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

$$B_{eq} = (4/3)\Sigma_i \Sigma_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ba(1)	0	0	1/4	0.43
Ba(2)	1/3	2/3	0.09671 (5)	0.52
Ti(1)	0	0	0	0.67
Ti(2)	1/3	2/3	0.84633 (14)	0.62
O(1)	0.5185 (6)	0.0370	1/4	0.65
O(2)	0.8349 (6)	0.6698	0.0802 (2)	0.66

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

Ti(1)O_6 octahedron					
O(2)—O(2)	3.965 (4)	× 3	O(2)—Ti(1)—O(2)	180.00 (1)	
O(2)—O(2)	2.8334 (3)	× 6	O(2)—Ti(1)—O(2)	91.2 (1)	
O(2)—O(2)	2.774 (7)	× 6	O(2)—Ti(1)—O(2)	88.8 (2)	
Ti(1)—O(2)	1.983 (2)	× 6			
Ti(1)—Ti(2)	3.940 (1)				
Ti(2)O_6 octahedron					
O(1)—O(2)	3.932 (2)	× 3	O(1)—Ti(2)—O(2)	169.1 (1)	
O(1)—O(1)	2.5434 (3)	× 3	O(1)—Ti(2)—O(1)	79.37 (6)	
O(2)—O(2)	2.8904 (3)	× 3	O(2)—Ti(2)—O(2)	95.1 (1)	
O(1)—O(2)	2.848 (4)	× 6	O(1)—Ti(2)—O(2)	92.3 (1)	
Ti(2)—O(1)	1.991 (1)	× 3			
Ti(2)—O(2)	1.959 (2)	× 3			
Ti(2)—Ti(2)	2.690 (4)				
Ba—O cuboctahedra					
Ba(1)—O(1)	2.868 (4)	× 6	Ba(2)—O(1)	2.820 (6)	× 3
Ba(1)—O(2)	2.881 (3)	× 6	Ba(2)—O(2)	2.871 (4)	× 6
			Ba(2)—O(2)	2.981 (3)	× 3

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71575 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1053]

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Structural Reinvestigation of $Ba_3Zr_2S_7$ by Single-Crystal X-ray Diffraction

BAI-HAO CHEN AND BRYAN EICHHORN

Center for Superconductivity Research and Department of Chemistry and Biochemistry, University of Maryland, Maryland 20742, USA

WINNIE WONG-NG

National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

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Abstract

Single crystals of barium zirconium sulfide, $Ba_3Zr_2S_7$, were prepared from BaS, Zr and S at 1323 K by using a $BaCl_2$ flux. The compound belongs to the Ruddlesden-Popper ($A_{n+1}B_nX_{3n+1}$) family with A = Ba, B = Zr, X = S and n = 2. It is isostructural to $Sr_3Ti_2O_7$ and crystallizes in alternately stacked double perovskite $BaZrS_3$ layers and rocksalt BaS layers.

Comment

A number of new Ruddlesden-Popper $A_{n+1}B_nX_{3n+1}$ compounds (Ruddlesden & Popper, 1957, 1958) have been discovered recently where A = Ba, B = Zr, Hf and X = S. The previous studies have shown that the Ba_2MS_4 phases (n = 1) are body-centered tetragonal, *I*4/*mmm* (No. 139) (Chen & Eichhorn, 1991; Saeki, Yajima & Onoda, 1991), the $Ba_3Zr_2S_7$ compound (n = 2) is *C*-centered orthorhombic, *Cccm* (No. 66) (Saeki, Yajima & Onoda, 1991), the n = 3, 4, 5 members are face-centered orthorhombic, *Fmmm* (No. 69) (Chen, Eichhorn & Fanwick, 1992; Chen, Wong-Ng & Eichhorn, 1993), and the $BaMS_3$ ($n = \infty$) compounds are orthorhombic, *Pnma* (No. 62) (Clearfield, 1963; Lelieveld & IJdo, 1980).

A review of these structures reveals that the lower n members of the Ruddlesden-Popper sulfides have high crystal symmetry (*I*4/*mmm*) whereas the higher n members ($\infty > n > 2$) display lower *Fmmm* crystal symmetry. The exception is the n = 2 member, $Ba_3Zr_2S_7$ (Saeki, Yajima & Onoda, 1991), which was shown by electron diffraction and Rietveld profile refinement to have *Cccm* symmetry. This phase was prepared by a different synthetic method and displayed trends in bond lengths at odds with those of the other members of the $Ba_{n+1}M_nS_{3n+1}$ series (Chen, Wong-Ng & Eichhorn, 1993). Therefore, a reinvestigation of the synthesis and structure (single-crystal X-ray diffraction) of $Ba_3Zr_2S_7$ was undertaken to address this structural discrepancy.

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A listing of atomic coordinates and equivalent isotropic displacement parameters is given in Table 1. Selected interatomic distances and angles are listed in Table 2. A ball-and-stick drawing and polyhedral representation of the structure are shown in Fig. 1.

As first described by Saeki, Yajima & Onoda (1991), the $Ba_3Zr_2S_7$ compound adopts a Ruddlesden–Popper structure of the $Sr_3Ti_2O_7$ type and is characterized by distorted double BaS rocksalt layers with double perovskite $BaZrS_3$ blocks intergrown along the *c* axis of the lattice. The perovskite $BaZrS_3$ blocks contain the usual ZrS_6 octahedra linked at their corners with the Ba atoms residing in the 12-coordinate voids of the framework. The Ba atoms in the BaS layers are nine-coordinate.

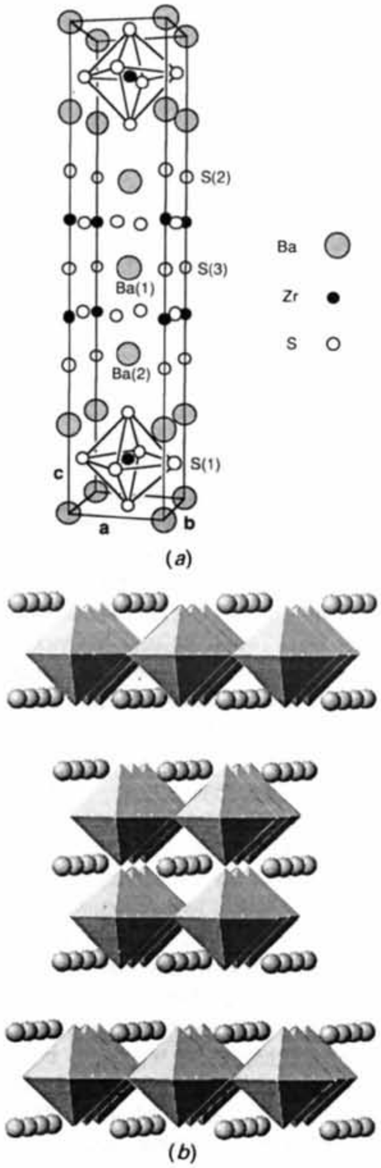

Fig. 1. (*a*) Ball-and-stick representation and (*b*) polyhedral representation of the $Ba_3Zr_2S_7$ structure.

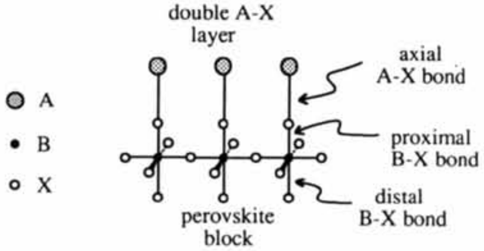

Fig. 2. Schematic drawings of the BX_6 octahedra at the double *AX*–perovskite interface in $A_{n+1}B_nX_{3n+1}$ compounds.

The trends in the bond lengths observed from this single-crystal study are remarkably close to those of the other members of the series (Chen, Wong-Ng & Eichhorn, 1993). The Ba(2)—S(2) bond length [3.073 (8) Å] parallel to the *c* axis in the BaS layer is similar to that [3.194 (1) Å] found in the cubic BaS (Guntert & Faessler, 1956) and significantly shorter than the other Ba—S contacts [3.334 (4)–3.558 (1) Å].

In addition, the Zr—S(3) bond [2.540 (2) Å], which is distal to the BaS layer, is longer than the others [2.501 (7) and 2.5016 (5) Å] as shown in Fig. 2. This distortion appears to be a common feature among the $Ba_{n+1}M_nS_{3n+1}$ compounds. It is interesting to note that distortions in the isostructural $Sr_3Ti_2O_7$ phase are opposite to those of the $Ba_{n+1}M_nS_{3n+1}$ compounds just described. In $Sr_3Ti_2O_7$, the Ti—O bonds distal to the double SrO layers are 0.012 Å shorter than the proximal Ti—O contacts (Elcombe *et al.*, 1991).

In the first report of $Ba_3Zr_2S_7$ (Saeki, Yajima & Onoda, 1991), the structure and composition of the phase were unequivocally established as that of a Ruddlesden–Popper compound; however, the authors reported the crystal symmetry to be *Cccm* (No. 66) with cell parameters a = 7.0697 (2), b = 25.4923 (7), c = 7.0269 (2) Å. Their structure comprised of buckled ZrS_6 octahedra in which the distal Zr—S bonds [2.538 (5) Å] were equal to or shorter than the other Zr—S contacts. These characteristics are similar to those of $Sr_3Ti_2O_7$ but contrast with the distortions in all of the other $Ba_{n+1}M_nS_{3n+1}$ compounds, which have elongated *M*—S contacts distal to the double BaS layers. The $Ba_3Zr_2S_7$ crystals isolated in our laboratories do not display *Cccm* symmetry or buckled octahedra, yet the electron diffraction data reported by Saeki, Yajima & Onoda (1991) are equally inconsistent with the *I*4/*mmm* symmetry observed in our study. Thus, it appears that $Ba_3Zr_2S_7$ may exist in at least two crystalline modifications, *I*4/*mmm* and *Cccm*, presumably determined by synthetic methods and phase conditions of the sample.

To summarize, the crystal structure of the n = 2 member of the $Ba_{n+1}Zr_nS_{3n+1}$ series is consistent with that of the other members prepared by the same synthetic method ($BaCl_2$ flux). The salient features of these Ruddlesden–Popper sulfides are the elongated Zr—S contacts distal to the double BaS layers and the short Ba—S bonds parallel to the c axis in the BaS layer. The overall structure is significantly less distorted than that reported by Saeki, Yajima & Onoda (1991), perhaps due to differences in synthetic conditions.

Experimental

Crystal data

$Ba_3Zr_2S_7$
$M_r = 818.98$
Tetragonal
$I4/mmm$
$a = 4.9983$ (7) Å
$c = 25.502$ (5) Å
$V = 637.1$ (2) Å^3
$Z = 2$
$D_x = 4.270$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$-$24°$
$\mu = 11.98$ mm^{-1}
$T = 295$ K
Brick shaped
$0.15 \times 0.15 \times 0.06$ mm
Dark brown

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{min} = 0.73$, $T_{max} = 0.99$
1041 measured reflections
415 independent reflections
299 observed reflections $[I \geq 3\sigma(I)]$

$R_{int} = 0.034$
$\theta_{max} = 33°$
$h = -1 \rightarrow 8$
$k = -8 \rightarrow 1$
$l = -1 \rightarrow 39$
3 standard reflections
frequency: 120 min
intensity variation: <1%

Refinement

Refinement on F
$R = 0.054$
$wR = 0.063$
$S = 1.83$
299 reflections
18 parameters
$w = 1/\sigma F^2$

$(\Delta/\sigma)_{max} = 0.02$
$\Delta\rho_{max} = 8.34$ e Å^{-3}
$\Delta\rho_{min} = -1.63$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table2.2B)

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

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ba(1)	0	0	0	1.90 (2)
Ba(2)	0	0	0.18180 (6)	2.38 (2)
Zr	0	0	0.40042 (7)	1.09 (2)
S(1)	0	1/2	0.4048 (2)	3.0 (1)
S(2)	0	0	0.3023 (2)	3.84 (9)
S(3)	0	0	1/2	4.5 (1)

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

Ba(1)—S(1)	3.484 (4)	Ba(2)—S(2)	3.073 (8)
Ba(1)—S(3)	3.5344 (1)	Zr—S(1)	2.5016 (5)
Ba(2)—S(1)	3.334 (4)	Zr—S(2)	2.501 (7)
Ba(2)—S(2)	3.558 (1)	Zr—S(3)	2.540 (2)
S(1)—Ba(1)—S(1)	91.6 (1)	S(1)—Ba(2)—S(2)	63.2 (1)
S(1)—Ba(1)—S(1)	88.3 (1)	S(1)—Ba(2)—S(2)	127.0 (1)
S(1)—Ba(1)—S(1)	60.9 (1)	S(1)—Ba(2)—S(2)	131.4 (1)
S(1)—Ba(1)—S(1)	180	S(2)—Ba(2)—S(2)	89.26 (3)
S(1)—Ba(1)—S(1)	119.0 (1)	S(2)—Ba(2)—S(2)	166.9 (2)
S(1)—Ba(1)—S(3)	59.53 (4)	S(2)—Ba(2)—S(2)	83.5 (1)
S(1)—Ba(1)—S(3)	120.5 (1)	S(1)—Zr—S(1)	174.9 (3)
S(3)—Ba(1)—S(3)	90	S(1)—Zr—S(1)	89.89 (2)
S(3)—Ba(1)—S(3)	180	S(1)—Zr—S(2)	92.6 (2)
S(1)—Ba(2)—S(1)	97.1 (2)	S(1)—Zr—S(3)	87.5 (2)
S(1)—Ba(2)—S(1)	64.0 (1)	S(2)—Zr—S(3)	180

A 1 g mixture of BaS, Hf powder and elemental S in a 2:1:3 ratio was ground and loaded into a silica ampule along with an additional 10 wt % $BaCl_2$ flux. The tube was sealed under vacuum and placed inside a larger silica tube which was also sealed under vacuum. The material was heated to 1323 K at 0.3 K min^{-1} and held at 1323 K for 10 h. The sample was then cooled to room temperature at 1 K min^{-1}. The resulting material was extracted with cool water to dissolve the $BaCl_2$ flux, filtered and then washed with acetone. Dark brown crystals of $Ba_3Zr_2S_7$ were obtained in *ca* 40% yield. Other $Ba_{n+1}Zr_nS_{3n+1}$ phases with $n > 2$ were also present.

In the process of determining the systematic extinctions, it was found that the majority of the observed reflections were indicative of I-centered space groups such as $I4$, $I\bar{4}$, $I4/m$, $I422$, $I4mm$, $I\bar{4}m2$ and $I4/mmm$. However, a small fraction of weak reflections (approximately 3%) appeared to violate the extinction conditions. In the structural solution process, space groups with symmetry lower than body centered, such as $P4/m$, $P4/mmm$ and $P4/nmm$, which also satisfy the basic Ruddlesden-Popper layer arrangements, were also tried. The initial atom coordinates were estimated using idealized positions based on a standard Ruddlesden-Popper type structure. Successful refinements were not achieved employing the lower symmetry primitive space groups. All refinements yielded unsatisfactory R values (> 15%) and unreasonable temperature factors.

Solution and refinement of the structure in the higher symmetry space group $I4/mmm$ (No. 139) was satisfactory. The structure was refined (*MolEN*; Fair, 1990) by full-matrix least squares with all atoms anisotropic in the final cycles. The non-position weighting scheme with $\rho = 0.4$ was used. Refinement in the orthorhombic space group $Fmmm$ yielded slightly higher residuals ($R = 0.060$). Therefore, the higher symmetry $I4/mmm$ refinement was chosen as the correct solution. The existence of spurious peaks could be caused by the quality of the crystal (*i.e.* small impurity surface crystallites) or by various experimental conditions such as harmonic reflections, overlap of neighboring strong reflections due to the long c parameter or mosaic spread of strong reflections.

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Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71590 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1076]

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Silver Insertion Mode in β-$Ag_xV_2O_5$ Tunnel Structure

ERIC DÉRAMOND, JEAN-MICHEL SAVARIAULT* AND JEAN GALY†

Centre d'Elaboration de Matériaux et d'Etudes Structurales du CNRS, 29 rue Jeanne Marvig, 31400 Toulouse, France

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Abstract

The β-$Ag_xV_2O_5$ phase of silver vanadate has a large homogeneity range, $0.29 \leq x \leq 0.41$; the $(V_2O_5)_n$ network of its crystal structure is typical of the β phase of the vanadium oxide bronzes with its oxygenated tunnels running along [010]. Ag atoms are inserted in a novel manner, being distributed onto two distinct crystallographic sites, which explains the overstepping of the theoretical boundary limit of the β phases, $x = 0.33$.

Comment

The structure type of β phases was depicted for the first time by Wadsley (1955) for the sodium vanadium oxide bronze β-$Na_xV_2O_5$. A wide family has followed, β-$M_xV_2O_5$, where M represents alkaline, alkaline earth, Cu, Ag, Cd or Pb metals. Galy and co-workers (Galy & Hardy, 1964; Galy, Darriet & Hagenmuller, 1971) studied $Li_xV_2O_5$ and demonstrated the existence of two phases, β and β', the difference between them being the mode of lithium insertion. Various possibilities have been analysed and discussed by Galy, Darriet, Casalot & Goodenough (1970).

To understand the homogeneity range for these phases, related directly to the M-atom insertion mode, several investigations have been undertaken. The β and β' phases are characterized by closely related networks of $[V_2O_5]_n$ which result from the association by edges and corners of triple infinite chains built up by $V(1)O_6$ and $V(2)O_6$ octahedra and $V(3)O_5$ square pyramids (Fig. 1). In the β phase of $Na_xV_2O_5$, the Na or M atoms are distributed over a crystallographic site, $M(1)$ [here Ag(1)]; this site, repeated by a centre of symmetry of the $C2/m$ space group, produces a type of 'M doublet' inserted in the large bicapped rhombic prism O(6*b*)[O(8)O(4)O(8*c*)-O(4*c*)]$_2$O(6*d*). Due to the short distance which separates $M(1)$ and $M(1c)$, only 50% of the sites are occupied, giving a theoretical upper limit of $M_{0.33}V_2O_5$ for the β phases.

Recently, in companion papers, Permer & Ferey (1993) and Savariault, Déramond & Galy (1993) reported investigations of the β' phases of iron and copper; in these phases both iron and copper occupy the oxygenated tetrahedra built up by O(8), O(4) and two O(6*b*) [or O(8*c*), O(4) and two O(6*d*)]. Such an insertion mode allows these phases to reach the maximum formula $M_{0.66}V_2O_5$. The problem with $Ag_xV_2O_5$, studied by Casalot & Pouchard (1967), is knowing if it belongs to the β or β' type, or both, *via* its silver insertion within the tunnels.

The crystal structure clearly establishes that the Ag atoms are distributed in the bicapped rhombic prism but unusually over four sites, Ag(1), Ag(2), Ag(1*c*) and Ag(2*c*). Clearly, $Ag_xV_2O_5$ is not a β' phase. Among the β phases, $Ag_xV_2O_5$ is the first exhibiting these two insertion sites. The Ag(1) site in the monocapped trigonal prism O(6*b*)[O(8)O(8*c*)O(4*c*)]$_2$ is similar to that of Na in Wadsley's phase (Wadsley, 1955) (Fig. 2). Ag(1*c*) being situated 1.925 (3) Å from Ag(1) implies that these sites can only be half occupied, which is confirmed by Ha-Eierdanz & Müller (1993).

The coordination number (CN) 7 of Ag(1) indicates regular Ag—O distances [Ag(1)—O = 2.390 (1)–2.655 (2) Å] which correspond to classical Ag^I—O interatomic distances according to Wells (1975). Ag(2), close to Ag(1) at a distance of 0.415 (2) Å, still in the monocapped trigonal prism, is displaced towards O(6*b*) [Ag(2)···O(6*b*) = 2.160 (4) Å]. The Ag—O distances range from 2.160 (4) to 2.854 (3) Å. Of course, Ag(1) and Ag(2) cannot be occupied simultaneously as well as Ag(2) and Ag(1*c*) [or Ag(1) and Ag(2*c*)], but Ag(2) and Ag(2*c*), with an interatomic distance of 2.750 (4) Å, can.

The theoretical $x = 0.33$ value for the existence of the β phase is not now the upper limit; the new limit is $x = 0.66$, as for the β' phase.

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† Mailing address: CEMES-LOE/CNRS, BP 4347, 31055 Toulouse CEDEX, France.