Europium-doped barium bromide iodide

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Europium-doped barium bromide iodide

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Single crystals of Ba0.96Eu0.04BrI (barium europium bromide iodide) were grown by the Bridgman technique. The title compound adopts the ordered PbCl2 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 = ±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 isotypic compounds, see: PbCl2 (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 Euii-activated barium halides, see: Schweizer (2001); Crawford & Brixner (1991); Selling et al. (2007); Bourret-Courchesne et al. (2009).

Experimental

Crystal data

Ba0.96Eu0.04BrI
M = 544.70
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 Kα radiation
μ = 24.97 mm–1
T = 153 K

Data collection

Bruker SMART 1000 CCD
diffractometer
Absorption correction: multi-scan
(Blessing, 1995)
T = 0.128, T = 0.316
2609 measured reflections
430 independent reflections
370 reflections with I > 2σ(I)
Rint = 0.027

Refinement

R[F2 > 2σ(F2)] = 0.015
wR(F2) = 0.033
S = 1.02
430 reflections

Table 1

Selected bond lengths (Å).
[Table entries follow]

Symmetry codes: (i) –x + 1, y, –z; (ii) –x + 1, y + 1, –z; (iii) –x + 2, y – 1, z + 1/2; (iv) –x + 1, y, z + 1/2; (v) y, y + 1, z; (vi) –x + 1, –y, z – 1/2; (vii) –x + 2, –y, z.

Data collection: APEX2 (Bruker, 2008); cell refinement: SAINT (Bruker, 2008); data reduction: SAINT; 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.

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

supplementary materials
Europium-doped barium bromide iodide

G. Gundiah, S. M. Hanrahan, F. J. Hollander and E. D. Bourret-Courchesne

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 $\gamma$-rays (Selling et al., 2007). The F-based compounds of the form BaFX ($X=\text{Cl, Br, I}$) 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 P2$_{2}$$\bar{1}$ and Pbam respectively (Lenus et al., 2002). We have synthesized single crystals of Ba$_{0.96}$Eu$_{0.04}$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 Pnna, 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 $4f^65d \rightarrow 4f^7$ 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 Ba$_{0.96}$Eu$_{0.04}$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.
supplementary materials

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

\(a = 8.684\ (3) \ \text{Å}\)

\(b = 5.0599\ (19) \ \text{Å}\)

\(c = 10.061\ (4) \ \text{Å}\)

\(V = 442.1\ (3) \ \text{Å}^3\)

\(Z = 4\)

\(F_{000} = 576.7\)

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

Mo \(K\alpha\) radiation, \(\lambda = 0.71073\ \text{Å}\)

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

430 independent reflections

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

\(R_{int} = 0.027\)

\(\theta_{\text{max}} = 25.0^\circ\)

\(\theta_{\text{min}} = 3.1^\circ\)

\(h = -9\rightarrow10\)

\(k = -6\rightarrow5\)

\(l = -11\rightarrow11\)

2609 measured reflections

Refinement

Refinement on \(F^2\)

Primary atom site location: heavy-atom method
supplementary materials

Least-squares matrix: full

\[ w = 1/\sigma^2(F_o^2) + (0.02P)^2 \]

where \( P = (F_o^2 + 2F_c^2)/3 \)

\[ \Delta \rho_{\text{max}} = 0.001 \]

\[ \Delta \rho_{\text{min}} = -0.78 \text{ e}\AA^{-3} \]

430 reflections

Extinction correction: SHELXL97 (Sheldrick, 2008),

\[ \text{Fe}^* = k\text{Fe}[1+0.001x\text{Fe}^3\gamma^3/\sin(20)]^{1/4} \]

21 parameters

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 (\( A^2 \))

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Atomic displacement parameters (\( A^2 \))

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Geometric parameters (\( A, \circ \))

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supplementary materials

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Ba1—II—Ba1ii 107.950 (19)  Br1i—Ba1—IIi 69.416 (14)
Ba1i—II—Ba1ii 87.92 (3)  Br1viii—Ba1—IIi 136.041 (16)
Ba1i—II—Ba1iii 100.44 (2)  II—Ba1—IIi 72.051 (19)
Ba1i—II—Ba1iii 151.463 (16)  IIi—Ba1—IIi 87.92 (3)
Ba1ii—II—Ba1iii 86.09 (3)  Br1v—Ba1—IIvi 138.42 (2)
Ba1i—II—Ba1iv 100.44 (2)  Br1—Ba1—IIvi 72.00 (3)
Ba1i—II—Ba1iv 86.09 (3)  Br1i—Ba1—IIvi 68.31 (2)
Ba1ii—II—Ba1iv 151.463 (16)  Br1vii—Ba1—IIvi 68.457 (18)
Ba1iii—II—Ba1iv 85.99 (3)  II—Ba1—IIvi 136.767 (14)
Br1v—Ba1—Br1 101.62 (3)  IIi—Ba1—IIvi 78.07 (2)
Br1—Ba1—Br1vi 129.163 (17)  Br1v—Ba1—IIviii 137.726 (19)
Br1—Ba1—Br1vi 129.163 (17)  Br1—Ba1—IIviii 72.00 (3)
Br1v—Ba1—Br1vii 70.719 (16)  Br1—Ba1—IIviii 138.42 (2)
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Br1vi—Ba1—Br1vii 119.523 (18)  Br1vii—Ba1—IIviii 68.457 (18)
Br1v—Ba1—II 69.62 (2)  II—Ba1—IIviii 136.767 (14)
Br1—Ba1—II 69.62 (2)  IIi—Ba1—IIviii 137.726 (19)
Br1vi—Ba1—II 125.42 (3)  IIi—Ba1—IIviii 78.07 (2)
Br1vii—Ba1—II 115.06 (2)  IIi—Ba1—IIviii 85.99 (3)
Br1v—Ba1—IIi 140.69 (2)  Ba1—Br1—Ba1ix 101.62 (3)
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Br1vii—Ba1—IIi 136.041 (16)  Br1v—Br1—Ba1vii 109.282 (16)
II—Ba1—IIi 72.051 (19)  Br1—Ba1—IIv 99.06 (2)
Br1v—Ba1—IIi 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, °)

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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.
supplementary materials

Fig. 1