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Crystal structure of $Ba_5In_2Al_2ZrO_{13}$

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Abstract

The crystal structure of anion-deficient hexagonal perovskite-like oxide $Ba_5In_2Al_2ZrO_{13}$ ($a = 5.8707(7)$ Å, $c = 24.445(3)$ Å, space group $P6_3/mmc$, $z = 2$) was determined using single crystal data. A least-squares refinement gave conventional and weighted R factors of 0.037 and 0.040 respectively. This structure is a 10L $(cchcc)_2$ sequence of close-packed BaO_3 and $BaO\square_2$ layers. The main feature of the structure is joint occupation of two 4f positions by In and Al atoms, which result in disordering of oxygen atoms and vacancies in the $BaO\square_2$ layers. It was shown that this structure can be considered formally as a result of the intergrowth of Ba_2InAlO_5-like blocks and $BaZrO_3$ ones along the c-axis of the hexagonal supercell.

1. Introduction

There are only a few anion-deficient hexagonal perovskite-like oxides where oxygen atoms and vacancies are completely ordered. Ordering of vacancies leads to the formation of coordination polyhedra for some of the B-cations with coordination number less than 6. So, the crystal structures $BaCoO_{2.6}$ [1], β-Ba_2ScAlO_5 [2] and Ba_2InAlO_5 [3] apart from octahedra BO_6 contain tetrahedra BO_4. The crystal structure of $Ba_7Sc_6Al_2O_{19}$ [4] has been described earlier. It was shown that this can be presented as an intergrowth structure with alternation of β-Ba_2ScAlO_5 and $Ba_3Sc_4O_9$ [5] blocks along the c-axis in a hexagonal supercell. It was suggested that it would be possible to synthesize similar structures, where different structural blocks alternate along the c-axis. To realize this idea Ba_2InAlO_5 and $BaZrO_3$ oxides were used. $BaZrO_3$ has an ideal cubic perovskite cell, which can be considered as a 3L $(c)_3$ close-packing along the three-fold axis. The hexagonal perovskite oxide Ba_2InAlO_5 has the same crystal structure as β-Ba_2ScAlO_5, where ordering of oxygen vacancies leads to the formation of close-packing of BaO_3 and $BaO\square_2$ layers.

2. Experimental details

Single crystals of $Ba_5In_2Al_2ZrO_{13}$ were obtained on the surface of the pellet during annealing of a stoichiometric mixture of $BaCO_3$, In_2O_3, Al_2O_3 and ZrO_2 at 1500 °C in air. For X-ray diffraction investigation, a flat crystal with dimensions $0.07 \times 0.06 \times 0.01$ mm^3 was chosen. Experimental and crystallographic parameters are summarized in Table 1. The structure determination package was used for structure solution and refinement. Initial data were treated for standard procedure for empirical absorption correction to take into account an absorption influence.

3. Results

The refinement of the crystal structure of $Ba_5In_2Al_2ZrO_{13}$ was carried out in isotropic and ani-

TABLE 1. Crystallographic and experimental data for $Ba_5In_2Al_2ZrO_{13}$

Space group	$P6_3/mmc$
a (Å)	5.8707(7)
c (Å)	24.445(3)
V (Å^3)	729.6(3)
Z	2
Calculated density (g cm^{-3})	5.778(2)
Absorption coefficient (cm^{-1})	175.69
Crystal size (mm^3)	$0.06 \times 0.07 \times 0.01$
Diffractometer	CAD-4
Scan mode	$\omega/1.33\Theta$
Radiation and wavelength	MoKα, $\lambda = 0.71069$Å
Weight scheme	Unit
Restriction	$\lvert F\rvert \geq 4\sigma(F)$
Min $\sin(\Theta/\lambda)$	0.1
Number of measured reflections	511
Number of unique reflections	308
Number of reflections in refinement	221
R_F, R_w	0.037, 0.040
No. of variables	33

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sotropic estimations, and led to values of $R_F = 0.037$ and $R_w = 0.040$. The thermal parameter of the delocalized oxygen atom was refined isotropically.

The crystal structure of $Ba_5In_2Al_2ZrO_{13}$ is a 10L $(cchcc)_2$ close-packing of BaO_{3-x} layers. The scheme of the polyhedra connections is shown in Fig. 1. Zr atoms are ordered and located in 2*a* positions, and have practically an ideal octahedral arrangement. In and Al atoms statistically occupy two 4f positions (0.85 In + 0.15 Al for $z = 0.397$ (In/Al) and vice versa for $z = 0.815$ (Al/In)). The refinement of the occupations for these atoms led to values of 0.84(2) for the first position and 0.86(2) for the second one. A refinement without statistical occupations led to enormous thermal parameters for In and Al atoms (2.1 Å^2 and -1.1 Å^2 respectively).

O3 atoms statistically occupy 1/3 of the 6*h* position which resulted from the 2*c* position owing to disordering of oxygen atoms in *x*, *y*, 1/4 and *x*, *y*, 3/4 planes. This arrangement can be presented as a tetrahedron with a statistically oriented vertex. It should be pointed out that the rather short distance Al/In–O (caused by delocalization of O3 atoms in the *x*, *y*, 1/4(3/4) plane) is realized in this structure (1.64 Å). However, there is a very weak electron maxima on a difference Fourier map with coordinates 0.34, 0.17, 3/4. The distance from the Al/In atom to this peak is 2.31 Å, which may confirm the presence of In atoms in the 2/3, 1/3, 0.397 position. Ba atoms have three different coordination arrangements. So, Ba3 atoms occupy cubooctahedra. The presence and ordering of oxygen atoms and vacancies lead to changing of the oxygen arrangement for the Ba1 and Ba2 atoms. There is a joint polyhedron for the Ba1 atoms in the 0,0,*z* and 0,0,1/2-*z* position (consisting of two half cubooctahedra). Ba3 atoms are situated in the trigonal prism and have six equatorial neighbours formed by O3 atoms, statistically occupied for 1/3, and shifted to a Ba–O bond length of 3.22(2) Å. Such type of coordination polyhedra result in a high value for the thermal parameter (and strong anisotropy for B_{33}) for the Ba3 atoms. Atomic parameters, anisotropic thermal parameters, main interatomic distances and angles for the $Ba_5In_2Al_2ZrO_{13}$ structure are represented in Tables 2(a, b) and 3 respectively.

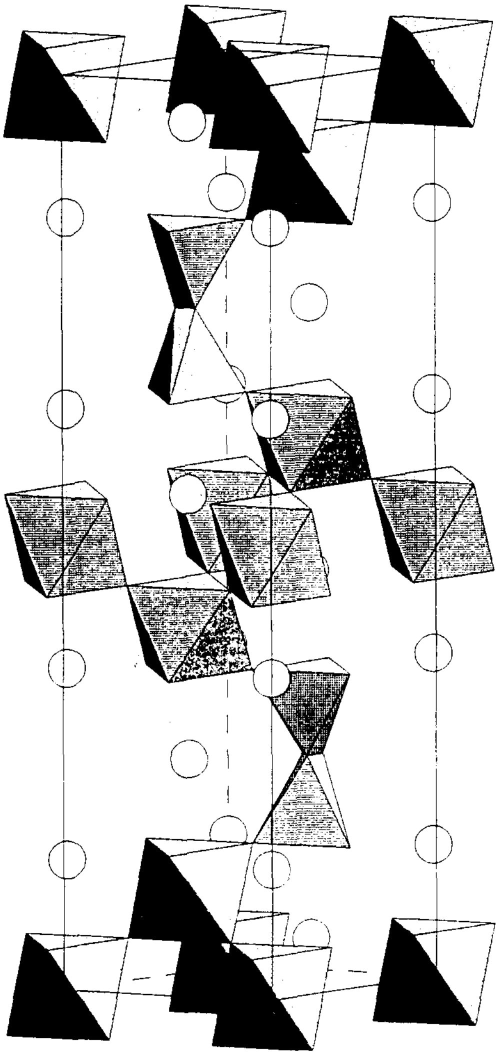

Fig. 1. Crystal structure of $Ba_5In_2Al_2ZrO_{13}$.

The $Ba_5In_2Al_2ZrO_{13}$ structure is a $(cchcc)_2$ close-packing, where the BaO_3 and $BaO\square_2$ layers with disordered placement of the oxygen atoms and vacancies alternate along the *c*-axis. Oxygen vacancies are localized in $BaO\square_2$ (*h*-type) layers around the 2*c* positions.

4. Discussion

As mentioned above, the crystal structure of $Ba_5In_2Al_2ZrO_{13}$ can be considered as an intergrowth structure with the alternation of Ba_2InAlO_5-like blocks and $BaZrO_3$ blocks along the *c*-axis in the hexagonal supercell. In Fig. 2 the 10L close-packing ($Ba_5In_2Al_2ZrO_{13}$) as a result of the intergrowth of 8L (Ba_2InAlO_5) and 3L ($BaZrO_3$) (presented as polyhedra schemes along 0,0,*z* and 2/3, 1/3, *z* columns) is shown. It is easy to see, that the $(cchcc)_2$ sequence of $Ba_5In_2Al_2ZrO_{13}$ is formed by adding one *c*-type layer into the $(cchc)_2$ sequence of Ba_2InAlO_5. According to this suggestion all polyhedra types present in the basic structures must also exist in the final one. However, in this case some differences occur; the main distinctions deal with considerable differences between *a*–*b* dimensions of initial close-packings (which is a geometrical criterion). So, the *a*-parameters of the unit cells are 5.79 Å and 5.93 Å for Ba_2InAlO_5 and $BaZrO_3$ (in hexagonal description) respectively. Such differences must lead to either strong distortions of the coordination polyhedra or disordering in some close-packed layers. These changes are quite necessary to obtain a matching between the initial close-packings and to ensure the

TABLE 2. $Ba_5In_2Al_2ZrO_{13}$: (a) Positional and isotropic thermal parameters

Atom	Position	x	y	z	B_{eq} (Å^2)
Ba(1)	4*e*	0	0	0.3565(1)	1.00(2)
Ba(2)	2*d*	2/3	1/3	1/4	2.83(5)
Ba(3)	4*f*	2/3	1/3	0.5446(1)	0.98(2)
Zr(1)	2*a*	0	0	0	0.40(5)
In/Al[a]	4*f*	2/3	1/3	0.3968(1)	0.63(3)
Al/In[b]	4*f*	2/3	1/3	0.8150(4)	1.5(1)
O(1)	12*k*	0.503(3)	2*x*	0.6536(6)	1.9(3)
O(2)	12*k*	0.167(3)	2*x*	0.5484(7)	2.1(3)
O(3)[c]	6*h*	0.295(5)	2*x*	1/4	1(1)[d]

[a] Occupancy (0.85In + 0.15Al).

[b] Occupancy (0.85Al + 0.15In).

[c] Occupancy 0.333O.

[d] Atom was refined isotropically.

Anisotropically refined atoms are given in the form of isotropic equivalent displacement parameter defined as: $(4/3)*[a^2*B(1,1)+b^2*B(2,2)+c^2*B(3,3)+ab(\cos\gamma)*B(1,2)+ac(\cos\beta)*B(1,3)+bc(\cos\alpha)*B(2,3)]$.

TABLE 2. $Ba_5In_2Al_2ZrO_{13}$: (b) Displacement parameters

Atom	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
Ba(1)	0.0072(3)	$B(1,1)$	0.00052(3)	$B(1,1)/2$	0	0
Ba(2)	0.031(1)	$B(1,1)$	0.00047(5)	$B(1,1)/2$	0	0
Ba(3)	0.0085(4)	$B(1,1)$	0.00038(3)	$B(1,1)/2$	0	0
Zr(1)	0.0034(7)	$B(1,1)$	0.00016(5)	$B(1,1)/2$	0	0
In/Al	0.0052(5)	$B(1,1)$	0.00027(3)	$B(1,1)/2$	0	0
Al/In	0.007(1)	$B(1,1)$	0.0012(2)	$B(1,1)/2$	0	0
O(1)	0.013(4)	0.013(6)	0.0011(3)	$B(2,2)/2$	−0.002(2)	$2B(1,3)$
O(2)	0.021(5)	0.019(6)	0.0006(2)	$B(2,2)/2$	0.001(3)	$2B(1,3)$

The form of the anisotropic displacement parameter is: $\exp[-(B(1,1)*h^2+B(2,2)*k^2+B(3,3)*l^2+B(1,2)*hk+B(1,3)*hl+B(2,3)*kl)]$.

TABLE 3. Main interatomic distances (Å) and angles (°) for $Ba_5In_2Al_2ZrO_{13}$

Ba(1)–O(1)	2.95(2)×6	Zr(1)–O(2)	2.07(2)×6
Ba(1)–O(2)	2.88(2)×3	In/Al–O(1)	2.12(2)×3
Ba(2)–O(1)	2.92(2)×6	In/Al–O(2)	2.16(2)×3
Ba(2)–O(3)	3.21(3)×6	Al/In–O(1)	1.83(2)×3
Ba(3)–O(1)	3.14(2)×3	Al/In–O(3)	1.64(1)×3
Ba(3)–O(2)	2.83(2)×3	O(3)–O(3)	0.68(4)×2
Ba(3)–O(2)	2.94(2)×6		
O(1)–In/Al–O(1)	89.6(6)	O(1)–Al/In–O(1)	103.7(8)
O(2)–In/Al–O(2)	85.5(7)	O(3)–Al/In–O(3)	23.8(11)
O(1)–In/Al–O(2)	92.4(7)	O(1)–Al/In–O(3)	107.4(10)
O(1)–In/Al–O(2)	177.2(7)	O(1)–Al/In–O(3)	128.5(11)
O(2)–Zr–O(2)	89.4(7)		
O(2)–Zr–O(2)	90.6(7)		
O(2)–Zr–O(2)	180.0(7)		

lability of them. In this case the lability is provided by a joint occupation of the 4f position by In and Al atoms and as a consequence disordering of oxygen atoms and vacancies in the $BaO\square_2$ layers. A similar disordering type exists in the α-Ba_2ScAlO_5 structure [6]. A four-coordinated arrangement is unusual for both In and Sc atoms. That is why the joint occupation of one crystallographic position together with Al atoms leads to a separation of oxygen atoms from the two-fold position to the six-fold one with a simultaneous decreasing of their occupancy. Positions in face-shared octahedra are occupied by (3/4Al + 1/4Sc) atoms in the α-Ba_2ScAlO_5 structure and by (0.85Al + 0.15In) atoms in the $Ba_5In_2Al_2ZrO_{13}$ one, this occupation may influence the degree of distortion of this pair of octahedra. The compositions of the BaO_{3-x} layers are different in these structures. So, $BaO_{1.5}\square_{1.5}$ layers are formed in the α-Ba_2ScAlO_5 structure, and in the $Ba_5In_2Al_2ZrO_{13}$ structure $BaO\square_2$ layers exist. The average composition of anion deficient layers remains the same as in the initial Ba_2InAlO_5 structure. Therefore, an analysis of cation and anion positions in $Ba_5In_2Al_2ZrO_{13}$ structure allows us to pick out the structural blocks of Ba_2InAlO_5 and $BaZrO_3$.

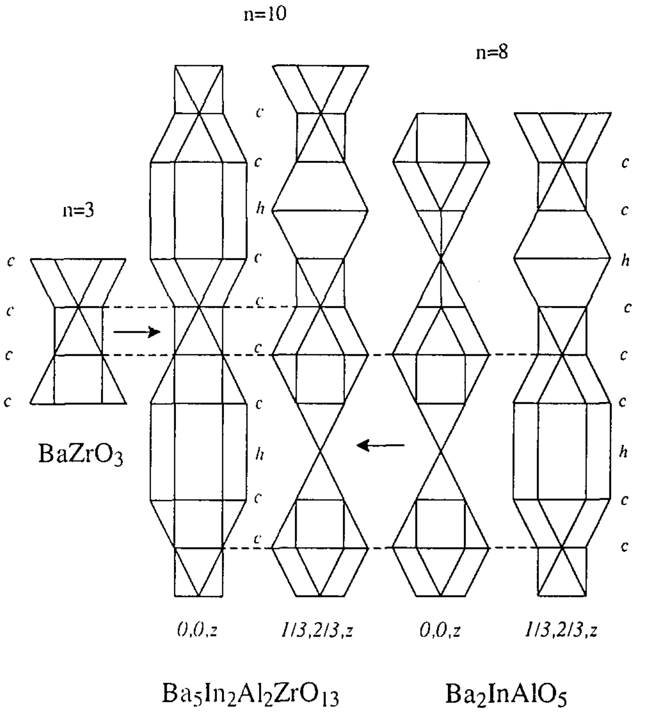

Fig. 2. The 10L $(cchcc)_2$ close-packing of $Ba_5In_2Al_2ZrO_{13}$ as a result of the intergrowth of 8L $(cchc)_2$ and 3L $(c)_3$ close-packings.

In contrast to $Ba_7Sc_6Al_2O_{19}$, the crystal structure of $Ba_5In_2Al_2ZrO_{13}$ is an hexagonal intergrowth structure where only one specific structural block (Ba_2InAlO_5-like) is present. Nevertheless, the direct synthesis of this complex oxide shows the real possibility for creation of new compounds with the same type of intergrowth structures.

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References

1 A.J. Jacobson and J.L. Hutchinson, *J. Solid State Chem., 35* (1980) 334.
2 R.V. Shpanchenko, E.V. Antipov, L.N. Lykova, L.M. Kovba, *Vestnik Mosk. Univers. (Russ.), Ser.2 Chim., 31* (1991) 555.
3 Hk. Müller-Buschbaum and M. Abed, *Z. Anorg. Allg. Chem., 591* (1990) 174.
4 R.V. Shpanchenko, E.V. Antipov, M.V. Paromova and L.M. Kovba, *Zh. Neorgan. Chim. (Russ.), 36* (1991) 1402.
5 L.M. Kovba and M.V. Paromova, *Vestnik Mosk. Univers. (Russ.), Ser.2 Chim.*, Vol. 11, No. 5 (1970) 621.
6 E.V. Antipov, R.V. Shpanchenko, L.N. Lykova and L.M. Kovba, *Crystallogr. (Russ.), 35* (1990) 213.