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ORIGINAL PAPER

Calcium-free Solid Solutions in the System $\text{Ba}_7\text{F}_{12}\text{Cl}_{2-x}\text{Br}_x$ ($x < 1.5$), a Single-component White Phosphor Host

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Abstract We have recently prepared solid solutions of $\text{Ba}_{-6.3}\text{Ca}_{-0.7}\text{F}_{12}\text{Cl}_{2-x}\text{Br}_x$ with x ranging from 0 to 2. In this work, the synthesis and single crystal X-ray structure of calcium-free crystals of $\text{Ba}_{-6.9}\text{Na}_{-0.2}\text{F}_{12}\text{Br}_{0.6}\text{Cl}_{1.4}$ (space group $P6_3/m$, $a = 10.6024(10)$, $c = 4.2034(4)$ Å), $\text{Ba}_{-6.9}\text{Na}_{-0.2}\text{F}_{12}\text{Br}_{1.4}\text{Cl}_{0.6}$ (space group $P6_3/m$, $a = 10.6155(9)$, $c = 4.2355(4)$ Å) and $\text{Ba}_{-6.9}\text{Na}_{-0.2}\text{Br}_{1.32}\text{Cl}_{0.68}\text{F}_{12}$ (space group $P6_3/m$, $a = 10.6218(9)$, $c = 4.2284(4)$ Å) are reported.

These crystals systematically present additional electron density at the $0\ 0\ 0.25$ position which is associated with the presence of small, but significant amounts of Na^+ ions in the crystal.

Keywords Barium fluorohalide · Solid solution · Single crystal X-ray diffraction

Introduction

Alkaline earth fluoro-halides are interesting host materials for optical applications. Crystals of the matlockite family

(PbFCl -structure) have attracted substantial interest because of several applications such as X-ray imaging or optical hole burning at ambient temperatures [1]. The new compound $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ and its derivatives have been patented as a new, single component white phosphor material [2]. $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ crystallizes in two modifications, one ordered (space group $P-6$) and one disordered (space group $P6_3/m$) [3]. Very recently, we have demonstrated that the disordered form contains small amounts of Na^+ ions, yielding a refined composition $\text{Ba}_{-6.9}\text{Na}_{-0.2}\text{F}_{12}\text{Cl}_2$ [4].

The formation of solid solutions (desirable to tune the optical properties of doped crystals) starting from nominally $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ can be approached both by replacing Ba with another divalent ion, and by replacing Cl with Br. We have previously reported the crystal structures of $\text{Ba}_6\text{EuF}_{12}\text{Cl}_2$ [5] and of the solid solutions $\text{Ba}_{-6.3}\text{Ca}_{-0.7}\text{F}_{12}\text{Cl}_{2-x}\text{Br}_x$ [6]. In this latter work, the experimental preparation conditions required the presence of Ca^{2+} in the reaction mixture to obtain bromide substituted single crystals.

In this work we address the formation of single crystals of $\text{Ba}_7\text{F}_{12}\text{Cl}_{2-x}\text{Br}_x$ ($x < 1.5$) without Ca. The effect of the substitution of chloride by bromide on the emission spectra of these white phosphors is briefly discussed.

Experimental

Single crystals were obtained by slow cooling (0.1 K/min) of melts containing alkali halides (LiCl, LiBr, NaCl and NaBr) and BaF_2 under inert atmosphere in graphite crucibles. Both pure and Eu(II)-doped (Eu:Ba ratio < 0.01) samples were prepared. The presence of Eu(II) in these concentrations did not influence the crystal structure.

Dedicated to the memory of Professor Erwin Parthé, deceased August 28 2006. The synthesis and single crystal X-ray structures of $\text{Ba}_7\text{F}_{12}\text{Cl}_{2-x}\text{Br}_x$ ($x \leq 1.4$) including small amounts of Na in the $0\ 0\ 0.25$ position are reported.

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Individual single crystals were mechanically separated and selected under polarized light for single crystal structure determinations.

Additional solid state reactions of stoichiometric mixtures of $\text{Ba}_7\text{F}_{12}\text{Cl}_{2-x}\text{Br}_x$ (starting from $6\text{BaF}_2 + (2-x)\text{BaCl}_2 + x\text{BaBr}_2$) over the entire composition range were performed.

X-ray measurements were obtained using a Siemens SMART diffractometer with a graphite monochromator and a SMART APEX detector.

Luminescence spectra were obtained using a Fluorolog instrument.

Results and Discussions

Synthesis

We have performed systematic solid state preparations of stoichiometric mixtures corresponding to $\text{Ba}_7\text{F}_{12}\text{Cl}_{2-x}\text{Br}_x$ over the entire composition range with an annealing temperature of 750 °C under inert atmosphere. X-ray powder diffraction shows that up to $x = 1.4$, the ordered form of $\text{Ba}_7\text{F}_{12}\text{Cl}_{2-x}\text{Br}_x$ is obtained (space group $P6_3$), as well as some BaF_2 (ca 20 wt%). For $x > 1.5$, the only phases found were BaF_2 and $\text{BaFCl}_{1-y}\text{Br}_y$. Es-Saski et al. [7] equally reported this limit of bromide substitution in $\text{Ba}_7\text{F}_{12}\text{Cl}_{2-x}\text{Br}_x$ by solid state reaction.

Single crystals of $\text{Ba}_{7-y}\text{Ca}_y\text{F}_{12}\text{Cl}_{2-x}\text{Br}_x$ with $y \approx 0.7$ (disordered modification, space group $P6_3/m$) have been prepared previously [6] from mixtures of: $\text{BaF}_2 + \text{CaF}_2 + \text{NaCl} + \text{NaBr}$. The corresponding lattice parameters are collected in Fig. 1 and compared with those of samples prepared in this study.

Initial experiments with mixtures of $\text{BaF}_2 + \text{NaCl} + \text{NaBr}$ did not appear to favour the introduction of bromide

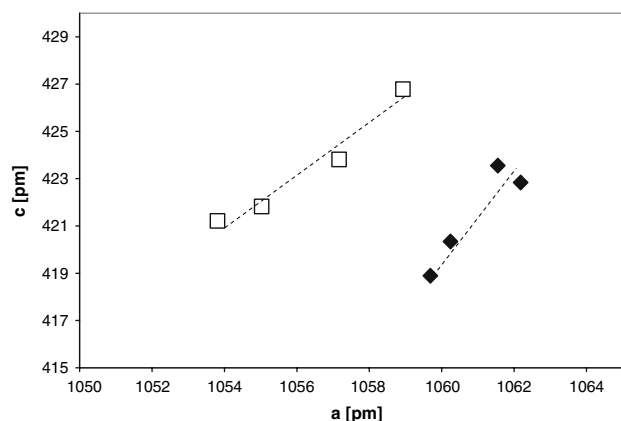


Fig. 1 Comparison of the lattice parameters for $\text{Ba}_{6.3}\text{Ca}_{0.7}\text{F}_{12}\text{X}_2$ [6] (open squares) and calcium-free (filled diamonds) $\text{Ba}_7\text{F}_{12}\text{X}_2$ ($\text{X} = \text{Cl}_{2-x}\text{Br}_x$) single crystals. The lines are drawn to guide the eye

ions in the structure. However, the addition of LiCl and LiBr to the reaction mixture resulted in the successful preparation of $\text{Ba}_7\text{F}_{12}\text{Cl}_{2-x}\text{Br}_x$. However, also with this flux composition the highest bromide content was limited to the composition $\text{Ba}_7\text{F}_{12}\text{Cl}_{0.6}\text{Br}_{1.4}$.

Typical reaction conditions leading to well developed crystalline needles of 2–3 mm length were: 5 g $\text{BaF}_2 + 0.44$ g $\text{NaBr} + 0.077$ g $\text{LiBr} + 0.144$ g LiCl , corresponding to a molar ratio of $\text{NaBr}:\text{LiBr}:\text{LiCl}$ of 5:1:4 respectively. This mixture was heated under inert atmosphere to 950 °C and then cooled in 50 h to 650 °C.

Besides the desired product, about 10 wt% of LiBaF_3 and 5 wt% of BaF_2 were identified by powder X-ray diffraction in the reaction mixtures.

Single Crystal Structure Determinations

Crystal structure data for the crystals $\text{Ba}_{-6.9}\text{Na}_{-0.2}\text{F}_{12}\text{Br}_{0.6}\text{Cl}_{1.4}$, $\text{Ba}_{-6.9}\text{Na}_{-0.2}\text{F}_{12}\text{Br}_{1.4}\text{Cl}_{0.6}$ and $\text{Ba}_{-6.9}\text{Na}_{-0.2}\text{Br}_{1.32}\text{Cl}_{0.68}\text{F}_{12}$ are collected in Tables 1 and 2. Similarly to our recent results for $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ [4], all single crystal refinements for these samples with space group $P6_3/m$ present an additional electron density at the 0 0 0.25 position. This electron density has been associated [4] with the presence of additional Na^+ ions in this six-fold fluoride coordinated site with typical Na–F bond length of 2.22–2.23 Å. For the final crystal structure refinements, the populations of the Ba2 and the Na site were refined independently to obtain an unbiased estimate of the Na content. In our previous work [4], the refined Na content was confirmed quantitatively by chemical analysis. Within the standard deviations, the charges are balanced.

The crystal structure is illustrated in Fig. 2. Ba1 is coordinated by fluoride and bromide (or chloride), while Ba2 is only coordinated by fluoride. The refined Na and Ba contents are very similar for all samples with different bromide content (see Table 2), and can be summarized with the overall formula $\text{Ba}_{-6.9}\text{Na}_{-0.2}\text{F}_{12}\text{X}_2$. As Na is monovalent and Ba bivalent, one obtains thus an overfilling of the 00z channel, as discussed in [4]. Further details of the crystal structure investigations may be obtained in writing from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein–Leopoldshafen, Germany, on quoting the depository numbers CSD 417033, 417020 and 417032.

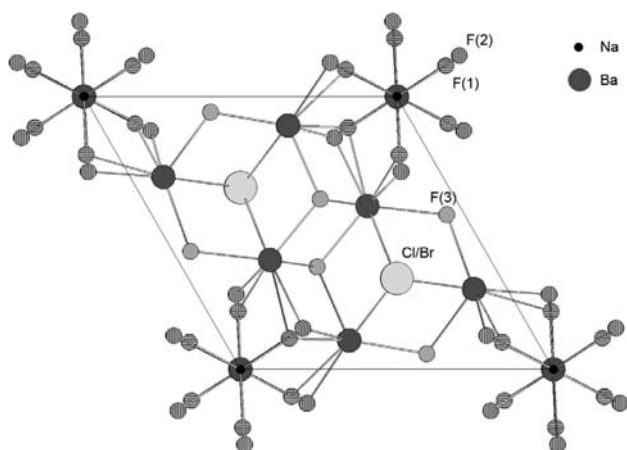
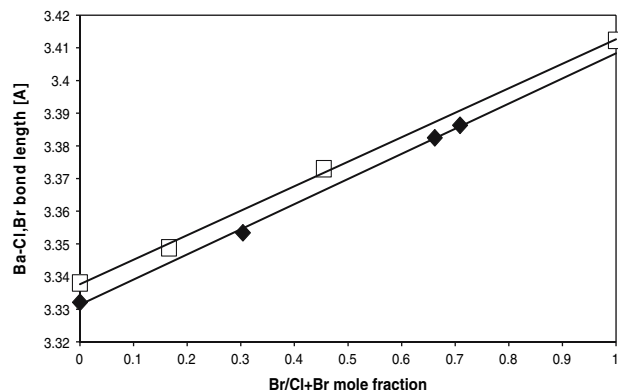
Comparison of the unit cell volume as a function of bromide content show that Vegard's law applies for this series of compounds, as it does for $\text{Ba}_{6.3}\text{Ca}_{0.7}\text{F}_{12}\text{X}_2$ [6]. Figure 3 compares the Ba–Cl,Br bond length for both series of compounds and shows that the refined bromide composition correlates even better with the Ba–Cl,Br bond length than with the lattice parameters a and c taken separately (see Fig. 1). It appears that this bond length is systematically larger in the Ca containing compounds.

Table 1 Crystal data

CSD number	417033	417020	417032
Formula	Ba _{-6.9} Na _{-0.2} F ₁₂ Br _{0.6} Cl _{1.4}	Ba _{-6.9} Na _{-0.2} F ₁₂ Br _{1.4} Cl _{0.6}	Ba _{-6.9} Na _{-0.2} F ₁₂ Br _{1.3} Cl _{0.7}
Mass [g mol ⁻¹]	1280.4	1308.4	1306.2
Crystal system/space group	Hexagonal, P6 ₃ /m		
<i>a</i> = <i>b</i> (Å)	10.6024(10)	10.6155(9)	10.6218(9)
<i>c</i> (Å)	4.2034(4)	4.2355(4)	4.2284(4)
<i>V</i> (Å ³)	409.20(9)	413.35(8)	413.15(11)
<i>Z</i>	1		
Density [g cm ⁻³]	5.30	5.25	5.25
Crystal size [mm]	130 × 60 × 35	130 × 70 × 50	170 × 50 × 35
Diffractometer type	Siemens SMART		
Radiation [Å]	MoK _α 0.71073		
Temperature [K]	293 K		
(range [°])	2.22–28.23	2.22–28.13	2.21–28.17
<i>n</i> _{ref} measured	2879	2888	2880
<i>n</i> _{ref} independent	383	385	386
<i>R</i> _{int} [%]	2.74	1.68	2.24
Absorption correction	Numerical		
Absorption coefficient <i>μ</i> [mm ⁻¹]	19.271	19.078	19.087
Program used	Xtal 3.2.		
<i>n</i> _{ref} with <i>I</i> > 3σ(<i>I</i>)	352	369	355
<i>R</i> (<i>R</i> _w) [%]	1.72 (1.61)	2.49 (2.07)	1.55 (1.50)
Goodness of fit [%]	1.80	2.35	2.00

Table 2 Refined populations and selected bond length

Sample	Ba _{-6.9} Na _{-0.2} F ₁₂ Br _{0.6} Cl _{1.4}	Ba _{-6.9} Na _{-0.2} F ₁₂ Br _{1.4} Cl _{0.6}	Ba _{-6.9} Na _{-0.2} F ₁₂ Br _{1.3} Cl _{0.7}
Population Ba2	0.438(1)	0.429(1)	0.437(1)
Population Cl	0.696(3)	0.291(3)	0.338(3)
Population Na22	0.083(5)	0.100(5)	0.094(4)
Ba–X (Å)	3.3534(3)	3.3863(3)	3.3825(2)
Na–F (Å)	2.228(3)	2.221(4)	2.229(3)

**Fig. 2** Projection along the *c*-axis of the crystal structure of Ba_{-6.9}Na_{-0.2}F₁₂Br_{1.4}Cl_{0.6}**Fig. 3** Ba–Cl, Br bond length versus refined bromide content in Ba_{6.3}Ca_{0.7}F₁₂X₂ [6] (squares) and in Ba_{-6.9}Na_{-0.2}F₁₂X₂ (diamonds)

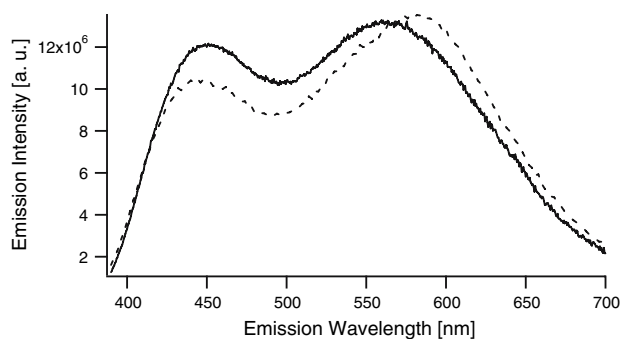


Fig. 4 Comparison of the emission spectra of Eu-doped $\text{Ba}_{-6.9}\text{Na}_{-0.2}\text{F}_{12}\text{Cl}_2$ (dashed line) and $\text{Ba}_{-6.9}\text{Na}_{-0.2}\text{F}_{12}\text{Br}_{1.32}\text{Cl}_{0.68}$ (full line). $T = 300^\circ\text{K}$, $\lambda_{\text{excitation}} = 340 \text{ nm}$

Figure 4 shows the effect of replacing chloride by bromide on the emission spectra of these single component white phosphors. Both materials present a large emission spectrum ranging over a vast part of the visible spectrum (from 400 to 700 nm). The lower wavelength emission band at $\sim 450 \text{ nm}$ is similar to the emission observed at 440 nm in Eu-doped $\text{Ba}_{12}\text{F}_{19}\text{Cl}_5$ [8] which presents a similar fluoride and chloride environment than the Ba1 in $\text{Ba}_7\text{F}_{12}\text{Cl}_2$. The band at 565–590 nm can be related to Eu(II) on the site of the Ba2 ion coordinated by 9 F atoms (in the 00z channel) [9].

The introduction of bromide shifts the higher emission band from about 590 to lower wavelength ($\sim 565 \text{ nm}$), which corresponds visually to the transition from a slightly yellowish emission to a white emission.

Conclusions

In contrast to the Ca-containing compounds $\text{Ba}_{-6.3}\text{Ca}_{-0.7}\text{F}_{12}\text{Cl}_{2-x}\text{Br}_x$, it appears that the maximum Br–Cl ratio

which can be obtained in the absence of other bivalent ions besides Ba^{2+} in $\text{Ba}_7\text{F}_{12}\text{Cl}_{2-x}\text{Br}_x$ is reached for $x \approx 1.5$. Crystals of the disordered modification show systematically additional electron density at the 0 0 0.25 site which corresponds to a small, but constant (independent of bromide substitution) amount of Na^+ ions in the structure.

Supplementary Data

Further details of the crystal structure investigations may be obtained in writing from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-417033, 417020 and 417032.

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