Synthesis and Structure of the new Fluoride Bromide $Ba_{6.668(2)}Ca_{0.332(2)}F_{12}Br_2$ and Solid Solutions with Composition $Ba_{7-x}Ca_xF_{12}(Cl_yBr_{1-y})_2$ with x = ~0.5, 0 < y < 1

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Abstract. Crystals of the chemical composition $Ba_7F_{12}Cl_2$ were modified by adding a small amount of Ca^{2+} to allow the synthesis of the corresponding bromine compound $Ba^{[Ca]}_7F_{12}Br_2$. These samples were prepared in a NaBr flux and characterized by single crystal x-ray diffraction. The new structure crystallizes in a disordered arrangement in the hexagonal space group $P6_3/m$ (176). The calcium ion has a coordination number of 6.
Solid solutions on the heavy halide position can be synthesised in a NaCl/NaBr flux to obtain the compounds $Ba_{7-x}Ca_xF_{12}(Cl_yBr_{1-y})_2$ with x = ~0.5 and 0 < y < 1.

Regardless the amount of calcium used in the preparation process, the Ca stoichiometry in the compound is always between 0.3 and 0.5. The lattice parameters differ depending on the Ca- and Br-content between 1053.81(5) $\leq$ a = b $\leq$ 1058.93(3) pm and 421.21 $\leq$ c $\leq$ 426.78(3) pm.

Keywords: Barium; Calcium; Fluoride bromide; Disordered structures; Crystal structures; Solid solutions

Synthese und Struktur einer neuen Fluorid-Bromid-Verbindung $Ba_{6.668(2)}Ca_{0.332(2)}F_{12}Br_2$ und von Mischkristallen $Ba_{7-x}Ca_xF_{12}(Cl_yBr_{1-y})_2$ mit x = ~0.5, 0 < y < 1

Inhaltsübersicht. Kristalle der Verbindung $Ba_7F_{12}Cl_2$ wurden durch den Einbau von kleinen Mengen an Calcium so modifiziert, dass die Verbindung $Ba^{[Ca]}_7F_{12}Br_2$ erhalten werden konnte. Die Kristalle wurden aus einer NaBr-Schmelze hergestellt und durch Einkristallstrukturanalyse charakterisiert. Die Verbindung kristallisiert in einer fehlgeordneten Variante der $Ba_7F_{12}Cl_2$-Struktur in der hexagonalen Raumgruppe $P6_3/m$ (176). Das eingebaute Calciumion hat die Koordinationszahl 6.

Mischkristalle wurden aus einer NaCl/NaBr-Schmelze synthetisiert. Dabei entstanden Verbindungen der Zusammensetzung $Ba_{7-x}Ca_xF_{12}(Cl_yBr_{1-y})_2$ mit x = ~0.5 und 0 < y < 1.
Ungeachtet der eingesetzten Menge an Ca wurde in den Verbindungen eine Calcium Stöchiometrie zwischen 0.3 und 0.5 bestimmt. Die Gitterkonstanten werden bei zunehmendem Br-Gehalt größer, wobei gilt: 1053.81(5) $\leq$ a = b $\leq$ 1058.93(3) pm und 421.21 $\leq$ c $\leq$ 426.78(3) pm.

Introduction

Recently a new host lattice for rare earth elements with the composition $Ba_7F_{12}Cl_2$ showing interesting optical properties was reported [1, 2, 3]. The compound crystallises in two modifications with space group $P\bar{6}$ and $P6_3/m$ according to the synthesis condition. The latter shows disorder within tricapped trigonal channels. Solid solutions with bivalent ions on the metal side are still under study; a complete substitution of the channel allowed to obtain the ordered compound $Ba_6EuF_{12}Cl_2$ (space group $P\bar{6}$) [4].

Similar studies were made for the corresponding lead-chlorine compound [5] where also both modifications could be established. The corresponding lead-bromine compound was reported lately [6].

Solid state synthesis did not allow to obtain the corresponding barium bromine compound. However, by adding a small amount of Ca^{2+}, the bromine sample could be stabilized as $Ba_{6.668(2)}Ca_{0.332(2)}F_{12}Br_2$. An unexpected disorder was found in the fluorine channel, where the Ca-ion is surrounded by six fluorides ($CN^{Ca}=6$). To confirm this unexpected result, solid solutions on the heavy halide position (Br $\rightarrow$ Cl) were made and analysed for $Ba_{7-x}Ca_xF_{12}(Cl_yBr_{1-y})_2$ with x = ~0.5 and 0 < y < 1. For all solid solutions, a roughly similar calcium concentration was detected. All refinements show, that calcium is surrounded by 6 fluorides.

Synthesis and structure analysis for these solid solutions will be described in this paper.

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Experimental Section

The samples were prepared in air or under controlled atmosphere using either a muffle furnace or a Czochralski and Bridgman crystal growth set-up. For all preparations in air, the starting alkaline earth halides (of typically "pro analysi" purity) together with NaCl/NaBr as flux were placed in covered platinum crucibles, while graphite crucibles were used under inert atmosphere to exclude a possible oxygen incorporation in the matrix. The mixtures were heated above the melting point (~900 °C) and slowly cooled down to 600 °C in 3h. Needle shaped crystals up to 1 mm in length can be obtained in addition to other phases such as BaF(Cl,Br). Our previous experiments [1] have shown that for disordered $Ba_7F_{12}Cl_2$ the flux composition of 0.75 BaF_2 + 0.25 (Na_2Cl_2) yields good crystals. For the calcium substituted samples, the same basic composition was kept, but BaF_2 was partly replaced by CaF_2. Typically, the calcium to barium ratio ranged from 1:6 to 2:5 in the flux, while in the resulting single crystals (see refinement results below) the highest Ca content which was observed corresponds to a ratio of 0.6: 6.4.

In a second series of experiments, NaCl was progressively replaced by NaBr to yield the partially bromide substituted crystals $Ba_{7-x}Ca_xF_{12}Cl_{2-y}Br_y$. In this case, the calcium to barium ratio was also increased up to 3:4 to obtain a nominally fully substituted "$Ba_6CaF_{12}Br_2$", however the calcium content in the crystals (obtained from the x-ray refinement) remained similar to the one found for the other crystals $Ba_{7-x}Ca_xF_{12}Cl_{2-y}Br_y$, i.e. x < 0.5. The end member $Ba_{6.668(2)}Ca_{0.332(2)}F_{12}Br_2$ was also obtained from a NaBr flux, but the calcium content was decreased down to a theoretical end member $Ba_{6.835}Ca_{0.165}F_{12}Br_2$. Nevertheless the calcium content in the crystals remained almost unaffected with a calcium content of about 0.332(2) (also obtained from the x-ray refinement).

In addition to these experiments several attempts were made to stabilize the bromide by replacing the small Ca-ion with other bivalent ions smaller than Ba^{2+}, e.g. Sr^{2+}. For all syntheses, no bromine compound was found.

Results and Discussion

Crystal Description

All flux grown crystals have hexagonal habit. Needles up to a size of 1 mm were observed. Inspection in polarized light showed no birefringence along the needle axis. Together with the crystal faces, a hexagonal or trigonal symmetry was found. The crystals can be cleaved easily along and perpendicular to the needle axis and plates can be obtained by cleavage.

X-Ray Diffraction

The lattice constants and diffraction data of selected crystals were measured on a CAD4, a SMART and a STOE diffractometer. Atomic coordinates for starting refinements were taken from ref. [1]. Details of the refined crystal data and refinement conditions are given in Table 1. The partially standardized [7] atomic positional and vibrational parameters for all samples are given in Table 2. The anisotropic displacement factors for the Ca-ion are summarized in Table 3.

Structure Description and Discussion

The description of this structure is given in detail in the publication of $Ba_7F_{12}Cl_2$ [1]. The barium atoms in the structure are surrounded by two chlorine or bromine atoms and seven fluorine atoms. Propeller-type arrangements with chlorine atoms located on the axis and fluorine atoms forming blades are observed. For Ca-substituted samples, a further disorder within the channels (see Figure 1) was observed and confirmed by x-ray diffraction analysis and from changes in the lattice parameters (see below). It consists of

Table 1 Crystal data and conditions of data collection and refinement for phases $Ba_{7-x}Ca_xF_{12}(Cl_yBr_{1-y})_2$ in the hexagonal space group $P6_3/m$ (176), Z = 1, measured with wavelength $MoK\alpha$ (71.073 pm), temperature 300K, used program XTAL 3.7

Empirical Formula	Ba / Ca	6.698(4) / 0.302(4)	6.704(2) / 0.296(2)	6.6862(16) / 0.3138(16)	6.6676(16) / 0.3324(16)
	Cl / Br	2 / −	1.664(8) / 0.336(8)	1.090(4) / 0.910(4)	− / 2
Formula mass		1231.2	1246.4	1270.2	1316.817
Unit cell dimensions /pm		$a = b = 1053.81(5)$	$a = b = 1055.03(5)$	$a = b = 1057.17(6)$	$a = b = 1058.93(3)$
		$c = 421.21(3)$	$c = 421.82(5)$	$c = 423.81(5)$	$c = 426.78(3)$
Volume /10^6 pm^3		405.09(5)	406.62(6)	410.20(7)	414.45(4)
Density /g/cm^3		5.047	5.090	5.142	5.276
Crystal size /mm^3		0.05x0.05x0.012	0.05x0.05x0.012	0.05x0.05x0.012	0.05x0.05x0.012
Diffractometer type		STOE	CAD4	CAD4	SMART
θ range for data collection		2.2 − 40.0	2.2 − 54.9	2.2 − 54.9	2.2 − 28.48
No. of reflections measured		4734	1872	1841	2721
No. of independent reflections		757	1872	1841	377
R_{int} =		0.0249	0.0211	0.0397	0.0152
No. of refl. with I > 3σ(I)		698	1572	1485	368
Absorption coefficient /cm^2/g		41.206	50.945	50.945	47.609
R (R_w)		0.025 (0.032)	0.021 (0.025)	0.040 (0.043)	0.0152 (0.0140)
Number of Parameters		27	28	28	27
Extinction (Zachariasen)		1.830(18)	0.091(2)	0.1373(15)	0.0133(7)
Goodness-of-fit		3.002	1.8015	3.7996	2.0435
$e_{min/max}$ density values /pm^{-3}		−1.49/4.99	−2.32/2.90	−2.93/3.47	−1.013/0.765
CSD-number		413375	413376	413374	413377

Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe D-76344 Eggenstein-Leopoldshafen (Germany), email: crysdata@FIZ-Karlsruhe.de, on quoting the deposition numbers CSD (as mentioned in this table), the name of the authors and citation of the paper.

Table 2 Standardized atomic positional parameters, population and atomic displacement factors (x100)

$Ba_{6.698(4)}Ca_{0.302(4)}F_{12}Cl_2$

Ion	Wyk	x	y	z	U_{eq}	pop
F(1)	6(h)	0.1154(3)	0.2155(3)	1/4	2.4(1)	0.5
F(2)	6(h)	0.1498(3)	0.2708(3)	1/4	2.4(1)	0.5
Ba(1)	6(h)	0.40311(1)	0.29278(1)	1/4	1.422(7)	
F(3)	6(h)	0.43346(11)	0.05625(12)	1/4	1.96(6)	
Cl(1)	2(c)	1/3	2/3	1/4	1.96(2)	
Ca(1)	2(b)	0	0	0	2.74(3)	0.150(1)*
Ba(2)	2(a)	0	0	1/4	2.74(3)	0.350(1)*

$Ba_{6.704(2)}Ca_{0.296(2)}F_{12}Cl_{1.664(8)}Br_{0.336(8)}$

Ion	Wyk	x	y	z	U_{eq}	pop
F(1)	6(h)	0.1178(2)	0.2198(2)	1/4	2.14(8)	0.5
F(2)	6(h)	0.1517(2)	0.2741(2)	1/4	1.67(3)	0.5
Ba(1)	6(h)	0.40244(1)	0.29313(1)	1/4	1.190(3)	
F(3)	6(h)	0.43372(9)	0.05658(8)	1/4	1.67(3)	
Cl(1)	2(c)	1/3	2/3	1/4	1.61(1)	0.832(4)*
Br(1)	2(c)	1/3	2/3	1/4	1.61(1)	0.168(4)*
Ca(1)	2(b)	0	0	0	2.57(2)	0.148(1)*
Ba(2)	2(a)	0	0	1/4	2.57(2)	0.352(1)*

$Ba_{6.6862(16)}Ca_{0.3138(16)}F_{12}Cl_{1.090(4)}Br_{0.910(4)}$

Ion	Wyk	x	y	z	U_{eq}	pop
F(1)	6(h)	0.1147(2)	0.2151(2)	1/4	3.1(1)	0.5
F(2)	6(h)	0.1466(2)	0.2672(2)	1/4	2.02(5)	0.5
Ba(1)	6(h)	0.40094(1)	0.29370(1)	1/4	1.303(4)	
F(3)	6(h)	0.43358(9)	0.05708(10)	1/4	2.02(5)	
Cl(1)	2(c)	1/3	2/3	1/4	1.66(1)	0.545(2)*
Br(1)	2(c)	1/3	2/3	1/4	1.66(1)	0.455(2)*
Ca(1)	2(b)	0	0	0	2.83(3)	0.1569(8)*
Ba(2)	2(a)	0	0	1/4	2.83(3)	0.3431(8)*

$Ba_{6.6676(16)}Ca_{0.3324(16)}F_{12}Br_2$

Ion	Wyk	x	y	z	U_{eq}	pop
F(1)	6(h)	0.1103(6)	0.2115(3)	1/4	2.5(3)	0.5
F(2)	6(h)	0.1439(6)	0.2673(3)	1/4	2.5(3)	0.5
Ba(1)	6(h)	0.39811(1)	0.29463(1)	1/4	1.40(1)	
F(3)	6(h)	0.43308(11)	0.05779(11)	1/4	1.89(8)	
Br(1)	2(c)	1/3	2/3	1/4	1.73(2)	
Ca(1)	2(b)	0	0	0	2.80(4)	0.1662(8)*
Ba(2)	2(a)	0	0	1/4	2.80(4)	0.3338(8)*

* constraint

Table 3 Anisotropic displacement factor

Compound	Ion	U_{11}	U_{22}	U_{33}	U_{12}
$Ba_{6.698(4)}Ca_{0.302(4)}F_{12}Cl_2$	Ca(1)	1.29(1)	1.29(1)	5.62(4)	0.648(6)
$Ba_{6.704(2)}Ca_{0.296(2)}F_{12}Cl_{1.664(8)}Br_{0.336(8)}$	Ca(1)	1.011(6)	1.011(6)	5.68(3)	0.506(3)
$Ba_{6.6862(16)}Ca_{0.3138(16)}F_{12}Cl_{1.090(4)}Br_{0.910(4)}$	Ca(1)	1.070(8)	1.070(8)	6.36(4)	0.535(4)
$Ba_{6.6676(16)}Ca_{0.3324(16)}F_{12}Br_2$	Ca(1)	1.168(21)	1.168(21)	6.05(5)	0.584(10)

The anisotropic displacement factor in the structure factor expression is: $U_{ij} = \exp-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^*)$. Note that $U_{13} = 0$ and $U_{23} = 0$.
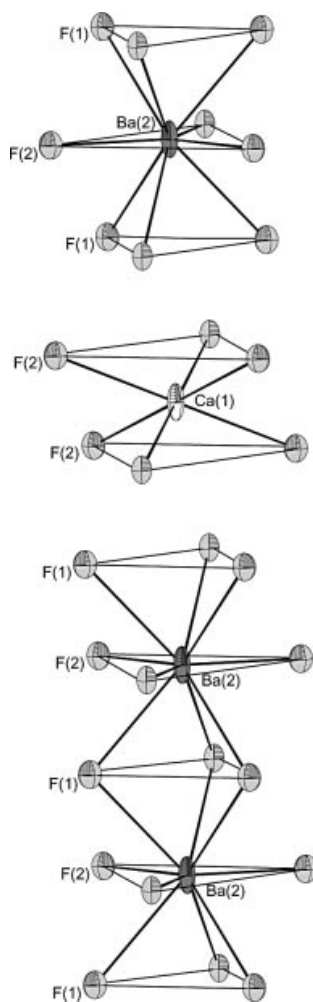
Figure 1 The connected fluoride triangles (open spheres) along c_{hex} are shown for $Ba_{6.668(2)}Ca_{0.332(2)}F_{12}Br_2$. The large ellipsoids represent the Ba(2) ions. Each one is surrounded by nine fluoride ions forming a tricapped trigonal prism. In between is a Ca-ion, surrounded by 6 fluoride ions.

partial occupancies of an additional position [Wykoff 2b] by Ca. No Ca-incorporation was found in the matrix of the Ba positions.
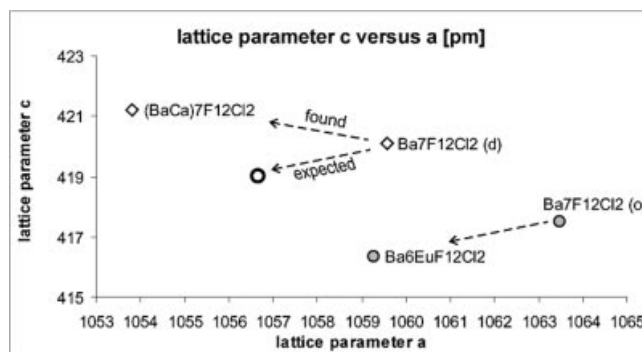

Figure 2 Lattice parameters of different modifications of $Ba_7F_{12}Cl_2$.

Figure 2 compares the lattice parameter behaviour, when barium is replaced by a smaller bivalent ion. Experimental results in space group $P\bar{6}$ show, that the lattice parameters a and c decrease if Ba^{2+} is replaced by Eu^{2+} [4] within the channels. The ratio of the cell parameters remain the same. However the new compounds in space group $P6_3/m$ with Ca^{2+} in the channels do not show this behaviour. The Ba–Cl:Ca compound shows a smaller lattice parameter a, but the parameter c is increased in comparison with $Ba_7F_{12}Cl_2$ (d) [1]. This effect may be explained by the further disordered position of the atoms in the structure. By replacing continuously the chlorine by bromine, the lattice parameters are increasing with higher bromine content (see Table 1).

The chemical environment and coordination can be compared between the pure Ba/Ca–Cl and the Ba/Ca–Br compound. For these two samples the positions of F(1) and F(2) are equally each half-occupied and are separated by 51.0 (4) pm for the chlorine compound and by 50.7 (7) pm for the bromine compound.

The shortest Ba–F distance of 256.2 (3) and 255.9(5) pm is within standard deviations the same in these two compounds. Differences in the distances could be found in the Ba(1)–F(3) distances with 264.61(11) for the chlorine compound vs. 267.44(10) pm for the bromine compound and 266.70(11) vs. 271.22(10) pm. All other interatomic dis-

Table 4 Selected interatomic distances

$Ba_{6.698(4)}Ca_{0.302(4)}F_{12}Cl_2$		$Ba_{6.704(2)}Ca_{0.296(2)}F_{12}Cl_{1.664(8)}Br_{0.336(8)}$		$Ba_{6.6862(16)}Ca_{0.3138(16)}F_{12}Cl_{1.090(4)}Br_{0.910(4)}$		$Ba_{6.6676(16)}Ca_{0.3324(16)}F_{12}Br_2$	
Ba(1)–F(2)	256.2(3)	Ba(1)–F(2)	255.08(18)	Ba(1)–F(2)	256.03(20)	Ba(1)–F(2)	255.9(6)
Ba(1)–F(3)	264.64(11)	Ba(1)–F(3)	264.78(8)	Ba(1)–F(3)	265.80(9)	Ba(1)–F(3) (2x)	266.75(6)
Ba(1)–F(3) (2x)	266.69(6)	Ba(1)–F(2) (2x)	266.25(11)	Ba(1)–F(3) (2x)	266.95(6)	Ba(1)–F(3)	267.44(10)
Ba(1)–F(3)	266.70(11)	Ba(1)–F(3) (2x)	266.74(5)	Ba(1)–F(3)	269.06(9)	Ba(1)–F(2) (2x)	269.3(3)
Ba(1)–F(2) (2x)	267.05(18)	Ba(1)–F(3)	267.61(8)	Ba(1)–F(2) (2x)	269.27(13)	Ba(1)–F(3)	271.22(10)
Ba(1)–F(1)	271.8(3)	Ba(1)–F(1)	270.04(19)	Ba(1)–F(1)	270.81(20)	Ba(1)–F(1)	271.6(6)
Ba(1)–F(1) (2x)	290.71(19)	Ba(1)–F(1) (2x)	288.82(13)	Ba(1)–F(1) (2x)	291.72(14)	Ba(1)–F(1) (2x)	293.4(3)
Ba(1)–Cl(1) (2x)	333.80(2)	Ba(1)–Cl(1)/Br(1) (2x)	334.88(2)	Ba(1)–Cl(1)/Br(1) (2x)	337.30(2)	Ba(1)–Br(1) (2x)	341.23(1)
Ba(2)–F(2) (3x)	247.6(3)	Ba(2)–F(2) (3x)	250.87(2)	Ba(2)–F(2) (3x)	245.03(2)	Ba(2)–F(2) (3x)	245.4(5)
Ba(2)–F(1) (6x)	288.29(19)	Ba(2)–F(1) (6x)	291.37(14)	Ba(2)–F(1) (6x)	289.40(14)	Ba(2)–F(1) (6x)	288.4(3)
Ca(1)-F(2) (6x)	269.1(3)	Ca(1)-F(2) (6x)	272.13(19)	Ca(1)-F(2) (6x)	266.95(19)	Ca(1)-F(2) (6x)	267.6(5)

tances are also slightly longer in the bromine compound (see Table 4).

In general the interatomic distances of all four compounds are significantly different for all barium surroundings. Most pronounced are the Ba−Cl/Ba−Br distance differences. The Ba−Br distance is 342.1 pm whereas the corresponding Ba−Cl distance (i.e. for the Ca doped sample) is 333.8 pm, similar to the undoped samples. A comparable behaviour was found for the solid solution on the heavy halide side for $Ba_{12}F_{19}(Cl,Br)_5$ [8].

Conclusion

The crystals of the disordered bromine compound of hypothetically $Ba_7F_{12}Cl_2$ can only be synthesised if small amounts of calcium are incorporated in the structure. Regardless of the concentration of calcium used in the preparation process, the incorporated compound gives always the stoichiometry of $Ba_{7-x}Ca_xF_{12}X_2$ with X = Br, Cl and x = ~0.5.

References

[1] F. Kubel, H. Bill, H. Hagemann, *Z. Anorg. Allg. Chem.* **1999**, *625*, 643.

[2] F. Kubel, H. Bill, H. Hagemann, *Z. Naturforsch.* **1999**, *54b*, 515.

[3] H. Bill, H. Hagemann, F. Kubel, PCT Int. Appl. (1999), [27 pp. CODEN: PIXXD2 WO 9917340 A1 19990408 CAN 130:259353 AN 1999:234098].

[4] F. Kubel, H. Bill, H. Hagemann, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1721.

[5] F. Kubel, H. Hagemann, H. Bill, *J. Solid State Chem.* **2000**, *149*, 56.

[6] M. Weil, F. Kubel, *Z. Anorg. Allg. Chem.* **2000**, *626*, 2481.

[7] L. M. Gelato, E. Parthé, *J. Appl. Chem.* **1987**, *20*, 137.

[8] F. Kubel, H. Hagemann, H. Bill, *Z. Anorg. Allg. Chem.* **1996**, *622*, 1374.