Crystal structure of barium antimony lead bismuth oxide, $\text{Ba}(\text{Pb}_{0.63}\text{Sb}_{0.26}\text{Bi}_{0.11})\text{O}_3$

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Abstract

$\text{BaBi}_{0.11}\text{O}_3\text{Pb}_{0.63}\text{Sb}_{0.26}$, cubic, $Fm\bar{3}m$ (No. 225),
 $a = 8.536(1) \text{ \AA}$, $V = 622.0 \text{ \AA}^3$, $Z = 8$, $R_{\text{gt}}(F) = 0.033$,
 $wR_{\text{all}}(F^2) = 0.119$, $T = 293 \text{ K}$.

Source of material

Single crystals (up to 1 mm^3) were grown by PbO-flux in platinum crucibles with Pb-, Sb- and Bi-oxides and Ba-carbonate as starting materials cooled down from 1420 K to 1020 K with 2–4 K/h [1].

The chemical composition $\text{BaPb}_{0.63(1)}\text{Sb}_{0.26(1)}\text{Bi}_{0.11(1)}\text{O}_3$ was determined by electron microprobe analysis (Cameca SX 100). In spite of the excess of PbO as flux the requested Pb-content decreased about 10 % in the crystals in respect to the starting composition $\text{BaPb}_{0.7}\text{Sb}_{0.2}\text{Bi}_{0.1}\text{O}_3$. That was only determined in Sb-bearing crystals of the $\text{Ba}(\text{Pb}, \text{Bi}, \text{Sb})\text{O}_3$ system. The crystals were homogeneous and didn't show zonations, twinings or intergrowth sections as known for other compositions.

Experimental details

The site occupancy factors were refined using some restraints as follows: The sum of the elements on the octahedral sites (0,0,0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ corresponds to the chemical composition determined by electron microprobe analysis. Furthermore the sum of the elements on both octahedral sites must be 1. Therefore all e.s.d.'s concerning these elements have the same values which are small because of the good agreement of the model and the refined parameters.

Discussion

$\text{Ba}(\text{Pb}_{0.63}\text{Sb}_{0.26}\text{Bi}_{0.11})\text{O}_3$ single crystals show a face centered cubic superstructure resulting from an ordering of Sb vs. Bi on the octahedral site producing an eightfold perovskite cell. The space group $Fm\bar{3}m$ belongs to the zero-tilt system No. 23 [2] with cation ordering. Additional measurements with synchrotron radiation (HASYLAB at DESY, Hamburg) near the Pb absorption edge in order to separate Pb and Bi using the anomalous dispersion [3] showed a statistical distribution of the Pb-cations on the octahedral sites. The site occupancy factors of the Pb-cations were fixed during refinement. No exchange of Pb on the cubooctahedral Ba-site was determined. Further investigations of superstructures vs. chemical composition and microscopic reflection colour related to electronic states were carried out [4].

Table 1. Data collection and handling.

Crystal:	black, wedge-shaped fragment, size $0.14 \times 0.21 \times 0.28 \text{ mm}$
Wavelength:	Mo K_{α} radiation ($0.71073 \text{ \AA}$)
μ :	548.98 cm^{-1}
Diffractionmeter, scan mode:	Siemens P4, ω
$2\theta_{\text{max}}$:	89.9°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	3182, 113
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 112
$N(\text{param})_{\text{refined}}$:	10
Programs:	SHELXS-90 [5], SHELXL-93 [6]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ba(1)	8c		1/4	1/4	1/4	0.0184(2)	U ₁₁	U ₁₁	0	0	0
Pb(1)	4a	0.63	0	0	0	0.0138(2)	U ₁₁	U ₁₁	0	0	0
Sb(1)	4a	0.3709(3)	0	0	0	0.0138	U ₁₁	U ₁₁	0	0	0
Bi(1)	4a	0.0000	0	0	0	0.0138	U ₁₁	U ₁₁	0	0	0
Pb(2)	4b	0.63	1/2	1/2	1/2	0.0126(2)	U ₁₁	U ₁₁	0	0	0
Sb(2)	4b	0.1489(4)	1/2	1/2	1/2	0.0126	U ₁₁	U ₁₁	0	0	0
Bi(2)	4b	0.2212	1/2	1/2	1/2	0.0126	U ₁₁	U ₁₁	0	0	0
O(1)	24e		0.246(1)	0	0	0.026(4)	0.049(4)	U ₂₂	0	0	0

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