–O distances in $EuGeBO_5$ are in the range of 1.694(6)–1.753(5) and 1.409(10) to 1.599(10) Å, respectively, which are consistent with the distances of Ge–O bonds found in $SrGe_2B_2O_8$ [19] and the B–O bonds found in $Cs_2B_4SiO_9$ [20]. The Eu–O bond lengths of 2.313(6) to 2.534(6) Å are in agreement with those in $Eu_2GeB_2O_8$ [7].

Although the crystal structure of $EuGeBO_5$ as we described above is relatively simple, the $REMM'O_5$ (M = Si, Ge; M' = B, Al) series demonstrates various structure types with different types of $(MM'O_5)^{3-}$ polyanions (Fig. 5). It is interesting to summarize and compare these polyanion structures. Except for the monoclinic phase, there are four other types of structures for the $REMM'O_5$ series reported, namely, the orthorhombic *Pbam* and $P2_12_12_1$ phases and the trigonal $P3_1$ and $P3_121$ phases. Among them, the space groups $P2_12_12_1$, $P3_1$, and $P3_121$ are suitable for homochiral structures, which make these $REMM'O_5$ compounds potential second-order nonlinear optical materials.

The $(MM'O_5)^{3-}$ polyanions in $PrGeBO_5$ (space group $P3_121$) [5], $LaGeBO_5$ (space group $P3_1$) [21], $LaSiAlO_5$ (space group $P2_12_12_1$) [22], and $YGeAlO_5$ (space group *Pbam*) [23] are totally different. In $PrGeBO_5$, BO_4 tetrahedra are isolated and GeO_4 tetrahedra share edges to form a chain along the *c* direction. In $LaGeBO_5$, the polyanion is constructed from BO_4 tetrahedra and a chain is formed with GeO_4 tetrahedra through corner sharing. In $LaSiAlO_5$, SiO_4 tetrahedra are isolated and AlO_4 tetrahedra share corners to construct chains along the *a* direction. Differently, Ge and Al in $YGeAlO_5$ are five- and six-coordinated with O atoms to form tetragonal pyramids and octahedra, respectively. AlO_6 octahedra share edges to form a chain along the *c* direction, and two GeO_5 pyramids always connect to form dimers to link neighboring Al atoms through corner sharing in the *ab* plane. In conclusion, the $(MM'O_5)^{3-}$ polyanions have different dimensionalities in the structures of

$LaGeBO_5$ (space group $P3_1$), $EuGeBO_5$ (space group $P2_1/a$), and $YGeAlO_5$ (space group *Pbam*), respectively. In $PrGeBO_5$ (space group $P3_121$) and $LaSiAlO_5$ (space group $P2_12_12_1$), the BO_4 and SiO_4 tetrahedra are isolated.

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