Crystal structure of pentastrontium tris(phosphate) bromide, $Sr_5(PO_4)_3Br$ and of pentabarium tris(phosphate) bromide $Ba_5(PO_4)_3Br$, *two bromoapatites*

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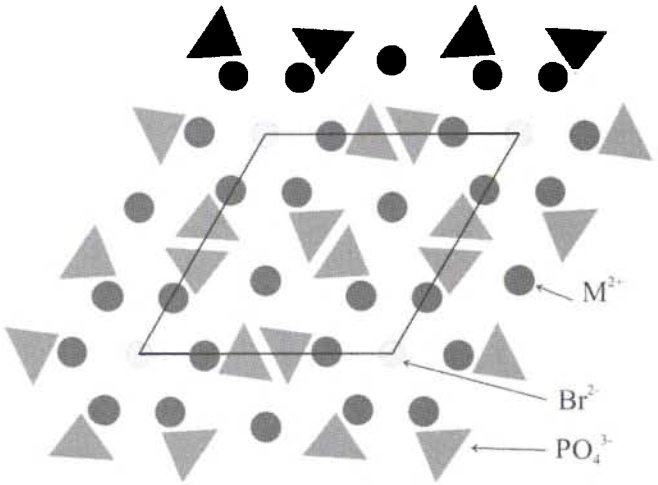

Abstract

$BrO_{12}P_3Sr_5$, hexagonal, $P6_3/m$ (No. 176), $a = 9.972(1)$ Å, $c = 7.214(1)$ Å, $V = 621.3$ Å^3, $Z = 2$, $R_{gt}(F) = 0.042$, $wR_{all}(F) = 0.024$, $T = 293$ K.

$Ba_5BrO_{12}P_3$, hexagonal, $P6_3/m$ (No. 176), $a = 10.342(2)$ Å, $c = 7.673(2)$ Å, $V = 710.7$ Å^3, $Z = 2$, $R_{gt}(F) = 0.022$, $wR_{all}(F) = 0.015$, $T = 293$ K.

Source of material

Single crystals of $Sr_5(PO_4)_3Br$ were grown from $Sr_3(PO_4)_2$ in excess of $SrBr_2$ melt at 1223K, in Pt-crucibles sealed in evacuated quartz tubes, (3 d, cooling down 3 K/min to 913 K and then at 10 K/min down to 293 K).

The $Ba_5(PO_4)_3Br$ crystals were grown from $Ba_3(PO_4)_3$ in excess $BaBr_2$ melt at identical conditions. Excess $SrBr_2$ (or $BaBr_2$) was removed by dissolving it in water.

Experimental details

A four-circle diffractometer was used in order to get an accurate determination of the cell axis whilst the data sets were collected on an area detector.

Discussion

Both, $Sr_5(PO_4)_3Br$ and $Ba_5(PO_4)_3Br$ crystallise with the apatite structure, and are isotypic with $Ca_5(PO_4)_3Br$ [1], with the bromine positioned at the $z = 0$. Increasing the size of the alkaline earth metal ions from Ca to Ba expands the structure and all M—O and M—Br distances increase in length. One typical example is the M(1)—O(1) distance that increases from 2.416(1) Å and 2.592(2) Å to 2.763(2) Å in the Ca, Sr and Ba apatites, respectively.

1. Pentastrontium tris(phosphate) bromide, $Sr_5(PO_4)_3Br$

Table 1. Data collection and handling.

Crystal:	colourless, hexagonal rod, size 0.028 × 0.028 × 0.127 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	249.14 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 100 exposures, $\Delta\varphi = 2°$
$2\theta_{max}$:	60.8°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7368, 657
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 3\ \sigma(I_{obs})$, 537
$N(param)_{refined}$:	39
Programs:	Jana98 [2], ATOMS [3]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sr(1)	4*f*	1/3	2/3	0.00163(6)	0.0122(1)	U_{11}	0.0079(2)	$U_{11}/2$	0	0
Sr(2)	6*h*	0.25550(4)	–0.00878(4)	1/4	0.0110(1)	0.0126(1)	0.0092(2)	0.0056(1)	0	0
P	6*h*	0.4087(1)	0.37260(9)	1/4	0.0075(3)	0.0090(4)	0.0078(5)	0.0034(3)	0	0
O(1)	6*h*	0.3433(3)	0.4840(3)	1/4	0.025(1)	0.021(1)	0.009(1)	0.018(1)	0	0
O(2)	6*h*	0.5882(2)	0.4648(2)	1/4	0.018(1)	0.009(1)	0.016(2)	0.0079(9)	0	0
O(3)	12*i*	0.3581(2)	0.2693(2)	0.0777(3)	0.0219(8)	0.0167(7)	0.012(1)	0.0119(7)	–0.0044(7)	–0.0045(7)
Br	2*b*	0	0	0	0.0129(2)	0.0129(2)	0.0140(4)	0.00643(8)	0	0

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2. Pentabarium tris(phosphate) bromide, $Ba_5(PO_4)_3Br$

Table 3. Data collection and handling.

Crystal:	colourless, hexagonal rod, size 0.040 × 0.044 × 0.370 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	169.38 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 100 exposures, $\Delta\varphi = 2°$
$2\theta_{max}$:	60.64°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8292, 723
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 3\ \sigma(I_{obs})$, 576
$N(param)_{refined}$:	40
Programs:	Jana98 [2], ATOMS [3]

Table 4. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba(1)	4*f*	1/3	2/3	0.00123(4)	0.00762(7)	U_{11}	0.0044(2)	$U_{11}/2$	0	0
Ba(2)	6*h*	0.25175(2)	–0.01588(2)	1/4	0.0059(1)	0.0069(1)	0.0048(1)	0.00323(9)	0	0
P	6*h*	0.4085(1)	0.3712(1)	1/4	0.0038(4)	0.0032(4)	0.0026(6)	0.0016(3)	0	0
O(1)	6*h*	0.3473(3)	0.4802(3)	1/4	0.020(1)	0.018(1)	0.012(2)	0.016(1)	0	0
O(2)	6*h*	0.5814(2)	0.4601(3)	1/4	0.006(1)	0.004(1)	0.014(2)	0.0004(9)	0	0
O(3)	12*i*	0.3583(2)	0.2724(2)	0.0875(3)	0.0207(9)	0.0107(8)	0.004(1)	0.0076(8)	–0.0067(7)	–0.0059(8)
Br	2*b*	0	0	0	0.0073(2)	0.0073(2)	0.0085(4)	0.00364(8)	0	0

References

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