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The Structure of Calcium Erbium Germanium Borate $Ca_3Er_3Ge_2BO_{13}$, a Sulphohalite-Related Compound

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Abstract

New series of fluorite-related phases in the system $(RE)_2O_3$–CaO–GeO_2 have been found to be stabilized by the addition of a small amount (1–2 wt%) of B_2O_3. A subsequent structure determination of one of the phases, $Ca_3Er_3Ge_2BO_{13}$, has revealed that the boron occupies interstitial sites in the fluorite-related structure. The compound has cubic symmetry, a = 10·452 (2) Å, space group $F\bar{4}3m$, containing eight fluorite subcells. The structure was refined to wR = 0·017 for 491 data. The RE/Ca atoms together with Ge atoms form a face-centred-cubic fluorite-like cation sublattice with Ge ordered at the cube corners and RE/Ca occupying the face centres. The displacement of O atoms along the subcell $\langle 111 \rangle$ directions to give tetrahedral coordination around the Ge atoms creates large interstitial sites at the subcell body centres. Half of the interstitial sites are occupied by (BO_4) tetrahedral clusters, and the other half are occupied by O atoms. An alternative description as a perovskite-derivative structure is presented and the structural relationship to sulphohalite is discussed.

Introduction

A number of oxide minerals form the bases for extensive solid-solution series, where the controlled substitution of cations in synthetic equivalents can lead to materials with important physical properties that make them suitable for device applications. These include spinels, perovskites and garnets. The latter materials have found particularly widespread application in magnetic bubble memories, microwave signal processing devices, lasers and optical telecommunications. Recently, material scientists have been trying to synthesize garnet compounds containing small rare earths on the octahedral sites. In attempts at Bell Laboratories by one of us (JPR) to grow single crystals of garnets of general composition $Ca_3RE_2Ge_3O_{12}$, RE = Er, Yb, Lu, Y, using a B_2O_3/PbO flux, it was observed that both Pb and B were incorporated in the reaction mixtures, resulting in the crystallization of new series of compounds with cubic symmetry and with X-ray diffraction patterns similar to those for (anion-deficient) fluorite-related structures. This paper reports the synthesis and the determination of the crystal structure for one of the new phases, with composition $Ca_3Er_3Ge_2BO_{13}$.

Experimental

Crystal growth

Crystals of $Ca_3Er_3Ge_2BO_{13}$ were obtained from a flux melt by weighing the following component powders into a 10^5 cm^3 pure platinum crucible: $CaCO_3$ 3·00, Er_2O_3 3·83, GeO_2 3·14, B_2O_3 4·00, PbO 6·00 g. The covered crucible was placed in a horizontally loaded, resistively fired, temperature-programmable furnace. The furnace was heated at an uncontrolled rate to 1523 K and controlled at that temperature for 3 h to effect reaction of the components and solution in the flux. A controlled cooling rate at 3·0 K h^{-1} was then initiated and continued to ~773 K when furnace power was shut off. The crucible was then removed and allowed to cool to room temperature. To extract the crystals from the solidified flux, the crucible was immersed in a hot, dilute solution of $HNO_3:H_2O$ in a ratio of 1:4 by volume. When the flux had been dissolved, the crystals were washed several times in deionized water and then dried.

Microprobe analyses

Microprobe analyses performed on different crystals from the same batch show variable substitution of

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Table 1. *Results of microprobe analyses* (%)

	Crystal 1	Crystal 2	Theoretical ($Ca_3Er_3Ge_2BO_{13}$)
Ca	12·1	12·5	12·2
Er	40·3	49·8	50·9
Pb	12·8	nil	nil
Ge	13·7	15·1	14·7
B	21·1*	22·6*	1·1
O			21·1

* These values were obtained by difference.

lead for erbium. Two extreme examples are given in Table 1. Also listed in Table 1 are theoretical weight percentages corresponding to the lead-free composition $Ca_3Er_3Ge_2BO_{13}$. It is seen that the analyses for crystal 2 correspond closely to the values for this composition. The substitution of Pb for Er is accompanied by a decrease in the Ge content, suggesting that Pb is stabilized in the structure in the tetravalent state, with charge balance achieved by vacancies on the Ge sites. The presence of boron as major constituent in the crystals was detected qualitatively by X-ray fluorescence. Also, the compound did not form unless the starting powders contained B_2O_3.

X-ray diffraction

Precession photographs taken with Mo $K\alpha$ radiation revealed that the single crystals of the mixed oxide were cubic with a lattice parameter of about 10·45 Å. The only systematic absences were those corresponding to an F lattice, namely $h + k, k + l, l + h = 2n + 1$. These absences and the equivalence between the hkl and the khl reflections indicated that the crystal symmetry belonged to one of the space groups $Fm3m$, $F\bar{4}3m$, or $F432$. For the intensity-data collection a sphere of 0·19 mm in diameter was mounted on a Philips PW1100 four-circle X-ray diffractometer using Ag $K\alpha$ radiation and a graphite monochromator. Least-squares refinement of 2θ values of 16 reflections chosen in the region where complete α_1/α_2 separation occurred gave the cubic cell parameter 10·452 (2) Å. All reflections in the θ interval of 3–33° were measured by the ω-scan technique with a variable scan width given by $\Delta\theta = (1{\cdot}40 + 0{\cdot}15 \tan\theta)^\circ$ and a speed of $0{\cdot}02^\circ\ s^{-1}$. The background was measured at each end of the interval for half the scan time. A total of 8507 reflections were measured which gave, after averaging, a total of 491 reflections. Since the structure proved to be noncentrosymmetric, the final averaging was done according to the $\bar{4}3m$ point group. The agreement factor between averaged intensities was 0·044. The average difference in intensity between Friedel pairs was of the same order of magnitude, which indicated that the anomalous-dispersion effect was negligible. The intensities were converted to structure factors by applying Lorentz, polarization and absorption corrections. Scattering-factor curves for neutral Ca, Er, Ge, B and O given in *International Tables for X-ray Crystallography* (1974) were used. The curves for Ca, Er and Ge were corrected for anomalous dispersion using the data of Cromer & Liberman (1970). All computing was performed on the CNRS computer using the Enraf–Nonius structure determination package and the XRAY 72 system of programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Structure determination and refinement

The centrosymmetric space group $Fm3m$ was assumed at the beginning of the structure determination. The heavy-atom positions were located from the three-dimensional Patterson function. The major Patterson peaks could all be explained by placing 24 Ca,Er atoms in position 24(e) (x00), with $x \sim 0{\cdot}23$ and 8 Ge atoms in position 8(c) $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$. An initial R factor of 0·30 was reduced to 0·24 after three cycles of refinement. A three-dimensional Fourier map was calculated, which revealed the presence of O atoms at (xxx) positions, with $x \simeq 0{\cdot}15$ and 0·42. A further peak at $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ was tentatively identified as boron. However, the placing of O atoms at the two 32-fold positions along the cube body diagonal was inconsistent with the stoichiometry (48 oxygens per unit cell) and the symmetry of the position 4(b) was incompatible with expected boron coordinations (tetrahedral or triangular). The dilemma was resolved by transferring to the noncentrosymmetric space group $F\bar{4}3m$, in which the (Ca,Er) site remained the same and the eight Ge positions were split into two fourfold positions, 4(c) $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$ and (4d) $(\frac{3}{4}\frac{3}{4}\frac{3}{4})$. The 48 O atoms were placed in three sets of 16-fold (xxx) positions, with $x_1 \simeq 0{\cdot}15$, $x_2 \simeq 0{\cdot}42$, and $x_3 \simeq 0{\cdot}85$, respectively, while the four B atoms were placed in the fourfold $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ positions. In the $F\bar{4}3m$ noncentrosymmetric space group these latter positions have a $\bar{4}3m$ site symmetry which allows a suitable coordination for the B atoms. Refinement of the scale, coordinates and isotropic temperature factors for this model reduced the R factor to 0·076. Refinement of the occupancy factor for the (Ca,Er) site (assumed up till now to be 0·5 Ca + 0·5 Er) gave a value greater than unity which was explained by the presence of some lead at this site. With a new composite scattering curve (0·5 Ca + 0·44 Er + 0·06 Pb) and inclusion of an isotropic extinction parameter, further refinement led to R and wR values of 0·054 and 0·038 respectively. The extinction correction was appreciable; for 11 reflections the $|F_o|$ was corrected by more than 25%. In the subsequent cycles these reflections were given zero weight. At this stage a difference-Fourier analysis revealed a single peak at the (000) position which in the Fourier map was of the same height as the other

Table 2. *Final positional and thermal parmeters*

		x	y	z	U (Å^2)
$Ca_{0.50}Er_{0.44}Pb_{0.06}$	24(f)	0·22807 (3)	0	0	0·00673 (8)
Ge(1)	4(c)	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0·0070 (2)
Ge(2)	4(d)	$\frac{3}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	0·0033 (2)
B	4(b)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0·0085 (17)
O(1)	16(e)	0·1512 (3)	0·1512	0·1512	0·0111 (10)
O(2)	16(e)	0·4180 (3)	0·4180	0·4180	0·0113 (10)
O(3)	16(e)	0·8461 (3)	0·8461	0·8461	0·0129 (10)
O(4)	4(a)	0	0	0	0·0103 (13)

Table 3. *Interatomic distances* (Å) *and angles* (°)

	Distance	O–M–O angle
(Ca,Er) polyhedron		
(Ca,Er)–O(1) × 2	2·375 (4)	
–O(2) × 2	2·325 (4)	
–O(3) × 2	2·403 (4)	
–O(4)	2·385 (4)	
Average	2·370	
O(1)–O(3) × 4	3·189 (5)	83·7 (1)
O(1)–O(4) × 2	2·737 (4)	70·2 (1)
O(3)–O(4) × 2	2·786 (4)	71·2 (1)
O(1)–O(2) × 2	2·970 (5)	78·4 (1)
O(3)–O(2) × 2	3·777 (5)	85·7 (1)
O(2)–O(2)	2·425 (5)	62·9 (1)
Ge(1) tetrahedron		
Ge(1)–O(1) × 4	1·789 (4)	First nearest neighbours
–O(2) × 4	3·041 (4)	Second nearest neighbours
O(1)–O(1) × 6	2·921 (5)	109·5
O(1)–O(2)	2·970 (5)	70·5
Ge(2) tetrahedron		
Ge(2)–O(3) × 4	1·740 (4)	
O(3)–O(3) × 6	2·842 (5)	109·5
B tetrahedron		
B–O(2) × 4	1·485 (4)	
O(2)–O(2) × 6	2·425 (5)	109·5

oxygen peaks. Inclusion of this extra oxygen, O(4), and subsequent refinement of all parameters [with the exception of x for O(2) because of high correlations with x for O(1), due to the pseudo centre of symmetry relating these two atoms] led to convergence at R and wR values of 0·026 and 0·017 respectively, for all reflections. During the last few cycles the occupancy factor of the Ge(2) site was allowed to vary; however, it remained very close to unity. These results clearly indicated that the formula of this compound was $Ca_3Er_3Ge_2BO_{13}$ with some Pb impurity substituting for the large cations. The final positional and thermal parameters are given in Table 2.* Calculated interatomic distances and angles are given in Table 3.

As we have shown above the structure of $Ca_3Er_3Ge_2BO_{13}$ is indeed non-centrosymmetric. However, if one neglects the differences in thermal parameters, the non-centrosymmetric character is actually due only to the O(2) anions and to the difference in scattering power between the B cations at ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$) and the O(4) anions at (000). As a consequence this compound failed all tests related to the non-centrosymmetric character, such as the piezoelectric, the anomalous-dispersion effect and the second-harmonic-generation tests.

Description of the structure

The unit-cell contents for $Ca_3Er_3Ge_2BO_{13}$ are viewed in perspective along [110] in Fig. 1. (1$\bar{1}$0) planes or slabs of atoms are viewed edge-on in this figure and it is apparent that (1$\bar{1}$0) planes of large cations (Ca,Er) alternate with (1$\bar{1}$0) slabs containing ⟨110⟩ strings of either (Ca,Er) + $(GeO_4)^{4-}$ tetrahedra or $(BO_4)^{5-}$ tetrahedra or O(4) oxygen atoms. These three types of ⟨110⟩ strings stack consecutively along ⟨001⟩ to form (1$\bar{1}$0) slabs with the sequence: O(4); (Ca,Er) + $(GeO_4)^{4-}$ tetrahedra; $(BO_4)^{5-}$ tetrahedra; (Ca,Er) + $(GeO_4)^{4-}$ tetrahedra; O(4); ... *etc.*

The structure of $(Ca,Er)_6Ge_2BO_{13}$ is closely related to the fluorite structure as illustrated in Fig. 2. The (Ca,Er) and Ge atoms form an ordered fluorite-like face-centred-cubic cation sublattice, with Ge ordered at the cube corners and (Ca,Er) at the face centres.

Consideration of the anion sublattice leads to the recognition of two distinct types of fluorite-like subcells which are shown outlined in Fig. 2. To illustrate the relationship more clearly, the origin has been moved from oxygen O(4) to the Ge atoms. In the subcell depicted on the right of Fig. 2, the anion sublattice remains intact [*i.e.* eight oxygens per subcell, 4 × O(1) + 4 × O(3)], but the anions are displaced along the

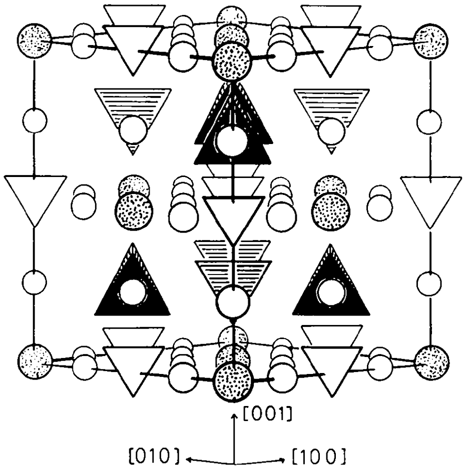

Fig. 1. The structure of $(Ca,Er)_6Ge_2BO_{13}$ viewed approximately along [110]. Shaded and unshaded tetrahedra correspond to $[GeO_4]^{4-}$ and $[BO_4]^{5-}$ respectively. Shaded and unshaded circles represent interstitial oxygen, O(4), and (Ca,Er) respectively. The unit-cell outline is marked.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36011 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

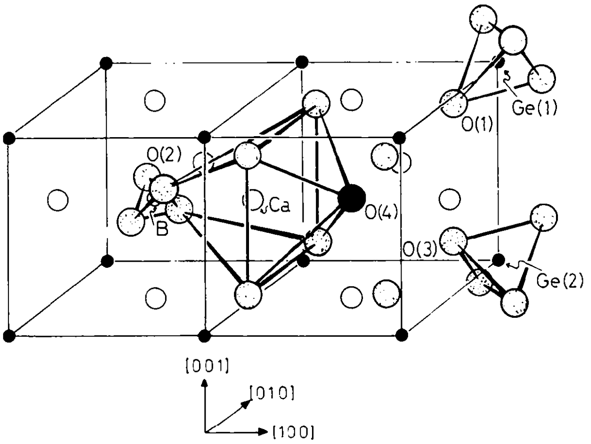

Fig. 2. Partial representation of the structure for $(Ca,Er)_6Ge_2BO_{13}$, showing its relationship to fluorite. Two fluorite-like face-centred cubic subcells are outlined. Small filled and open circles represent Ge and B respectively; medium circles correspond to (Ca,Er) and large stippled circles to oxygen. The large filled circle represents the interstitial oxygen, O(4). Oxygen polyhedra around independent cations are outlined. Two (Ca,Er) atoms have been omitted for clarity. Note that the origin of the cubic cell of $(Ca,Er)_6Ge_2BO_{13}$ is on the O(4) oxygen atom.

⟨111⟩ body diagonals towards the cube corners to give tetrahedral coordination around the Ge atoms. The displacements are 0·52 Å for O(3) and 0·47 Å for O(1) from the ideal fluorite positions, resulting in the formation of a large hole at the $(\frac{1}{2}\frac{1}{2}\frac{1}{2})_{\text{fl}}$ interstitial anion site. This site is fully occupied by oxygen, O(4), in $(Ca,Er)_6Ge_2BO_{13}$. In the subcell depicted on the left of Fig. 2, half the anions are missing from the ideal fluorite array, and the remaining four are displaced along the ⟨111⟩ body diagonals towards the cube centre. In this case the displacements from ideal fluorite positions are 0·78 Å, resulting in the formation of a tetrahedral cluster of O atoms, coordinated to a B atom at the cube centre.

The large cation, (Ca,Er), is displaced by 0·23 Å from the fluorite-like cube face centres towards the O(4) interstitial oxygen site and is coordinated to seven O atoms. The coordination polyhedron is described most simply as a modified octahedron in which one apical oxygen is replaced by an O(2)—O(2) pair, as shown in Fig. 2.

The structure of $Ca_3Er_3Ge_2BO_{13}$ may equally be described as a perovskite-derivative structure ABX_3, in which two types of B atoms, represented here by O(4) and the BO_4 tetrahedra, are octahedrally coordinated to the (Ca,Er) atoms (*i.e.* X) and form a three-dimensional array by corner-sharing. The GeO_4 tetrahedra occupy the large holes created by such an array, namely the cuboctahedral A sites of the perovskite structure. The ordering of the two types of B atoms in alternate sites along the cube edges gives rise to an F-centred 2 × 2 × 2 perovskite superlattice.

Bond lengths and angles for the various polyhedra are given in Table 3. The average M—O bond lengths are all very close to those calculated using ionic radii tabulated by Shannon (1976), *e.g.* a B—O distance of 1·49 Å is calculated for tetrahedrally coordinated boron compared with 1·485 (4) Å observed. The calculated Ge—O tetrahedral bond length of 1·77 Å (Shannon, 1976) is intermediate between the mean values observed for Ge(1)—O, 1·789 (4) Å, and Ge(2)—O, 1·740 (4) Å. The longer bond length is associated with the germanium atom, Ge(1), which has four further oxygen neighbours, O(2), at 3·041 (4) Å. For comparison, the second nearest oxygen neighbours for Ge(2) are more than 4 Å away. The observed average M—O bond length for the large cation, 2·370 (4) Å, agrees with a value of 2·37 Å for a mixed cation site $(Ca^{2+}_{0\cdot 50}Er^{3+}_{0\cdot 44}Pb^{4+}_{0\cdot 06})$. For comparison, a value of 2·40 Å is calculated assuming Pb^{2+}.

Relationship to sulphohalite

Sulphohalite, $2Na_2SO_4.NaCl.NaF$, has a structure very closely related to that of $(Ca,Er)_6Ge_2BO_{13}$. The relationship is easily visualized by comparing the formulae as shown below:

$$(Ca,Er)_6Ge_2BO_{13} = (Ca,Er)_6.(GeO_4)_2(BO_4).O$$
$$\text{sulphohalite} = Na_6.(SO_4)_2.Cl.F.$$

The structures are directly related, with interchange of $(SO_4)^{2-}$ tetrahedra for $(GeO_4)^{4-}$ tetrahedra, Cl^- for $(BO_4)^{5-}$, F^- for O^{2-}, and Na^+ for (Ca^{2+},Er^{3+}). The replacement of the tetrahedral group $(BO_4)^{5-}$ by Cl^- gives octahedral coordination around the large cation, and the structure is described in the centrosymmetric space group $Fm3m$ (Pabst, 1934).

In the sulphohalite structure the network of corner-sharing octahedra is formed by the Na atoms. The cuboctahedral holes of this arrangement are occupied by the $(SO_4)^{2-}$ tetrahedra while the two types of octahedra are occupied by the Cl and F atoms, respectively.

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