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Synthesis and structural characterization of $Ca_{12}Ge_{17}B_8O_{58}$

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Abstract: $Ca_{12}Ge_{17}B_8O_{58}$ was prepared by high-temperature solid state synthesis at 1100°C in a platinum crucible from calcium carbonate, boric acid, and germanium(IV) oxide. The compound crystallizes in the tetragonal crystal system in the space group $P\bar{4}$ (No. 81) isotypically to $Cd_{12}Ge_{17}B_8O_{58}$. The structure was refined from single-crystal X-ray diffraction data: $a = 15.053(8)$, $c = 4.723(2)$ Å, $V = 1070.2(2)$ Å^3, $R1 = 0.0151$, and $wR2 = 0.0339$ for all data. The crystal structure of $Ca_{12}Ge_{17}B_8O_{58}$ consists of $[Ge_4O_{12}]_n$ chains composed of GeO_4 tetrahedra and GeO_6 octahedra. The chains are interconnected into a $[Ge_4O_{10.5}]_n$ network *via* corner sharing. By additional $[Ge(B_2O_7)_4]^{28-}$ clusters, these units are connected to a three-dimensional $[Ge_{17}B_8O_{58}]^{24-}$ framework. The open structure forms three types of tunnels with five-, six-, and seven-membered rings (MRs) along the *c* axis, where the Ca^{2+} are located.

Keywords: calcium borogermanate; crystal structure; IR spectroscopy; solid-state reaction.

1 Introduction

In the last few years, the interest in the class of metal borogermanates has steadily been increasing. Borogermanates are known for their interesting physical properties like luminescence, ferro-, pyro-, or piezoelectricity and nonlinear optical (NLO) effects [1–8]. The compounds could be used as second harmonic generation (SHG) materials in laser applications, e.g. the SHG response of $K_2GeB_4O_9 \cdot 2\,H_2O$ is two times higher than that of the well known reference KDP [6, 7]. Other compounds like $Eu_2GeB_2O_8$ and $Tb_2GeB_2O_8$ are luminescent materials for red and green light emission, respectively [8].

At the beginning of our project, a variety of alkali borogermanates such as $A_2GeB_4O_9$ (A = Rb, Cs), $AGeB_3O_7$ (A = Rb, Cs), $Rb_4Ge_3B_6O_{17}$, $K_2GeB_4O_9 \cdot 2\,H_2O$ [1, 3, 6, 7], and alkaline earth borogermanates like $Ba_3Ge_2B_6O_{16}$, $Ba_3[Ge_2B_7O_{16}(OH)_2](OH)(H_2O)$, $Ca_{10}Ge_{16}B_6O_{51}$, $SrGe_2B_2O_8$, and $Sr_3Ge_2B_6O_{16}$ were known [1, 2, 4]. In the year 2014, our group successfully synthesized the compound $Sr_{3-x/2}B_{2-x}Ge_{4+x}O_{14}$ ($x = 0.32$) as the first boron containing member of the langasite family [9]. Furtheron, we focused our research on the system $CaCO_3$-GeO_2-H_3BO_3, where it was possible to synthesize a new colorless compound, which could not be identified using database reports. A single-crystal structure determination of the new unknown phase has revealed a novel calcium borogermanate with the composition $Ca_{12}Ge_{17}B_8O_{58}$, being isotypic to $Cd_{12}Ge_{17}B_8O_{58}$ [2]. In this work, we report the synthesis, the single crystal structure determination, and IR spectroscopic investigations of this new compound.

2 Experimental section

2.1 Synthesis

According to Eq. 1, a stoichiometric mixture of the starting materials $CaCO_3$ (99.95%, Stream Chemicals, Newburyport, MA, USA), GeO_2 (99.99%, ChemPur, Karlsruhe, Germany), and H_3BO_3 (99.5%, Merck, Darmstadt, Germany) was finely ground in an agate mortar and filled into a platinum FKS 95/5 crucible (feinkornstabilisiert, 95% Pt, 5% Au, Ögussa, Wien, Austria).

$$12\,CaCO_3 + 17\,GeO_2 + 8\,H_3BO_3 \xrightarrow{1100^\circ C} Ca_{12}Ge_{17}B_8O_{58} + 12\,CO_2 + 12\,H_2O \qquad (1)$$

Calcination was performed in an electric resistance furnace (Nabertherm muffle furnace). The sample was heated up to 1100°C with a rate of 275°C h^{-1} and maintained at that temperature for 20 h. After that, the temperature was lowered to 500°C with a rate of 3°C h^{-1} before switching off the furnace. The product naturally cooled down to room temperature.

The new compound $Ca_{12}Ge_{17}B_8O_{58}$ could be obtained in form of colorless, air- and water-resistant crystals. The

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powder diffraction pattern (Fig. 1) showed reflections of $Ca_{12}Ge_{17}B_8O_{58}$ as the major phase. The eight reflections marked with asterisks could not be assigned up to now.

2.2 Crystal structure analysis

The powder diffraction pattern of $Ca_{12}Ge_{17}B_8O_{58}$ was obtained in transmission geometry from a flat sample of the reaction product, using a Stoe Stadi P powder diffractometer with Ge (111)-monochromatized Mo$K_{\alpha1}$ (λ = 70.93 pm) radiation. The comparison of the experimental powder pattern with the theoretical pattern simulated from the single-crystal data in Fig. 1 exhibited that they match well.

Small single crystals of $Ca_{12}Ge_{17}B_8O_{58}$ were selected by mechanical fragmentation using a polarization microscope. A Bruker D8 Quest Kappa diffractometer with Mo-K_α radiation (λ = 71.073 pm) was used to collect the single crystal intensity data at room temperature. A multi-scan absorption correction (SADABS-2014 [10]) was applied to the intensity data sets. All relevant details of the data collection and the refinement are listed in Table 1. According to the systematic extinctions, the tetragonal space group $P\bar{4}$ (No. 81) was derived for the crystal. Due to the fact that $Ca_{12}Ge_{17}B_8O_{58}$ is isotypic to $Cd_{12}Ge_{17}B_8O_{58}$ [2], the structural refinement was performed by using the positional parameters of $Cd_{12}Ge_{17}B_8O_{58}$ as starting values (SHELXL-13 [11, 12]). All atoms were refined anisotropically and the final difference Fourier synthesis did not reveal any significant residual peaks, leading to values of 0.0151 and 0.0339 for $R1$ and $wR2$, respectively. The refinement exhibited that the measured crystal was a twin, with the twin law $(0\bar{1}0, \bar{1}00, 00\bar{1})$. The atomic coordinates, anisotropic displacement parameters, and interatomic distances are listed in the Tables 2–4. Graphical representations of the structure were produced with the program DIAMOND [13].

Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-431201.

Table 1: Crystal data and structure refinement of $Ca_{12}Ge_{17}B_8O_{58}$ (standard deviations in parentheses).

Empirical formula	$Ca_{12}Ge_{17}B_8O_{58}$
Molar mass, g·mol^{-1}	2730.27
Crystal system	Tetragonal
Space group	$P\bar{4}$ (No. 81)
Powder data	
Powder diffractometer	STOE Stadi P
Radiation	Mo$K_{\alpha1}$ (λ = 70.93 pm)
a, Å	15.005(6)
c, Å	4.701(4)
V, Å^3	1058.4(8)
Single crystal data	
Single crystal diffractometer	Bruker D8 Quest Kappa
Radiation	MoK_α (λ = 71.073 pm)
a, Å	15.053(8)
c, Å	4.723(2)
V, Å^3	1070.2(2)
Formula units per cell	1
Calculated density, g cm^{-3}	4.24
Crystal size, mm^3	0.08 × 0.05 × 0.03
Temperature, K	275(2)
Absorption coefficient, mm^{-1}	13.4
F(000), e	1288
θ range, deg	2.7–36.5
Range in hkl	±25, ±25, ±7
Total no. of reflections	54 998
Independent reflections	5232
Reflections with $I \geq 2\sigma(I)$	5169
Data/parameters	5169/216
Absorption correction	Multi-scan
Goodness-of-fit on F_i^2	1.065
Final $R1/wR2$ [$I \geq 2\,\sigma(I)$]	0.0146/0.0338
Final $R1/wR2$ (all data)	0.0151/0.0339
BASF	0.5019
Flack parameter	0.002(4)
Largest diff. peak/hole, e Å^{-3}	0.54/−1.07

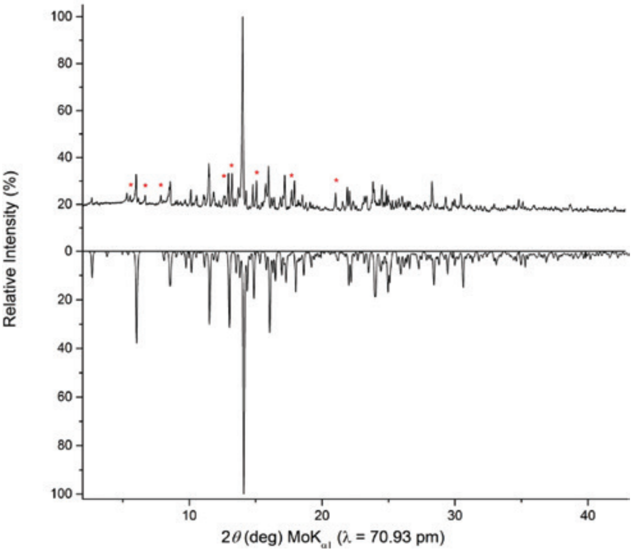

Fig. 1: Top: experimental powder pattern of $Ca_{12}Ge_{17}B_8O_{58}$. The reflections marked with a red asterisk could not be assigned until now. Bottom: theoretical powder pattern of $Ca_{12}Ge_{17}B_8O_{58}$ based on single-crystal diffraction data.

Table 2: Atomic coordinates and equivalent isotropic displacement parameters U_{eq} (Å^2) of $Ca_{12}Ge_{17}B_8O_{58}$ with standard deviations in parentheses.

Atom	Wyckoff position	*x*	*y*	*z*	U_{eq}[a]
Ca1	4*h*	0.89082(3)	0.85484(3)	0.9925(2)	0.00638(7)
Ca2	4*h*	0.36340(3)	0.75106(3)	0.9949(2)	0.00682(7)
Ca3	4*h*	1.00858(3)	0.67048(3)	0.9908(2)	0.00763(8)
Ge1	4*h*	0.71772(2)	0.81076(2)	0.50096(11)	0.00420(4)
Ge2	4*h*	0.57951(2)	0.78370(2)	1.00144(11)	0.00416(4)
Ge3	1*b*	0	0	1/2	0.00412(7)
Ge4	4*h*	0.53978(2)	0.64481(2)	0.50562(11)	0.00460(4)
Ge5	4*h*	0.48693(2)	0.89366(2)	0.50148(12)	0.00443(4)
B1	4*h*	0.81247(19)	0.97612(18)	0.5378(7)	0.0059(6)
B2	4*h*	0.70838(17)	1.12165(17)	0.5284(8)	0.0047(5)
O1	4*h*	0.77131(14)	0.89579(14)	0.6865(4)	0.0059(3)
O2	4*h*	0.90365(13)	0.98363(14)	0.7020(4)	0.0059(3)
O3	4*h*	0.81886(15)	0.96965(13)	0.2455(5)	0.0070(3)
O4	4*h*	0.76121(14)	1.05043(14)	0.6546(4)	0.0063(3)
O5	4*h*	0.61612(14)	1.11002(15)	0.6738(4)	0.0078(3)
O6	4*h*	0.74411(15)	1.20473(13)	0.6749(5)	0.0072(4)
O7	4*h*	0.70577(14)	1.12664(14)	0.2330(4)	0.0068(3)
O8	2*g*	1/2	0	0.3341(7)	0.0098(5)
O9	4*h*	0.56710(14)	0.88733(15)	0.7716(4)	0.0065(3)
O10	4*h*	0.44194(14)	0.60329(15)	0.3442(5)	0.0097(4)
O11	4*h*	0.60642(13)	0.68580(13)	0.2306(4)	0.0062(3)
O12	4*h*	0.48337(13)	0.81459(14)	0.2299(5)	0.0065(3)
O13	4*h*	0.50129(14)	0.71818(14)	0.7689(4)	0.0063(3)
O14	4*h*	0.67190(14)	0.74558(14)	0.7702(4)	0.0061(3)
O15	4*h*	0.65114(14)	0.85616(13)	0.2354(4)	0.0065(3)

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

Table 3: Anisotropic displacement parameters U_{ij} (Å^2) of $Ca_{12}Ge_{17}B_8O_{58}$ with standard deviations in parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ge1	0.00402(8)	0.00452(8)	0.00404(8)	0.00038(19)	−0.00017(18)	−0.00014(7)
Ge2	0.00382(8)	0.00445(8)	0.00422(8)	−0.00006(18)	0.00016(18)	−0.00001(6)
Ge3	0.00379(10)	0.00379(10)	0.00479(17)	0	0	0
Ge4	0.00454(8)	0.00432(8)	0.00494(9)	0.00012(19)	0.00075(17)	0.00009(6)
Ge5	0.00429(8)	0.00466(8)	0.00435(9)	−0.00002(19)	−0.00039(19)	0.00017(7)
Ca1	0.00668(15)	0.00592(15)	0.00653(18)	0.0002(3)	−0.0010(3)	0.00090(13)
Ca2	0.00477(15)	0.00818(16)	0.00752(17)	−0.0007(4)	0.0002(3)	−0.00097(12)
Ca3	0.00622(16)	0.00886(16)	0.00780(19)	0.0003(3)	0.0009(3)	0.00160(13)
O1	0.0072(8)	0.0037(7)	0.0069(8)	0.0008(7)	−0.0018(6)	−0.0035(6)
O2	0.0037(7)	0.0070(8)	0.0072(8)	0.0003(6)	0.0014(6)	−0.0002(6)
O3	0.0090(8)	0.0065(8)	0.0055(8)	−0.0006(7)	0.0006(7)	0.0009(6)
O4	0.0087(8)	0.0053(8)	0.0050(7)	0.0000(6)	−0.0007(7)	0.0030(6)
O5	0.0036(8)	0.0122(9)	0.0075(8)	0.0019(7)	0.0000(6)	−0.0006(7)
O6	0.0112(9)	0.0034(8)	0.0070(9)	0.0000(6)	0.0020(7)	−0.0024(6)
O7	0.0078(9)	0.0068(8)	0.0057(8)	0.0000(7)	−0.0004(7)	0.0013(6)
O8	0.0175(14)	0.0032(11)	0.0086(12)	0	0	0.0010(10)
O9	0.0073(8)	0.0067(8)	0.0055(8)	0.0013(7)	−0.0028(7)	−0.0006(6)
O10	0.0058(8)	0.0134(9)	0.0100(10)	−0.0010(7)	0.0003(7)	−0.0063(7)
O11	0.0060(8)	0.0062(8)	0.0064(8)	0.0025(6)	0.0018(7)	−0.0012(7)
O12	0.0049(7)	0.0072(8)	0.0073(8)	−0.0036(7)	0.0009(6)	−0.0003(6)
O13	0.0054(7)	0.0072(7)	0.0063(8)	−0.0036(7)	0.0003(7)	0.0007(6)
O14	0.0060(8)	0.0061(7)	0.0063(8)	0.0025(7)	0.0025(6)	0.0006(6)
O15	0.0062(8)	0.0064(8)	0.0070(8)	0.0012(7)	−0.0035(6)	−0.0003(6)
B1	0.0050(9)	0.0055(9)	0.0072(17)	−0.0004(9)	−0.0006(9)	−0.0002(7)
B2	0.0051(9)	0.0032(8)	0.0058(15)	0.0003(10)	0.0004(10)	0.0007(6)

Table 4: Interatomic distances (Å) in $Ca_{12}Ge_{17}B_8O_{58}$ (standard deviations in parentheses).

Ge1–O15	1.745(2)	Ge2–O14	1.859(2)	Ge3–O2	1.733(2)
Ge1–O14	1.748(2)	Ge2–O12	1.864(2)	Ge3–O2	1.733(2)
Ge1–O1	1.749(2)	Ge2–O11	1.873(2)	Ge3–O2	1.733(2)
Ge1–O6	1.749(2)	Ge2–O13	1.888(2)	Ge3–O2	1.734(2)
		Ge2–O15	1.889(2)		
		Ge2–O9	1.910(2)		
Ø	1.748(2)	Ø	1.881(2)	Ø	1.733(2)
Ge4–O11	1.753(2)	Ge5–O12	1.751(2)		
Ge4–O13	1.761(2)	Ge5–O5	1.753(2)		
Ge4–O10a	1.767(2)	Ge5–O9	1.759(2)		
Ge4–O10b	1.772(2)	Ge5–O8	1.796(2)		
Ø	1.763(2)	Ø	1.765(2)		
B1–O3	1.387(4)	B2–O7	1.398(4)		
B1–O4	1.467(4)	B2–O4	1.462(4)		
B1–O1	1.530(4)	B2–O6	1.527(4)		
B1–O2	1.581(4)	B2–O5	1.559(4)		
Ø	1.491(4)	Ø	1.487(4)		
Ca1–O4	2.355(2)	Ca2–O14	2.311(2)	Ca3–O15	2.318(2)
Ca1–O3a	2.364(2)	Ca2–O6	2.312(2)	Ca3–O4	2.337(2)
Ca1–O2a	2.383(2)	Ca2–O12	2.326(2)	Ca3–O7	2.354(2)
Ca1–O1	2.388(2)	Ca2–O13	2.386(2)	Ca3–O9	2.477(2)
Ca1–O3b	2.443(2)	Ca2–O7	2.395(2)	Ca3–O3	2.518(2)
Ca1–O2b	2.489(2)	Ca2–O11	2.534(2)	Ca3–O5	2.523(2)
Ca1–O7	2.498(2)	Ca2–O5	2.602(2)	Ca3–O1	2.588(2)
Ca1–O6	2.705(2)	Ca2–O10	3.011(2)	Ca3–O8	2.993(2)
Ø	2.453(2)	Ø	2.485(2)	Ø	2.514(2)

2.3 Vibrational spectra

The transmission FT-IR spectrum of a single crystal of $Ca_{12}Ge_{17}B_8O_{58}$ was measured in the spectral range of 600–4000 cm^{-1} with a Vertex 70 FT-IR spectrometer (spectral resolution 4 cm^{-1}), which is equipped with a KBr beam splitter, an LN-MCT (*M*ercury *C*admium *T*elluride) detector and a Hyperion 3000 microscope (Bruker, Vienna, Austria). 320 scans of the sample were acquired using a Globar (silicon carbide) rod as mid-IR source and a 15× IR objective as focus. During the measurement, the sample was positioned on a BaF_2 window. A correction of atmospheric influences was performed with the software OPUS 6.5.

3 Results and discussion

3.1 Crystal structure of $Ca_{12}Ge_{17}B_8O_{58}$

The new calcium borogermanate $Ca_{12}Ge_{17}B_8O_{58}$ crystallizes isotypically to $Cd_{12}Ge_{17}B_8O_{58}$ [2] in the tetragonal space group $P\bar{4}$ (No. 81). The structure is composed of $[Ge_4O_{12}]_n$ chains (Fig. 2a). These chains are interconnected into a $[Ge_4O_{10.5}]_n$ network *via* corner sharing (Fig. 2b). Together with the $[Ge(B_2O_7)_4]^{28-}$ clusters (Fig. 2c) a three-dimensional $[Ge_{17}B_8O_{58}]^{24-}$ framework (Fig. 2d) is built, forming tunnels of five-, six-, and seven-membered rings along the *c* axis which are occupied by Ca^{2+} cations (Fig. 3).

The $Ge(1)O_4$, $Ge(4)O_4$, and $Ge(5)O_4$ tetrahedra as well as the $Ge(2)O_6$ octahedra are interconnected *via* vertex sharing building up the above mentioned $[Ge_4O_{12}]_n$ chains (Fig. 2a). Each of these chains is connected with three others to form a three-dimensional $[Ge_4O_{10.5}]_n$ network *via* corner sharing (Fig. 2b). The three-dimensional $[Ge_4O_{10.5}]_n$ network builds up small four-membered and large 24-membered rings forming tunnels along the *c* axis (Fig. 2b). A B_2O_7 dimer is formed by the $B(1)O_4$ and $B(2)O_4$ tetrahedra sharing a common oxygen atom. Four of those dimers are connected to the $Ge(3)O_4$ tetrahedron *via* vertex sharing building up the $[Ge(B_2O_7)_4]^{28-}$ clusters (Fig. 2c). The clusters are positioned in the large 24-membered ring tunnels of the three-dimensional $[Ge_4O_{10.5}]_n$ network *via* corner sharing, forming the three-dimensional $[Ge_{17}B_8O_{58}]^{24-}$ anionic structure with tunnels of five-, six-, and seven-membered rings along the *c* axis (Fig. 2d) where the Ca^{2+} cations are located (Fig. 3). The five-membered ring is composed of three BO_4 and two GeO_4 tetrahedra. The six-membered ring consists of two BO_4 tetrahedra, three GeO_4 tetrahedra, and one GeO_6 octahedron, whereas the seven-membered ring is formed by one BO_4 tetrahedron, four GeO_4 tetrahedra, and two GeO_6 octahedra.

All three Ca atoms are eight-fold coordinated to oxygen anions with Ca–O distances ranging from 2.311(2) to 3.011(2) Å. The values correspond very well to the Ca–O distances of $Ca_{10}Ge_{16}B_6O_{51}$ ranging from 2.256(5) to 3.023(4) Å [2]. The two B atoms are coordinated by four oxygen atoms forming distorted tetrahedra with B–O distances ranging from 1.387(4) to 1.581(4) Å. Like in $Cd_{12}Ge_{17}B_8O_{58}$ [2], the B–O bond lengths exhibit a large variation, which stems from the different coordination environments of the oxygen atoms in the BO_4 tetrahedra. The atom Ge3 is located on the four-fold axis, whereas all other Ge atoms are on general positions. Ge2 is octahedrally coordinated to oxygen anions with Ge–O distances ranging from 1.859(2) to 1.910(2) Å, whereas Ge1, Ge3, Ge4, and Ge5 are tetrahedrally coordinated by oxygen atoms with Ge–O distances between 1.733(2) and 1.796(2) Å. Table 4 shows the interatomic distances of $Ca_{12}Ge_{17}B_8O_{58}$. Table 5 compares the unit cell parameters of $Ca_{12}Ge_{17}B_8O_{58}$ and $Cd_{12}Ge_{17}B_8O_{58}$.

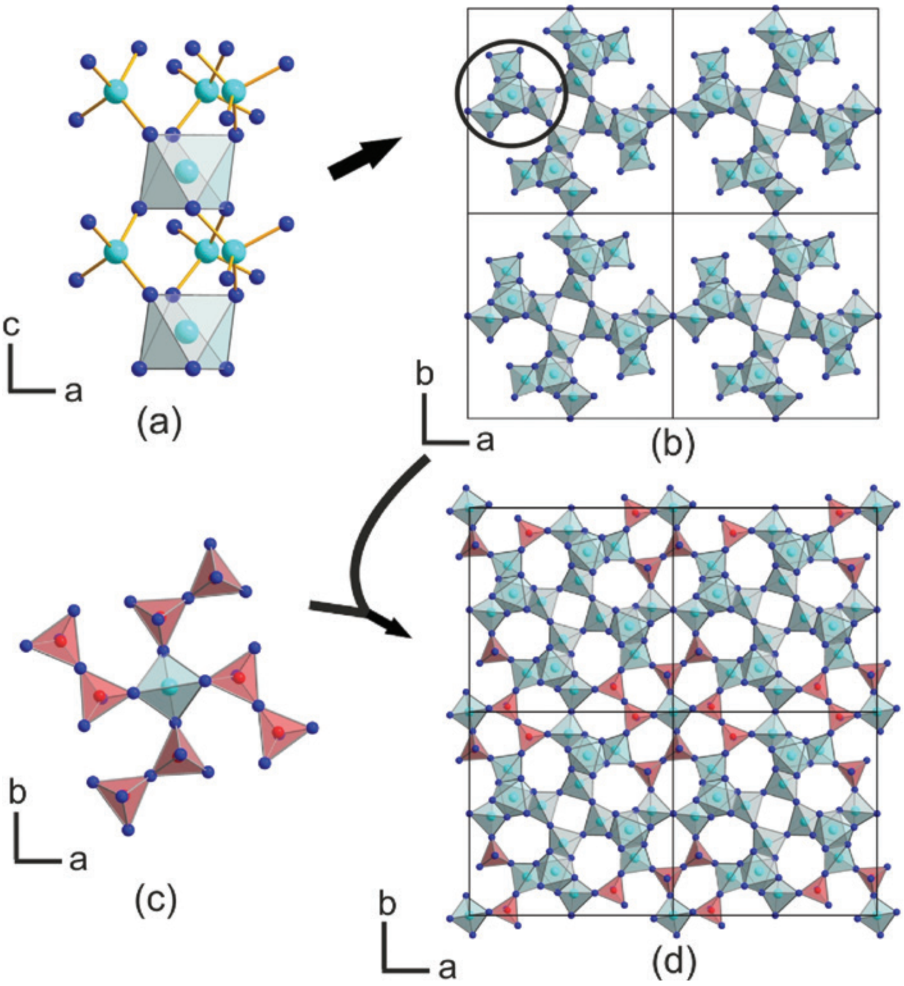

Fig. 2: Scheme showing the $[Ge_4O_{12}]_n$ chain (a); construction of the $[Ge_4O_{10.5}]_n$ network (b); $[Ge(B_2O_7)_4]$ unit (c); the three-dimensional $[Ge_{17}B_8O_{58}]^{24-}$ anionic structure (d).

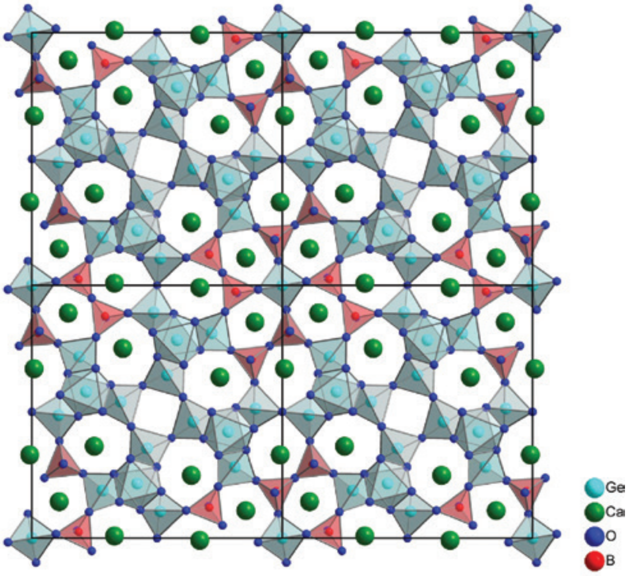

Fig. 3: Crystal structure of $Ca_{12}Ge_{17}B_8O_{58}$ along the *c* axis.

3.2 IR spectroscopy

Figure 4 displays the results of the IR spectroscopic measurement, which was performed on a single crystal of $Ca_{12}Ge_{17}B_8O_{58}$. The spectrum shows a series of different absorption bands with frequencies below 1500 cm^{-1} and from 2800–3000 cm^{-1}, which can be associated with various vibrations of the different units in the crystal. The absorption bands between 645 and 875 cm^{-1} can be related to various modes within the different GeO_4 tetrahedra, GeO_6 octahedra and BO_4 tetrahedra [14–18]. The region of 925–1200 cm^{-1} is due to bands of the symmetric stretching and asymmetric stretching modes of BO_4 tetrahedra [18–21]. The two small peaks between 1380 and 1450 cm^{-1} might represent a combinational tone of two vibration modes of Ge–O–Ge bonds [22]. Due to the overlap of the various bands, a precise assignment of the individual bands is impossible. The absorption bands at

Table 5: Comparison of the isotypic structures $Ca_{12}Ge_{17}B_8O_{58}$ and $Cd_{12}Ge_{17}B_8O_{58}$ (standard deviations in parentheses).

Empirical formula	$Ca_{12}Ge_{17}B_8O_{58}$	$Cd_{12}Ge_{17}B_8O_{58}$
Reference	This work	[2]
Molar mass, g mol^{-1}	2730.3	3598.3
Unit cell dimensions		
a, Å	15.053(8)	14.928(2)
c, Å	4.723(2)	4.698(1)
V, Å^3	1070.2(2)	1046.8(3)

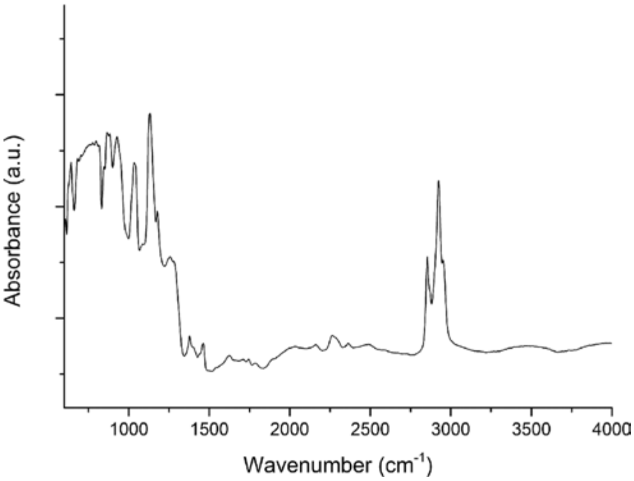

Fig. 4: FT-IR reflectance spectrum of $Ca_{12}Ge_{17}B_8O_{58}$.

2800–3000 cm^{-1} belong to the grease, which was used to fix the crystal on the class fiber. In summary, it can be stated that the IR spectrum confirms the existence of tetrahedrally and octahedrally coordinated germanium, and tetrahedrally coordinated boron atoms.

4 Conclusions

With the syntheses of $Ca_{12}Ge_{17}B_8O_{58}$, the list of known alkaline earth borogermanates could be extended to include an additional compound. It crystallizes in the tetragonal space group $P\bar{4}$ (No. 81), being isotypic to $Cd_{12}Ge_{17}B_8O_{58}$ [2]. The main structural characteristics are $[Ge_4O_{12}]_n$ chains which are composed of GeO_4 tetrahedra and GeO_6 octahedra. The chains form a three-dimensional $[Ge_4O_{10.5}]_n$ network *via* corner sharing. Together with the $[Ge(B_2O_7)_4]^{28-}$ clusters, the three-dimensional $[Ge_{17}B_8O_{58}]^{24-}$ anionic structure with tunnels of five-, six-, and seven-membered rings is built. The tunnels are occupied by the Ca^{2+} cations. Our future research interests will be focused on the exploration of other alkaline earth and divalent transition metal borogermanates.

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