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$Ba_3Zr_2S_7$, the Low-Temperature Polymorph

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Abstract

The synthesis and crystal structure of the low-temperature polymorph of barium zirconium sulfide is reported. The title compound contains double $BaZrS_3$ perovskite layers separated by BaS layers. The compound is the $n = 2$ member of the $Ba_{n+1}Zr_nS_{3n+1}$ Ruddlesden–Popper sulfides. This polymorph of $Ba_3Zr_2S_7$ was crystallized at 1203 K in a $BaCl_2$/CsCl eutectic flux and has $P4_2/mnm$ crystal symmetry in contrast to the high-temperature polymorph which has $I4/mmm$ crystal symmetry.

Comment

The synthesis of $Ba_3Zr_2S_7$ was first accomplished by Saeki, Yajima & Onoda (1991) from the reaction of $BaCO_3$ and $BaZrO_3$ under flowing CS_2 at 1373 K. The structure and composition of the product was determined from an analysis of electron-diffraction data and a Rietveld profile analysis of the powder X-ray diffraction data. Their studies clearly showed the compound to be a novel example of the $Ba_{n+1}Zr_nS_{3n+1}$ Ruddlesden–Popper sulfides and a rare example of a perovskite-related sulfide phase. In a concurrent study in our laboratory, we investigated the chemistry of the $Ba_{n+1}M_nS_{3n+1}$ Ruddlesden–Popper sulfides where M = Zr and Hf by way of high-temperature $BaCl_2$ flux synthesis in sealed silica ampules (Chen & Eichhorn, 1991; Chen, Eichhorn & Fanwick, 1992; Chen, Wong-Ng & Eichhorn, 1993; Chen, Eichhorn & Wong-Ng, 1994). We were able to prepare the n = 1–5 members of this series in single crystal form. The single crystal studies revealed a progression of crystal symmetries as a function of n (Eichhorn, 1994). During the course of our studies, we prepared single crystals of $Ba_3Zr_2S_7$ in a $BaCl_2$ flux at 1323 K that possessed $I4/mmm$ symmetry (Chen *et al.*, 1994). This structure displayed metric parameters quite similar to those of the other $Ba_{n+1}Zr_nS_{3n+1}$ phases which contrasted with the low-temperature $Cccm$ structure reported by Saeki *et al.* (1991). Here, we report the single crystal structure of the $Ba_3Zr_2S_7$ low-temperature polymorph crystallized at 1203 K. We found that the compound has $P4_2/mnm$ crystal symmetry and also possesses metric parameters similar to the other $Ba_{n+1}Zr_nS_{3n+1}$ phases characterized by single-crystal X-ray diffraction.

The structure contains double $BaZrS_3$ perovskite layers of corner-shared ZrS_6 octahedra and 12-coordinate Ba^{2+} ions. Each double perovskite block is separated from the next by a BaS layer where the Ba^{2+} ions are nine-coordinate. The structure is virtually identical to the high temperature $I4/mmm$ polymorph (Chen *et al.*, 1994) with a few exceptions listed below. The compound is a member of the general class of $Ba_{n+1}Zr_nS_{3n+1}$ phases that are isostructural with the $Sr_{n+1}Ti_nO_{3n+1}$ Ruddlesden–Popper series (Ruddlesden & Popper, 1957, 1958). The Zr—S distances range from 2.4972 (3) to 2.5557 (7) Å, where the long Zr—S2 contact of 2.5557 (7) Å is distal to the BaS layer. This behavior is the same as all of the other $Ba_{n+1}Zr_nS_{3n+1}$ compounds that have been characterized by single crystal X-ray diffraction (Chen & Eichhorn, 1991; Chen, Eichhorn & Fanwick, 1992; Chen, Wong-Ng & Eichhorn, 1993; Chen, Eichhorn & Wong-Ng, 1994) but contrasts with the $Ba_3Zr_2S_7$ structure reported by Saeki *et al.* (1991). The Ba—S contacts are in the range 3.1857 (13)–3.697 (2) Å with a short contact of 3.0833 (15) Å between Ba1 and S3. Unlike the $I4/mmm$ polymorph (Chen *et al.*, 1994), the ZrS_6 octahedra are buckled with Zr—S—Zr angles of 161.9 (1)–175.0 (1)°.

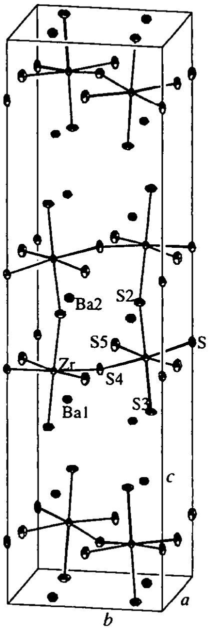

Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the $Ba_3Zr_2S_7$ unit cell. Only the Zr—S bonds are shown for clarity. The displacement ellipsoids are drawn at the 70% probability level.

Experimental

The title compound was prepared from the reaction of intimately ground BaS, Zr, and S powders (molar ratios 2:1:2) fired at 1373 K for four days in a sealed silica ampule. The resulting powder was then intimately mixed with 20 wt% $BaCl_2$/CsCl eutectic flux ($BaCl_2$/CsCl molar ratio 1:2) and sealed in an evacuated carbon-coated silica ampule. The reaction mixture was heated to 1203 K at 30 K h^{-1} and fired at 1203 K for four days. The reactants were then cooled to 773 K at a rate of 2 K h^{-1} and then cooled to room temperature over a 24 h period. The dark brown crystalline product was separated from the flux by dissolving the latter in deionized water. The product represented approximately 10% of the reaction mixture. Energy-dispersive X-ray analysis of the single crystals showed only Ba, Zr and S. All sample manipulations were conducted in a nitrogen drybox.

Crystal data

$Ba_3Zr_2S_7$
$M_r = 818.88$
Tetragonal
$P4_2/mnm$
$a = 7.0565\ (7)$ Å
$c = 25.371\ (4)$ Å
$V = 1263.3\ (3)$ Å^3
$Z = 4$
$D_x = 4.305$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 17.5$–$23.7°$
$\mu = 11.909$ mm^{-1}
$T = 153\ (2)$ K
Block
0.125 × 0.100 × 0.100 mm
Dark brown

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: semi-empirical ψ scans (*CAD*-4 *EXPRESS*; Enraf–Nonius, 1994)
$T_{min} = 0.222$, $T_{max} = 0.289$
3356 measured reflections
1833 independent reflections

1247 reflections with $F > 4\sigma(F)$
$R_{int} = 0.0321$
$\theta_{max} = 37.44°$
$h = -12 \rightarrow 0$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 43$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.094$
$S = 1.027$
1833 reflections
41 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0398P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 2.18$ e Å^{-3}
$\Delta\rho_{min} = -2.20$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.00042 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ba1	0.76051 (3)	$1 - x$	0.31854 (1)	0.00843 (8)
Ba2	0.74618 (4)	$1 - x$	1/2	0.01078 (10)
Zr1	1.25031 (4)	$x - 1$	0.40025 (2)	0.00511 (10)
S1	1	0	0.41591 (8)	0.0089 (3)
S2	0.2859 (2)	x	1/2	0.0133 (4)
S3	1.2218 (2)	$x - 1$	0.30203 (5)	0.0123 (2)
S4	1/2	1/2	0.39111 (8)	0.0104 (3)
S5	1/2	0	0.40450 (7)	0.0114 (2)

Table 2. *Selected geometric parameters (Å, °)*

Ba1—S3^{i}	3.0833 (15)	Ba2—S5^{iv}	3.4780 (13)
Ba1—S4	3.1857 (13)	Ba2—S4	3.697 (2)
Ba1—S3^{ii}	3.2842 (11)	Zr1—S5^{v}	2.4972 (3)
Ba1—S5^{iii}	3.3153 (12)	Zr1—S4^{v}	2.5025 (5)
Ba1—S1	3.437 (2)	Zr1—S3	2.5082 (14)
Ba2—S2	3.256 (2)	Zr1—S1	2.5294 (6)
Ba2—S1	3.3117 (14)	Zr1—S2^{v}	2.5557 (7)
S5^{v}—Zr1—S5^{iii}	175.04 (9)	S5^{v}—Zr1—S2^{v}	87.56 (4)
S5^{v}—Zr1—S4^{v}	90.301 (11)	S3—Zr1—S2^{v}	178.53 (6)
S5^{v}—Zr1—S3	92.45 (4)	Zr1^{ii}—S1—Zr1	161.92 (10)
S4^{v}—Zr1—S3	91.21 (6)	Zr1^{vi}—S2—Zr1^{vii}	164.02 (10)
S5^{v}—Zr1—S1	89.540 (12)	Zr1^{viii}—S4—Zr1^{vi}	169.38 (10)
S4^{v}—Zr1—S1	176.27 (7)	Zr1^{ii}—S5—Zr1^{vi}	175.05 (9)
S3—Zr1—S1	92.52 (6)		

Symmetry codes: (i) $\frac{1}{2}+y, \frac{3}{2}-x, \frac{1}{2}-z$; (ii) $2-x, -y, z$; (iii) $1-y, 1-x, z$; (iv) $1+y, x, 1-z$; (v) $1+x, y, z$; (vi) $x-1, y, z$; (vii) $x-1, y, 1-z$; (viii) $2-x, 1-y, z$.

All crystallographic calculations were performed on a PC with a 486 DX2/66 processor and 16 Mb of extended memory. Intensities were corrected for Lorentz and polarization factors, absorption and reduced to F_o^2 and (σF_o^2) using the program *XCAD*-4 (Harms, 1993). Systematic absences yielded the centrosymmetric tetragonal space group $P4_2/mnm$ (No. 136) or two possible non-centrosymmetric possibilities, namely, $P\bar{4}n2$ (No. 118) or $P4_2nm$ (No. 102). Intensity statistics indicated the centrosymmetric possibility. Successful refinements were not achieved employing either the face-centered or *I*-centered space groups. The twinning test was also applied and showed there was less than a 0.1% twinning possibility. The structure was successfully determined with the location of all but one of the unique atoms comprising the asymmetric unit in $P4_2/mnm$. A subsequent difference Fourier map revealed the location of the final S atom. The structure was refined to convergence with all atoms anisotropic in the final cycle. A final difference Fourier map possessed large peaks within 1 Å of the heavy atoms and $|\Delta\rho| = 2.18$ e Å^{-3}; the remainder of the map was featureless. An empirical correction for extinction was also applied to the data in the form $(F_c^2, \text{corr}) = k[1 + 0.001\chi F_c^2\lambda^3/\sin(2\theta)]^{-1/4}$ where $k = 0.03439$ is the overall scale factor. The value determined for χ was 0.00042 (6).

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *XCAD*-4 (Harms, 1993), *SHELXTL* (Sheldrick, 1994). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) in *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1173). Services for accessing these data are described at the back of the journal.

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Hexa-μ-nitrato-μ_4-oxo-tetraberyllium

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Abstract

Crystal structure determination of the title compound, [$Be_4O(NO_3)_6$], confirms the expectation of a molecular structure similar to that of basic beryllium acetate [Tulinsky & Worthington (1959). *Acta Cryst.* **12**, 626–634].

Comment

The basic nitrate is the first crystallographically characterized nitrato–metal complex in which all nitrate ligands within the (tetranuclear) molecule are bridging bidentate (*syn–syn*) (Addison, Logan, Wallwork & Garner, 1971).

Each molecule lies on a crystallographic threefold axis in the cubic unit cell. This imposes just one threefold axis on the molecule but it is found that each has full tetrahedral symmetry within experimental error. A central O atom (lying approximately at a quarter or three-quarters of the way along a body diagonal of the cell) is surrounded by a tetrahedron of Be atoms, each pair of which is bridged in a bidentate manner by a planar nitrate group, resulting in the expected tetrahedral coordination of each Be. However, the plane of each such nitrate group is slightly twisted and folded relative to the line of the two bridged Be atoms (clockwise, when viewed along the terminal N—O bond towards the centre of the tetrahedron), as shown in Fig. 1. This permits a reduction in the Be—O—N angles which, nevertheless, are all still greater than 120°.

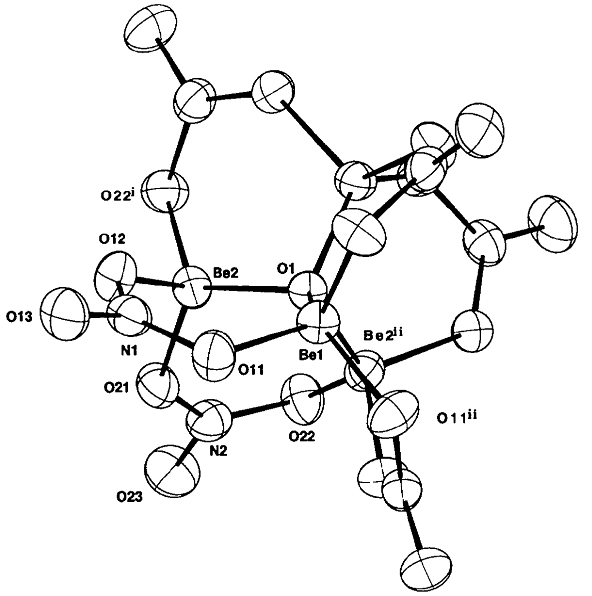

Fig. 1. The molecule of basic beryllium nitrate with displacement ellipsoids drawn at the 50% probability level. Symmetry codes: (i) *z*, *x*, *y*; (ii) *y*, *z*, *x*.

The eight molecules in the cell are centred near the eight permutations of 1/4 and 3/4 in groups of three. If they were exactly at these positions and all had the same orientation, the arrangement would correspond to simple cubic with a repeat distance equal to half of the actual cell dimension. The strength of some of the reflections with odd indices is an indication of the distortion from that arrangement. The two molecules situated at approximately 1/4 and 3/4 of the way along each body diagonal are centrosymmetrically related to each other, so the three nitrate planes on the molecule at 1/4 that face the corresponding three on the molecule at 3/4 along the same diagonal are staggered relative to each other. This must allow closer packing than if they were eclipsed and, combined with the overall molecular shape, results in an atomic pattern very different from a translational repeat.

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† Deceased.