

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Europium-doped barium bromide iodide

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Received 24 July 2009; accepted 8 October 2009

Key indicators: single-crystal X-ray study; $T = 153$ K; mean $\sigma(\text{Ba}-\text{Br}) = 0.0014$ Å; disorder in main residue; R factor = 0.015; wR factor = 0.033; data-to-parameter ratio = 20.5.

Single crystals of $\text{Ba}_{0.96}\text{Eu}_{0.04}\text{BrI}$ (barium europium bromide iodide) were grown by the Bridgman technique. The title compound adopts the ordered PbCl_2 structure [Braekken (1932). *Z. Kristallogr.* **83**, 222–282]. All atoms occupy the fourfold special positions (4c, site symmetry m) of the space group $Pnma$ with a statistical distribution of Ba and Eu. They lie on the mirror planes, perpendicular to the b axis at $y = \pm 0.25$. Each cation is coordinated by nine anions in a tricapped trigonal prismatic arrangement.

Related literature

For details of crystal growth by the Bridgman technique, see: Robertson (1986). For structural details of isotopic compounds, see: PbCl_2 (Braekken, 1932); EuBrI (Liao *et al.*, 2004); SrBrI (Hodorowicz & Eick, 1983); and BaBrCl (Hodorowicz *et al.*, 1983). For structural details of PbFCl compounds, see: Liebich & Nicollin (1977). For the structure of compounds with similar compositions by powder diffraction, see Lenus *et al.* (2002). For the luminescent properties of some Eu^{2+} -activated barium halides, see: Schweizer (2001); Crawford & Brixner (1991); Selling *et al.* (2007); Bourret-Courchesne *et al.* (2009).

Experimental

Crystal data

 $\text{Ba}_{0.96}\text{Eu}_{0.04}\text{BrI}$ $M_r = 344.70$ Orthorhombic, $Pnma$ $a = 8.684$ (3) Å $b = 5.0599$ (19) Å $c = 10.061$ (4) Å $V = 442.1$ (3) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 24.97$ mm⁻¹ $T = 153$ K $0.14 \times 0.09 \times 0.06$ mm

Data collection

Bruker SMART 1000 CCD

diffractometer

Absorption correction: multi-scan

(Blessing, 1995)

 $T_{\min} = 0.128$, $T_{\max} = 0.316$

2609 measured reflections

430 independent reflections

370 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.027$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.015$ $wR(F^2) = 0.033$ $S = 1.02$

430 reflections

21 parameters

 $\Delta\rho_{\max} = 0.89$ e Å⁻³ $\Delta\rho_{\min} = -0.78$ e Å⁻³

Table 1

Selected bond lengths (Å).

I1–Ba1 ⁱ	3.6448 (10)	Ba1–Br1 ^v	3.2643 (10)
I1–Ba1 ⁱⁱ	3.6448 (10)	Ba1–Br1	3.2643 (10)
I1–Ba1 ⁱⁱⁱ	3.7101 (9)	Ba1–Br1 ^{vi}	3.2931 (13)
I1–Ba1 ^{iv}	3.7101 (9)	Ba1–Br1 ^{vii}	3.3065 (14)

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

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINTE* (Bruker, 2008); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

This work was supported by the US Department of Homeland Security and carried out at the Lawrence Berkeley National Laboratory under Department of Energy Contract No. DE-AC02-05CH11231. The authors gratefully acknowledge useful discussions with Dr Stephen E. Derenzo and Dr Gregory Bizarri. This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or The Regents of the University of California.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FI2082).

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supplementary materials

Acta Cryst. (2009). E65, i76-i77 [doi:10.1107/S1600536809041105]

Europium-doped barium bromide iodide

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Comment

Barium mixed halides activated by Eu^{2+} have been extensively studied as X-ray phosphors (Schweizer, 2001; Crawford & Brixner, 1991) and scintillators for the detection of γ -rays (Selling *et al.*, 2007). The F-based compounds of the form BaFX ($X = \text{Cl}, \text{Br}, \text{I}$) have a tetragonal, matlockite structure similar to PbFCl (Liebich & Nicollin, 1977). Among the other barium mixed halides, the structure of BaBrCl has been found to be the PbCl_2 -type (Hodorowicz *et al.*, 1983). Lenus *et al.* recently solved the structures of BaBrI and BaClI from X-ray powder diffraction data in the space groups $P222_1$ and $Pbam$ respectively (Lenus *et al.*, 2002). We have synthesized single crystals of $\text{Ba}_{0.96}\text{Eu}_{0.04}\text{BrI}$ and present details of the structure. Eu is introduced as a dopant and substitute for Ba. The doping was not expected to change the structure of the parent material BaBrI . However, we determine the structure to have a space group $Pnma$, similar to that of isomorphous compounds EuBrI (Liao *et al.*, 2004) and SrBrI (Hodorowicz & Eick, 1983), but not the structure published by Lenus *et al.* for powders of BaBrI (Lenus *et al.*, 2002).

The title compound adopts the orthorhombic PbCl_2 structure. All atoms occupy the fourfold special positions (4c) of the space group $D_{2h}^{16}-Pnma$. They lie on the mirror planes, perpendicular to the b axis at $y = (\pm)0.25$. Each Ba/Eu cation is coordinated by 9 anions in a tricapped trigonal prismatic arrangement (Fig. 1). The anions are not equidistant from the Ba cation but present in two different positions. The smaller bromide anions occupy one of the anionic positions at distances between 3.26 and 3.30 Å. The larger iodide anions occupy the second anionic position (distances 3.62 - 3.71 Å), giving a completely ordered structure for the anions. The same ordering has been observed in isomorphous compounds EuBrI (Liao *et al.*, 2004) and SrBrI (Hodorowicz & Eick, 1983).

The Eu content of 4% has been determined from the refinement of the structure. The presence of divalent Eu is also confirmed by measuring the emission curve under X-ray excitation. The characteristic $4f^6 5d^1 \rightarrow 4f^7$ transition of Eu^{2+} was observed. A detailed study of the luminescent properties is currently underway and will be presented in a future publication (Bourret-Courchesne *et al.*, 2009).

Experimental

Single crystals with the composition $\text{Ba}_{0.96}\text{Eu}_{0.04}\text{BrI}$ were grown by the vertical Bridgman techniques. BaBr_2 , BaI_2 , EuBr_2 and EuI_2 were obtained commercially, mixed in the molar ratio 0.48: 0.48: 0.02: 0.02 and sealed in a quartz ampoule under a dynamic vacuum of 1.10^{-6} Torr. The sealed ampoule, about 1 cm in diameter, was heated in a 24 zone Mellen furnace to a temperature of 1123 K and directionally cooled to provide a growth rate of 1 mm/hour. The reactants and products are moisture-sensitive and all manipulations were carried out inside an Argon-filled glove box. The crystal obtained is colorless.

Refinement

The doping of Eu(ii) on the Ba(ii) site was modeled with a fractional Eu atom fixed in the same location and with the same thermal parameters as the Ba(ii) atom. The relative occupancy factor refined to 0.963 (13) Ba, 0.037 (13) Eu.

Figures

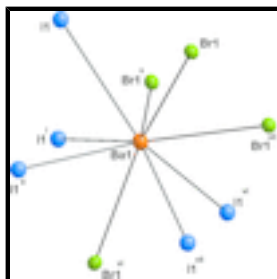


Fig. 1. Arrangement of anions around each Ba atom. The displacement ellipsoids are given at 50% probability. The symmetry codes are: (i) $-x + 1, -y, -z$; (ii) $-x + 1, -y + 1, -z$; (iii) $-x + 3/2, -y + 1, z + 1/2$; (iv) $-x + 3/2, -y, z + 1/2$; (v) $x, y + 1, z$; (vi) $-x + 3/2, -y, z - 1/2$; (vii) $-x + 2, -y, -z$; (viii) $-x + 3/2, -y + 1, z - 1/2$; (ix) $x, y - 1, z$.

barium europium bromide iodide

Crystal data

$\text{Ba}_{0.96}\text{Eu}_{0.04}\text{BrI}$

$M_r = 344.70$

Orthorhombic, $Pnma$

Hall symbol: $-P\ 2ac\ 2n$

$a = 8.684\ (3)\ \text{\AA}$

$b = 5.0599\ (19)\ \text{\AA}$

$c = 10.061\ (4)\ \text{\AA}$

$V = 442.1\ (3)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 576.7$

$D_x = 5.179\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1548 reflections

$\theta = 4.5\text{--}25.4^\circ$

$\mu = 24.97\ \text{mm}^{-1}$

$T = 153\ \text{K}$

Block, colourless

$0.14 \times 0.09 \times 0.06\ \text{mm}$

Data collection

Bruker SMART 1000 CCD diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: $8.192\ \text{pixels mm}^{-1}$

$T = 153\ \text{K}$

φ and ω scans

Absorption correction: multi-scan (Blessing, 1995)

$T_{\min} = 0.128, T_{\max} = 0.316$

2609 measured reflections

430 independent reflections

370 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\text{max}} = 25.0^\circ$

$\theta_{\text{min}} = 3.1^\circ$

$h = -9 \rightarrow 10$

$k = -6 \rightarrow 5$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2

Primary atom site location: heavy-atom method

Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.02P)^2]$
	where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.015$	$(\Delta/\sigma)_{\max} = 0.001$
$wR(F^2) = 0.033$	$\Delta\rho_{\max} = 0.89 \text{ e } \text{\AA}^{-3}$
$S = 1.02$	$\Delta\rho_{\min} = -0.78 \text{ e } \text{\AA}^{-3}$
430 reflections	Extinction correction: SHELXL97 (Sheldrick, 2008),
21 parameters	$F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
	Extinction coefficient: 0.0151 (5)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

The doping of Eu(ii) on the Ba(ii) site was modeled with a fractional Eu atom fixed in the same location and with the same thermal parameters as the Ba(ii) atom. The relative occupancy factor refined to 0.963 (13) Ba, 0.037 (13) Eu.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Il	0.52804 (5)	0.2500	0.16976 (4)	0.01285 (18)	
Ba1	0.76955 (4)	0.2500	-0.12472 (4)	0.01213 (17)	0.963 (13)
Eu1	0.76955 (4)	0.2500	-0.12472 (4)	0.01213 (17)	0.037 (13)
Br1	0.85573 (8)	-0.2500	0.06634 (6)	0.0107 (2)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Il	0.0119 (3)	0.0139 (3)	0.0128 (2)	0.000	0.00011 (16)	0.000
Ba1	0.0110 (3)	0.0126 (3)	0.0128 (2)	0.000	-0.00069 (15)	0.000
Eu1	0.0110 (3)	0.0126 (3)	0.0128 (2)	0.000	-0.00069 (15)	0.000
Br1	0.0096 (4)	0.0119 (5)	0.0105 (3)	0.000	-0.0008 (2)	0.000

Geometric parameters (\AA , $^\circ$)

Il—Ba1	3.6299 (11)	Ba1—Br1 ^{vii}	3.3065 (14)
Il—Ba1 ⁱ	3.6448 (10)	Ba1—Il ⁱ	3.6448 (10)
Il—Ba1 ⁱⁱ	3.6448 (10)	Ba1—Il ⁱⁱ	3.6448 (10)
Il—Ba1 ⁱⁱⁱ	3.7101 (9)	Ba1—Il ^{vi}	3.7101 (9)
Il—Ba1 ^{iv}	3.7101 (9)	Ba1—Il ^{viii}	3.7101 (9)

supplementary materials

Ba1—Br1 ^v	3.2643 (10)	Br1—Ba1 ^{ix}	3.2643 (10)
Ba1—Br1	3.2643 (10)	Br1—Ba1 ^{iv}	3.2930 (13)
Ba1—Br1 ^{vi}	3.2931 (13)	Br1—Ba1 ^{vii}	3.3065 (14)
Ba1—I1—Ba1 ⁱ	107.950 (19)	Br1—Ba1—I1 ⁱⁱ	140.69 (2)
Ba1—I1—Ba1 ⁱⁱ	107.950 (19)	Br1 ^{vi} —Ba1—I1 ⁱⁱ	69.416 (14)
Ba1 ⁱ —I1—Ba1 ⁱⁱ	87.92 (3)	Br1 ^{vii} —Ba1—I1 ⁱⁱ	136.041 (16)
Ba1—I1—Ba1 ⁱⁱⁱ	100.44 (2)	I1—Ba1—I1 ⁱⁱ	72.051 (19)
Ba1 ⁱ —I1—Ba1 ⁱⁱⁱ	151.463 (16)	I1 ⁱ —Ba1—I1 ⁱⁱ	87.92 (3)
Ba1 ⁱⁱ —I1—Ba1 ⁱⁱⁱ	86.09 (3)	Br1 ^v —Ba1—I1 ^{vi}	138.42 (2)
Ba1—I1—Ba1 ^{iv}	100.44 (2)	Br1—Ba1—I1 ^{vi}	72.00 (3)
Ba1 ⁱ —I1—Ba1 ^{iv}	86.09 (3)	Br1 ^{vi} —Ba1—I1 ^{vi}	68.31 (2)
Ba1 ⁱⁱ —I1—Ba1 ^{iv}	151.463 (16)	Br1 ^{vii} —Ba1—I1 ^{vi}	68.457 (18)
Ba1 ⁱⁱⁱ —I1—Ba1 ^{iv}	85.99 (3)	I1—Ba1—I1 ^{vi}	136.767 (14)
Br1 ^v —Ba1—Br1	101.62 (3)	I1 ⁱ —Ba1—I1 ^{vi}	78.07 (2)
Br1 ^v —Ba1—Br1 ^{vi}	129.163 (17)	I1 ⁱⁱ —Ba1—I1 ^{vi}	137.726 (19)
Br1—Ba1—Br1 ^{vi}	129.163 (17)	Br1 ^v —Ba1—I1 ^{viii}	72.00 (3)
Br1 ^v —Ba1—Br1 ^{vii}	70.719 (16)	Br1—Ba1—I1 ^{viii}	138.42 (2)
Br1—Ba1—Br1 ^{vii}	70.718 (16)	Br1 ^{vi} —Ba1—I1 ^{viii}	68.31 (2)
Br1 ^{vi} —Ba1—Br1 ^{vii}	119.523 (18)	Br1 ^{vii} —Ba1—I1 ^{viii}	68.457 (18)
Br1 ^v —Ba1—I1	69.62 (2)	I1—Ba1—I1 ^{viii}	136.767 (14)
Br1—Ba1—I1	69.62 (2)	I1 ⁱ —Ba1—I1 ^{viii}	137.726 (19)
Br1 ^{vi} —Ba1—I1	125.42 (3)	I1 ⁱⁱ —Ba1—I1 ^{viii}	78.07 (2)
Br1 ^{vii} —Ba1—I1	115.06 (2)	I1 ^{vi} —Ba1—I1 ^{viii}	85.99 (3)
Br1 ^v —Ba1—I1 ⁱ	140.69 (2)	Ba1—Br1—Ba1 ^{ix}	101.62 (3)
Br1—Ba1—I1 ⁱ	72.41 (2)	Ba1 ^{ix} —Br1—Ba1 ^{iv}	118.69 (2)
Br1 ^{vi} —Ba1—I1 ⁱ	69.416 (14)	Ba1—Br1—Ba1 ^{vii}	109.282 (16)
Br1 ^{vii} —Ba1—I1 ⁱ	136.041 (16)	Ba1 ^{ix} —Br1—Ba1 ^{vii}	109.282 (16)
I1—Ba1—I1 ⁱ	72.051 (19)	Ba1 ^{iv} —Br1—Ba1 ^{vii}	99.06 (2)
Br1 ^v —Ba1—I1 ⁱⁱ	72.41 (2)		

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

Table 2

Selected geometric parameters (Å, °)

Ba1—I1 ⁱ	3.6448 (10)	Ba1—I1 ⁱⁱ	3.6448 (10)
Ba1—I1 ^{vi}	3.7101 (9)	Ba1—I1 ^{viii}	3.7101 (9)
Ba1—Br1 ^{vii}	3.3065 (14)	Ba1—Br1 ^v	3.2643 (10)
Ba1—Br1	3.2643 (10)	Ba1—Br1 ^{vi}	3.2931 (13)
Br1 ^v —Ba1—Br1	101.62 (3)	Br1—Ba1—I1 ⁱⁱ	140.69 (2)
Br1 ^v —Ba1—Br1 ^{vi}	129.163 (17)	Br1 ^{vi} —Ba1—I1 ⁱⁱ	69.416 (14)
Br1—Ba1—Br1 ^{vi}	129.163 (17)	Br1 ^{vii} —Ba1—I1 ⁱⁱ	136.041 (16)

Br1 ^v —Ba1—Br1 ^{vii}	70.719 (16)	Br1 ^v —Ba1—I1 ^{vi}	.138.42 (2)
Br1—Ba1—Br1 ^{vii}	70.718 (16)	Br1—Ba1—I1	69.62 (2)
Br1 ^{vi} —Ba1—Br1 ^{vii}	119.523 (18)	Br1 ^v —Ba1—I1	69.62 (2)
I1 ⁱ —Ba1—I1 ⁱⁱ	87.92 (3)	Br1—Ba1—I1 ^{vi}	72.00 (3)
I1—Ba1—I1 ^{vi}	136.767 (14)	Br1 ^{vi} —Ba1—I1 ^{vi}	68.31 (2)
I1 ⁱ —Ba1—I1 ^{vi}	78.07 (2)	Br1 ^{vii} —Ba1—I1 ^{vi}	68.457 (18)
I1 ⁱⁱ —Ba1—I1 ^{vi}	137.726 (19)	Br1 ^{vi} —Ba1—I1	125.42 (3)
.I1—Ba1—I1 ⁱⁱ	.72.051 (19)	Br1 ^{vii} —Ba1—I1	115.06 (2)
Br1—Ba1—I1 ⁱ	72.41 (2)	Br1 ^v —Ba1—I1 ⁱ	140.69 (2)
I1—Ba1—I1 ⁱ	72.051 (19)	Br1 ^{vi} —Ba1—I1 ⁱ	69.416 (14)
Br1 ^{vii} —Ba1—I1 ⁱ	136.041 (16)	Br1 ^v —Ba1—I1 ⁱⁱ	.72.41 (2)

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

Fig. 1

