CRYSTAL STRUCTURE OF BaTm\(_2\)F\(_8\)

CRYSTALLOGRAPHY

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Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

Abstract

Full Text

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CRYSTALLOGRAPHY

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CRYSTAL STRUCTURE OF $BaTm_2F_8$

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In the systems BaF_2—TRF_3 (TR–Ln from Er to Yb and Y), double compounds $BaF_2 \cdot 2TRF_3 = BaTR_2F_8$ are formed. Single crystals of one representative of this class, $BaTm_2F_8$, were grown by the Stockbarger method in a fluorinating atmosphere. Structural analogues of $BaTm_2F_8$ have not been found in the literature.

The x-ray experimental material was obtained from a spherical specimen with $d = 0.35$ mm. The principal difficulty in the determination of the $BaTm_2F_8$ structure was the very high contrast in the scattering power of the two types of atoms, which complicated the determination of the coordinates of the F atoms. In this connection, reflection intensities were measured on a single-crystal nonautomatic diffractometer with a scintillation counter (Mo radiation).

Fig. 1. Difference projection $\rho_{\text{exp}} - \rho_{(\text{Ba, Tm})}$ along [001]. Contours are drawn at intervals of 10 el/Å^2

The structure was solved by the heavy-atom method from the projections $hk0$ and $0kl$, on the basis of experimental material from 256 reflections in the $hk0$ zone and 160 $0kl$ reflections ($\max \sin\theta/\lambda = 1.40$ Å^{-1}). Laue patterns and rotation x-ray photographs revealed monoclinic symmetry of the crystals. The parameters of the elementary cell were then refined on the diffractometer: $a = 6.935 \pm$

Fig. 2. Projections of the structure along [001] (A), [100] ( ). Black circles are Ba atoms.

± 0.001 Å; $b = 10.457 \pm 0.002$ Å; $c = 4.243 \pm 0.001$ Å; $\beta = 99°40'(\pm 2')$.

This cell contains two formula units of $BaTm_2F_8$. Systematic extinctions and analysis of the distribution of peaks of the interatomic function led to the space group $C_{2h}^3 = C2/m$.

From the character of the distribution of maxima on Patterson projections along [001] and [100], it was established that the Ba and Tm atoms occupy

Table 1

Atomic coordinates and individual thermal factors in the structure of $BaTm_2F_8$

Atoms	x/a	y/b	z/c	Multiplicity	$B_j = B + u_j$
Ba	0	0	0	2	−0.58
Tm	0.5	0.1761	0.5	4	−0.35
F_1	0.187	0.140	0.560	8	−0.75
F_2	0.393	0	0.227	4	−0.70
F_3	0.5	0.239	0	4	−0.83

different crystallographic positions in the space group $C2/m$. Two Ba atoms are located at centers of symmetry related by the oblique translation (000 and $\frac{1}{2}\frac{1}{2}0$), while four Tm atoms occupy a fourfold set (on twofold axes). The cations of the two types in the structure are arranged in alternating layers parallel to (001).

The F atoms appeared on electron-density projections along [001] and [100]. They occupy three different positions: one eightfold—general—and two fourfold positions (on mirror planes and on twofold rotation axes).

The atomic coordinates and individual isotropic thermal corrections were refined by the method of least squares, and also by constructing difference projections (with Ba and Tm atoms removed) along [001] and [100] (Fig. 1).

The final atomic coordinates in the structure of $BaTm_2F_8$ are given in Table 1. The discrepancy factors for all nonzero reflections are: $R_{hk0} = 5.98\%$ and $R_{0kl} = 6.16\%$. If the four* strongest reflections weakened by extinction are excluded, then $R_{hk0} = 5.09\%$ and $R_{0kl} = 5.66\%$ (overall thermal factor $B = -0.42$).

The Tm atom is surrounded by 8 F anions, forming a slightly distorted Thomson cube. The Tm polyhedra, sharing edges, form layers parallel to the (001) plane consisting of six-membered rings (Fig. 2A), which are connected by the vertices of the polyhedra into a continuous three-dimensional motif (Fig. 2B). These layers are translationally identical and are arranged one above another; the rings form channels penetrating the structure along the z axis. Ba atoms in 12-fold coordination are located in the channels at the same levels as the F anions common to two neighboring layers. The Ba polyhedra, sharing common bases, form slightly skewed columns, and with the Tm polyhedra have only common edges. All the large Ba and F ions are concentrated in layers parallel to the (201) plane; between these layers are the smaller Tm ions.

Each F_1 atom is bonded to two Ba and two Tm atoms; F_2 and F_3, to one Ba and two Tm atoms. In the structure studied, Pauling' s second rule is well fulfilled; the sum of the bond strengths converging on a Fe atom is 1.0 ± 0.09.

The average value of the interatomic distance Tm–F is close to the sum of the ionic radii according to Ahrens ([1]): 0.89 Å +1.33 Å = 2.22 Å; the average distance F–F = 2.76 Å and especially Ba–F = 2.82 Å are substantially greater

* For $hk0$: 060, 200, 130, 330; for $0kl$: 060, 002, 021, 0,4

sum of the ionic radii for 12-fold coordination of Ba. Since the structure is characterized by a rigid three-dimensional framework of TR polyhedra, the Ba –F distances are determined by the cell dimensions of this framework, or, ultimately, by the radius of the rare-earth ion. In the case of larger TR^{3+} ions,

Table 2

Interatomic distances (Å) in the structure of $BaTm_2F_8$

Tm polyhedron	Tm polyhedron	Ba polyhedron
Tm–F_1 2.25	F_1–F_1 2.55	Ba–F_2 2.73
Tm–F_1 2.30	F_1–F_1 2.54	Ba–F_3 2.73
Tm–F_2 2.23	F_2–F_2 2.50	Ba–F_1 2.88
Tm–F_3 2.17	F_1–F_3 2.81	Ba–F_1 2.86
	F_2–F_3 2.83	
	F_1–F_3 2.76	
	F_1–F_3 2.70	
	F_1–F_2 3.25	
	F_1–F_2 2.63	
avg. 2.23	avg. 2.76	avg. 2.82

the Ba–F distances would evidently already be too large, and therefore such ions do not form compounds of this structural type.

The structure that has been deciphered initiates a new structural type for fluorides. The sharp difference in the coordination numbers of the two cations (12 for Ba and 8 for Tm) determines the strict stoichiometry of this type of compound and the absence, in the systems BaF_2–TRF_3 (TR–Ln from Er to Yb), of appreciable regions of homogeneity based on it.

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Note: Figure translations are in progress. See original paper for figures.