

On the crystallochemical origin of the disordered form of $\text{Ba}_7^{(\text{EuII})}\text{F}_{12}\text{Cl}_2$ and the structural changes induced at high temperature

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The crystal structure of the disordered modification of $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ has been carefully re-examined on several new crystals prepared under different conditions of synthesis. All single crystal structure refinements reveal a residual electron density of $\sim 3 \text{ e}/\text{\AA}^3$ in the 0,0,0 position which is explained by the introduction of a small amount of sodium ions in the crystal. The title compound transforms from a disordered to an ordered modification at $\sim 800^\circ\text{C}$. New structural data show a change in space group from $\text{P6}_3/\text{m}$ to $\text{P}\bar{6}$. During this process, a slight chemical change and the formation of nano-channels in the crystals is observed by electron microscopy. These changes were further studied by electron microprobe analysis, by spectroscopic methods and thermal analysis.

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1 Introduction

The discovery of the new compound $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ [1,2], a white phosphor, has stimulated an extensive research effort to probe the extent of chemical modifications in this compound [eg. 3,4]. It was quite surprising to observe the presence of two crystalline forms, one ordered, and another disordered one.

Further, chemical substitutions such as Sr for Ba and/or Br for Cl provide a “chemical pressure” which allows to modulate in a controlled fashion the surroundings (crystal field) of the dopant ions and therefore also the emission properties for potential applications. For instance, the effect of chemical pressure and composition on the emission spectra of Sm^{2+} in solid solutions $\text{SrFCl}_x\text{Br}_{1-x}$ leads to spectral shifts and inhomogeneous broadening which have been quantitatively analyzed [5] in the context of potential application for optical data storage by persistent spectral hole burning [6]. We have recently shown that it is possible to fully replace Cl by Br in the disordered modification of $\text{Ba}_7\text{F}_{12}\text{Cl}_2$, provided one allows for a partial simultaneous substitution of Ba by Ca, leading to a stoichiometry of $\text{Ba}_{6.3}\text{Ca}_{0.7}\text{F}_{12}\text{Br}_2$ [3]. The new result for the crystal structure of $\text{Ba}_{6.3}\text{Ca}_{0.7}\text{F}_{12}\text{Br}_2$ is the fact that Ca does not occupy one of the Ba sites, but rather prefers to enter an interstitial position which yields a six-fold coordination instead of the nine-fold coordination of the neighboring Ba ion.

This discovery prompted us to investigate whether other substitutions on this six-fold coordinated site can be observed. New single crystal X-ray diffraction structure determinations of the disordered modification of $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ revealed the reproducible presence of small but significant electron density on this site. Further, we observed an irreversible structural change occurring above 800°C for this compound. These results will be presented in the following.

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2 Experimental

Synthesis The single crystals studied were prepared from mixtures composed of $3 \text{ BaF}_2 + 2 \text{ NaCl}$ which were placed into graphite crucibles and grown under nitrogen atmosphere by slow cooling (10K per hour) starting from 950°C . Both nominally pure and Eu(II)-doped samples (Eu:Ba = 0.004) were prepared and analyzed. Another starting composition was $\text{BaFCl} + 1.2 \text{ NaF}$ and yielded the same crystals.

High temperature treatment Crystals of the disordered modification were separated from the growth flux by washing using an ultrasonic bath ($\text{Ba}_7\text{F}_{12}\text{Cl}_2$ does not appear to be significantly soluble in water). The dried crystals (0,450 g) were placed into a graphite crucible and heated at 850°C for 20h in a nitrogen atmosphere. No significant mass loss was observed during this treatment (0,4495g after). Differential thermal analysis (DTA) measurements were performed under inert atmosphere (N_2 , argon) in graphite crucibles using a Setaram TAG24 instrument.

Structure analysis Single crystal X-ray diffraction measurements were done using Mo K_α 0.71073\AA radiation and a Bruker diffractometer equipped with a SMART CCD area detector (Siemens). Refinement was made using the XTAL 3.2 refinement package [7]. Table 1 gives the details of the refinement conditions.

Electron microscopy A scanning electron microscope (EDAX - JEOL-6400, with energy dispersive detector, type SUTW - Sapphire) and EDAX software Genesis was used. The samples were coated with graphite.

Spectroscopic studies Raman experiments were performed at room temperature using a Labram Raman microscope (laser excitation wavelength 532nm) and using a Kaiser Optical Holospec Monochromator in conjunction with liquid nitrogen cooled CCD camera in a 90 degree geometry (excitation wavelength 488nm). Luminescence measurements were obtained using a Jobin-Yvon Fluorolog FL3-22 instrument.

Chemical analysis Laser ablation ICP-MS experiments were done by Dr F. Bussy at the University of Lausanne (Switzerland), flame atomic absorption analysis by Dr M. Pelletier at the University of Geneva.

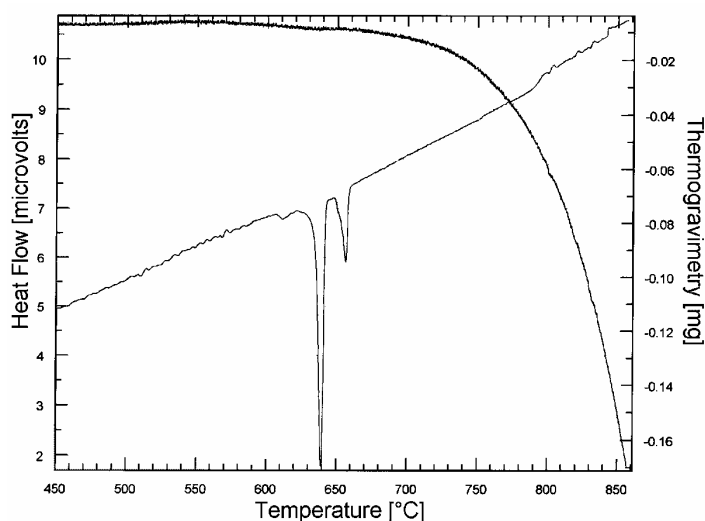


Fig. 1 DTA and TG heating trace of a mixture of composition $3 \text{ BaF}_2 + 2 \text{ NaCl}$ under inert atmosphere.

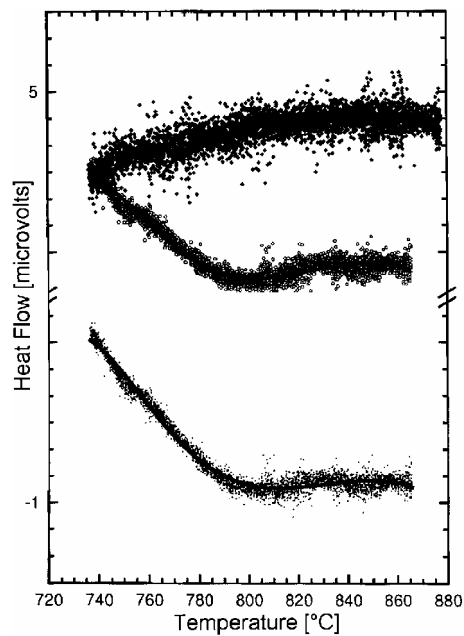


Fig. 2 DTA heating trace of disordered $\text{Ba}_7\text{F}_{12}\text{Cl}_2$. Top trace: empty graphite crucible, middle trace, disordered $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ in graphite crucible, bottom trace, difference signal.

3 Results and discussion

Synthesis In order to obtain single crystals of $\text{Ba}_7\text{F}_{12}\text{Cl}_2$, we performed a series of preparations using alkali halide fluxes. All the published phase diagrams of the type $\text{Ba}_m\text{M}/\text{F}_n\text{Cl}_l$ where $\text{M}=\text{Li}, \text{Na}, \text{K}, \text{Rb}$, [eg. 8,9]

indicate crystallization fields for BaF_2 , BaFCl and BaCl_2 , but no other barium fluoro-chloride. The experiments using Li and Na salts as fluxes allowed to obtain needle shaped crystals of $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ (by slow cooling of the melt) in addition to other phases, provided in principle that the stoichiometry of the reaction mixture corresponds to the crystallization field labelled BaF_2 in the published phase diagrams [8,9]. In general, one may use a mixture of typically 0.75-0.85mol% BaF_2 + 0.25-0.15mol% $(\text{AX})_2$ with $\text{A}=\text{Li}$, Na and $\text{X} = \text{Cl}$, or a mixture thereof, to obtain single crystals of $\text{Ba}_7\text{F}_{12}\text{Cl}_2$.

Single crystals can be easily obtained both in air and inert atmosphere. The presence of small amounts of rare earth dopants (R.E. to Ba ratio smaller than 0.01) has no measurable effect on the crystal structure. It is important to note that the disordered modification of $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ is only obtained when Na is present in the reaction mixture. The alternate preparations (which yielded the ordered modification) involved salts such as NH_4Cl , LiCl and $(\text{Li,K})\text{Cl}$. One of the most efficient methods of preparations (with the highest yield of $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ (>90%)) formation relative to other phases such as BaF_2 and BaFCl is realized with the initial stoichiometry of $3 \text{BaF}_2 + 2 \text{NaCl}$.

The DTA heating curve of this mixture is shown in figure 1. One observes two eutectic transitions at 638°C and 660°C as well as the small melt signal at ca 780°C. It is interesting to note the onset of some mass loss above 750°C. This experiment shows that single crystals of $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ are formed at temperatures below 780°C. We then performed DTA measurements on both ordered and disordered forms of $\text{Ba}_7\text{F}_{12}\text{Cl}_2$. The disordered form shows a weak endothermic signal (or change of slope) around 780-800°C (see figure 2) which is not observed neither in a second heating run nor for the ordered modification.

Table 1 Crystal data and structure refinement of “ $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ ” before and after heating.

Compound	$\text{Ba}_{6.905(2)}\text{Na}_{0.173(14)}\text{F}_{12}\text{Cl}_2$	$\text{Ba}_{6.978(2)}\text{Na}_{0.054(8)}\text{F}_{12}\text{Cl}_2$
Crystal system	hexagonal	hexagonal
Formula weight	1251.10	1258.49
Space group	$\text{P6}_3/\text{m}$ (No. 176)	$\text{P}\bar{6}$ (No. 174)
Cell parameters		
a,b (Å)	10.5969(10)	10.6237(9)
c (Å)	4.1889(4)	4.1722(3)
Unit cell volume (Å ³)	407.37(9)	407.80(8)
Z	1	1
Density (calculated) Mg/m ³	5.146	5.141
Crystal size (mm)	0.180x0.050x0.050	0.210x0.120x0.050
Diffractometer	Bruker SMART CCD area detector	
Radiation wavelength (Å)	Mo K α 0.71073Å	
Scan mode	ω	
	-14 < h < 9	-13 < h < 14
	-14 < k < 12	-14 < k < 14
	-5 < l < 5	-5 < l < 3
Temperature (K)	295	
sin θ/λ range (°)	0.665 to 0.055	0.665 to 0.054
Number of measured reflections	2678	2816
Number of independent reflections	381	762
Number of observed reflections >3 σ	381	762
Number of parameters	30	48
Program used	XTAL 3.7.1	
R _{int} =	0.024	0.020
R(wR) (on intensity)	0.015(0.015)	0.015(0.015)
Goodness-of-fit on intensity	1.85	2.15
Extinction coefficient	92(8)	269(13)
Flack parameter:	-	0.64(4)
Residual minimum/maximum		
electron density (in Å ⁻³)	0.9/-1.3	1.4/-2.2
CSD number	415766	415765

Structure analysis Structure analyses of several selected crystals of the disordered form of $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ both with and without rare-earth dopants were made at room temperature. Within statistical error, doped (Ba to

rare earth ratio < 0.005) and undoped single crystals gave the same results. In addition, one crystal was studied at -150°C (to sharpen the Difference Fourier map and to analyze vibrational parameters). Low temperature data do not differ significantly from expected values, so only the room temperature data are given. Low temperature structural data can be obtained from the authors on request. Table 1 gives the refinement conditions and table 2 the atomic positions. Selected interatomic distances are published in table 3.

Table 2 Positional, displacement and site occupation parameters with e.s.d.'s in parenthesis.

Atom	x/a	y/b	z/c	U(eq) Å ²	Population parameter	
Compound: Ba _{6.905(2)} Na _{0.173(14)} F ₁₂ Cl ₂						
Ba(1)	0.40472(1)	0.29370(1)	1/4	0.0128(1)		
Ba(2)	0	0	1/4	0.0204(3)	0.452(1)	
F(1)	0.1167(4)	0.2156(5)	1/4	0.020(2)	0.498(5)**	
F(2)	0.1536(5)	0.2759(4)	1/4	0.020(2)	0.502(5)**	
F(3)	0.6227(1)	0.5664(1)	1/4	0.0178(8)		
Cl	2/3	1/3	-1/4	0.0182(4)		
Na(22)	0	0	0	0.018(6)*	0.087(7)	
Atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ba(2)	2U ₁₂	2U ₁₂	0.0385(4)	0.0056(1)	0	0
Compound: Ba _{6.978(2)} Na _{0.054(8)} F ₁₂ Cl ₂						
Ba(1)	0.28860(3)	0.40183(3)	1/2	0.0112(2)		
Ba(2)	0.40947(3)	0.10957(3)	0	0.0118(2)		
Ba(3)	0	0	0	0.0165(3)	0.917(2)	
Cl(1)	2/3	1/3	1/2	0.017(1)		
Cl(2)	1/3	2/3	0	0.017(1)		
F(1)	0.0509(3)	0.4363(3)	1/2	0.016(2)		
F(2)	0.2173(4)	0.1179(4)	1/2	0.027(3)		
F(3)	0.1208(3)	0.2747(3)	0	0.019(2)		
F(4)	0.4310(3)	0.3694(4)	0	0.016(2)		
Ba(33)	0	0	1/2	0.0165(3)**	0.061(2)	
Na(33)	0	0	0.25(-)	0.0165(3)**	0.027(4)	
Atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ba(3)	2U ₁₂	2U ₁₂	0.0272(4)	0.00555(9)**	0	0
Ba(33)	2U ₁₂	2U ₁₂	0.0272(4)	0.00555(9)**	0	0
Na(33)	2U ₁₂	2U ₁₂	0.0272(4)	0.00555(9)**	0	0

*isotropic refinement, **constrained

Structural data and chemical composition The global structure of both forms of Ba₇F₁₂Cl₂ is given in [2]. Generally speaking, Ba₇F₁₂Cl₂ is described as a matrix of matlockite-like arrangement of BaX₉ (X = F, Cl) units. In the cavities of these units, a channel like system of threecapped trigonal prisms is formed. Two positions with different coordination number, M9 and M6, can be occupied as found for the Ca doped sample [3]. For reasons of size (ionic radius), the bigger alkaline earth ion occupies position with coordination number 9 and a smaller cation may (in the same channel) occupy the position with CN 6. A similar crystallochemical behaviour is also observed in alkali containing lead fluoro-chlorides such as Na₂Pb₁₁F₁₈Cl₆ [10]. In this family of compounds with space group P6₃/m, a matrix of a solid solution of lead/alkali in a matlockite like environment and a similar tricapped trigonal channel as in Ba₇F₁₂Cl₂ was found. For all samples it was observed that sodium occupies a position with CN 6 (site (0,0,0)) and the bigger potassium is located in a position with CN 3+6 (site (0,0,0.75)).

After refinement of the structures based on the model of [2], but additionally refining the positional occupation of the Ba(2) site, a small but significant residual electron density was found for position with CN 6 (see figure 3). This residual electron density can be absorbed when adding (Na⁺) in small amounts in the structure. A final refined composition of Ba_{6.905(2)}Na_{0.173(14)}F₁₂Cl₂ is then obtained with excellent agreement

factors ($R_w = 0.015$) which is close to idealized $Ba_{6.9}Na_{0.2}F_{12}Cl_2$. This new structural description of the disordered form only of $Ba_7F_{12}Cl_2$ includes thus small amounts of Na^+ within the structure localized in the channels.

This result is in reasonable agreement with charge compensation but “stuffs” the channel with more than expected ions. The composition is close to $Ba_{6.9}Na_{0.2}F_{12}Cl_2$, so charges are compensated. It is however unexpected to refine an overpopulation of elements within the channel (1.1 instead of 1). Nevertheless this stuffing can be possible, if the formation of Na clusters is assumed. Figure 4a shows all possible positions in the channel after refinement. Occupying Na in CN 6 and 9 allows concentrating cations in the channel, so having a slight over-occupation. This can be seen in figure 4b. Interatomic distances are reasonable and close to those found in NaF.

Table 3 Interatomic distances in Å with e.s.d.'s in parenthesis.

Compound: $Ba_{6.905(2)}Na_{0.173(14)}F_{12}Cl_2$			
Ba1-F3	2.648(1)	Ba1-Cl 2x	3.3321(3)
Ba1-F2 2x	2.659(3)	Ba2-F2 3x	2.538(4)
Ba1-F3 2x	2.6647(7)	Ba2-F1 6x	2.883(3)
Ba1-F3	2.682(1)	Na22-F1 6x	2.241(4)
Ba1-F1	2.734(4)	Na22-F2- 6x	2.745(4)
Ba1-F1 2x	2.920(3)		
Compound: $Ba_{6.978(2)}Na_{0.054(8)}F_{12}Cl_2$			
Ba1-F3 2x	2.636(2)	Ba2-F4	2.641(4)
Ba1-F1	2.654(3)	Ba2-F4	2.653(3)
Ba1-F4 2x	2.698(2)	Ba2-F2 2x	2.951(2)
Ba1-F2	2.718(3)	Ba2-Cl1 2x	3.3126(3)
Ba1-F1	2.727(3)	Ba3-F3 3x	2.534(3)
Ba1-Cl2 2x	3.3401(3)	Ba3-F2 6x	2.891(3)
Ba2-F3	2.591(3)	Na33-F2 3x	2.257(3)
Ba2-F1 2x	2.624(2)	Na33-F3 3x	2.740(3)

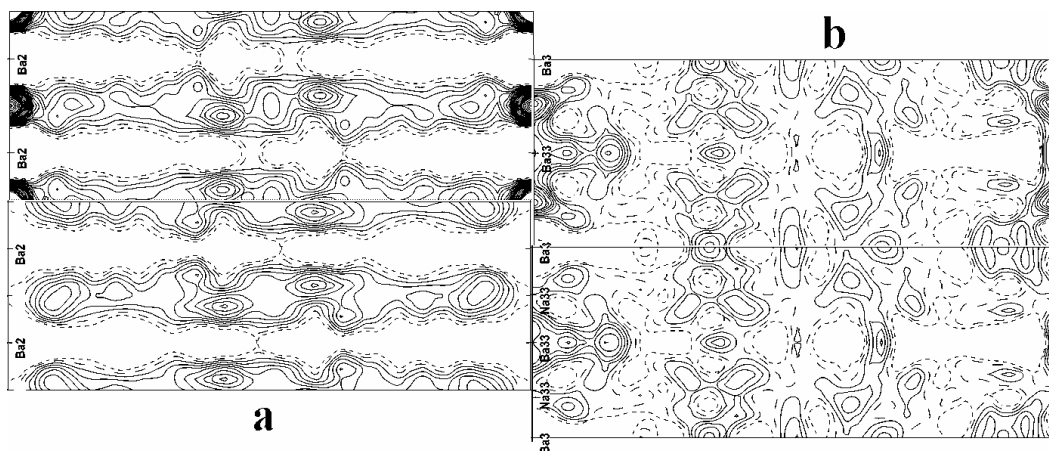


Fig. 3 Electron density map for a) $P6_3/m$, b) $P\bar{6}$. Relative residual electron density map of $Ba_7F_{12}Cl_2$ before (a) and after (b) structural changes (heated crystal). Top: initial refinement without Na^+ ; Bottom: after introducing small amounts of Na^+ in CN 6 in the refinement.

A similar refinement was made for a crystal at low temperature using a liquid nitrogen cooling device. Almost the same structural parameters such as chemical composition and atomic positional parameters were found. In contrast, the vibrational parameters of the matrix forming elements decrease about 50% whereas the vibrational parameters along the c -axis of the Ba in the channel changes only slightly from 0.0385(4) to 0.0301(2) which may indicate a static displacement of the Ba-ions.

The presence of Na^+ in the channels can be additionally justified for the following reasons:

The disordered modification of $Ba_7F_{12}Cl_2$ is only obtained when Na is present in the reaction mixture.

Alternate preparations involving salts such as NH_4Cl , LiCl and $(\text{Li},\text{K})\text{Cl}$ yield the ordered modification.

A crystal of the disordered modification was subjected to laser ablation ICP-MS, taking care not to measure possible contaminations on the outside of the sample. Laser ablation on the side of a single crystal was performed on several spots to a maximum depth of ca 30 microns. The presence of sodium was clearly detected. The averaged results show a Na:Ba mass ratio of 0.007 (with an error of about 10%), which would result in the stoichiometry $\text{Ba}_{6,9}\text{Na}_{0,29}\text{F}_{12}\text{Cl}_2$. We cannot fully exclude a small contamination of the instrument, as a nominally sodium-free sample of the ordered modification (prepared in the absence of Na in LiCl), yielded the very small Na:Ba mass ratio of 0.0014. Taking into account a slight overestimation of the quantity of Na measured by ICP-MS, we obtain a reasonable agreement with the composition resulting from the single crystal structure determination.

Chemical analysis of crystals dissolved in dilute perchloric acid by flame atomic absorption spectroscopy confirmed the presence of Na and yielded the Na :Ba mass ratio of 0.0042 ± 0.0002 . This ratio corresponds to the composition $\text{Ba}_{6,9}\text{Na}_{0,17}\text{F}_{12}\text{Cl}_2$, in remarkable agreement with the populations obtained by refinement of the X-ray diffraction data.

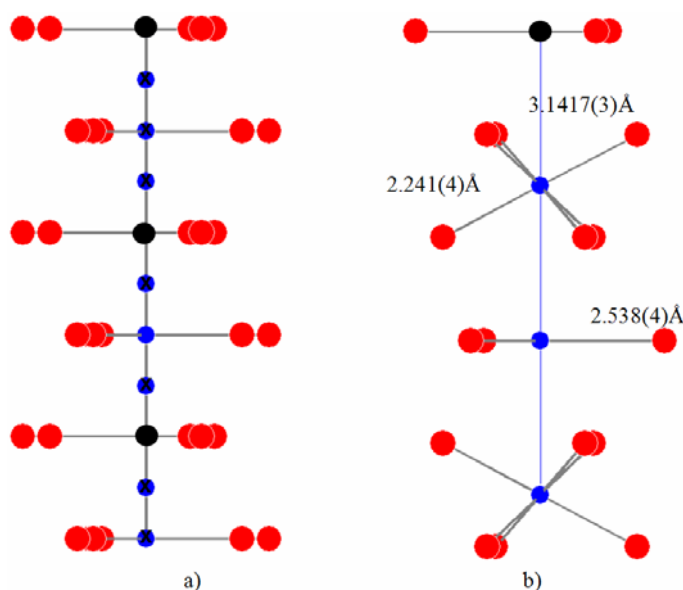


Fig. 4 a) Possible atomic positions of cations in the channel of disordered Ba_7 , possible sites in the channel marked with crosses; Ba: black, Na blue spheres. Filling Na-clusters in the channel allows an “overoccupation”. b) Na to Na and Na to F distances (in NaF: Na-Na 3.275 Å, Na-F 2.31 Å) for dense packing (or stuffing the channels).

Structural and morphological changes after heating to 850°C The crystals which were heated to 850°C present significant differences with the unheated ones. The single crystal X-ray diffraction shows (see tables 1 and 2) that this heat treatment induces a transformation to an ordered structure with space group $\text{P}\bar{6}$.

The structure refinement reveals that the channel seems to be filled with a higher amount of Ba and only a small electron density occupies position with CN 6 (absorbed when including very small amounts of Na^+ in this position). The refined composition is $\text{Ba}_{6,978(2)}\text{Na}_{0,054(8)}\text{F}_{12}\text{Cl}_2$ which is very close to stoichiometric $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ as found before [2].

The structural change is also seen using spectroscopic measurements. Raman spectra of samples before and after heating to 850°C are shown in figure 5. The spectrum of the heated sample is characterized by 3 strong bands at 255, 230 and 190 cm^{-1} which are clearly distinguishable from the Raman spectrum of the initial sample. These Raman bands can be assigned to Ba-F vibrations. One observes also some very weak bands above 300 cm^{-1} which may be associated, similarly as for $\text{Ba}_{12}\text{F}_{19}\text{Cl}_5$ [11], to the very short Ba-F distances (close to 250 pm) found in these structures. Raman spectra of ordered crystals (prepared from LiCl fluxes) are identical with those of the heated sample.+

The luminescence spectra of Eu-doped crystals show strong and broad bands in the visible region (see figure 6), generating thus a white emission from a single component sample. The first emission band (around 450 nm) is rather typical for the $4f^65d \rightarrow 4f^7$ emission of Eu(II). In the similar compound $\text{Ba}_{12}\text{F}_{19}\text{Cl}_5$, this emission band has been observed around 440 nm [12]. The second emission band is more unusual and will be discussed in a forthcoming publication. After the transformation at 850°C, one observes that the relative

intensities of the emission bands (using the same excitation at 340nm) change significantly. The initial sample emits a rather “warm” (yellowish) white, while the heated sample shows a “colder” (blue-shaded) white. The detailed analysis of optical properties of these crystals will be presented elsewhere.

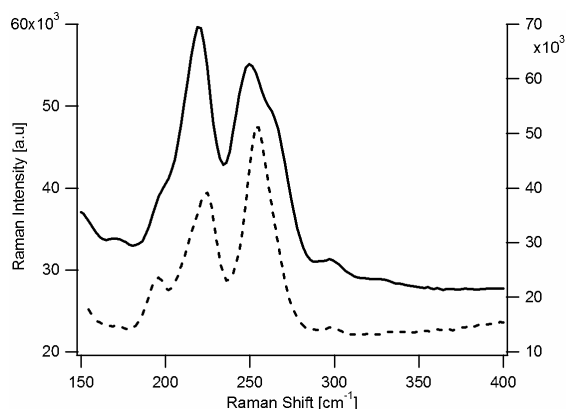


Fig. 5 Room temperature Raman spectra (excited with 488nm) of powdered samples before (full line) and after (dotted line) annealing at 850°C.

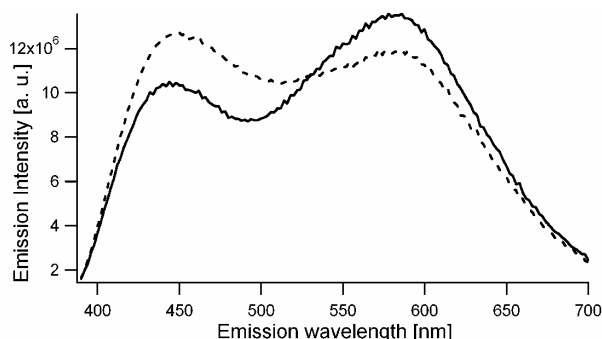


Fig. 6 Emission spectra excited at 340nm at 296K of Eu-doped samples before (full line) and after (dotted line) annealing at 850°C.

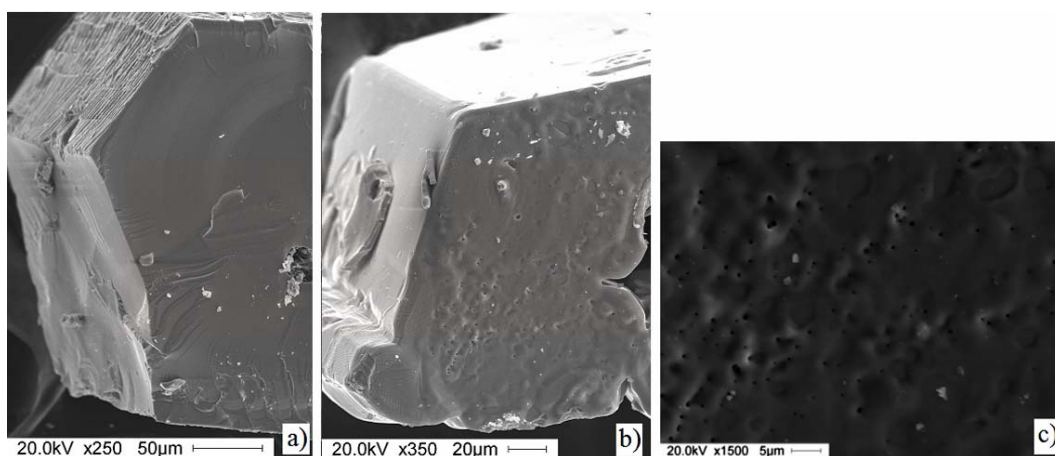


Fig. 7 Electron microscopy images of freshly broken 0001 surfaces of $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ before (a) and after (b,c) structural changes (heated crystal). Pictures (b) and (c) reveal the nanochannels formed after heating.

Electron microscopy shows after heating nano-sized channels parallel to the c-axis (see figure 7). This suggests a local fusion due to an eutectic melting within the crystal, leaving however the global crystal intact. Here it must be assumed, that the structure rearranges to a $\text{Ba}_{6.978(2)}\text{Na}_{0.054(8)}\text{F}_{12}\text{Cl}_2$ which is very close to $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ compound as found before. The irregular surface of the heated sample might be related with ferroelectric domains present in the ordered structure with the polar space group $\text{P}\bar{6}$.

4 Conclusions

In this work, we have demonstrated that the observation of the disordered modification of $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ is associated with the presence of small, but measurable, amounts of Na ions in the channels. The ordered form, which is thermodynamically more stable, does not require the presence of Na^+ , although some residual quantities may remain in the crystal.

The disordered modification transforms irreversibly into the ordered one above 800°C. The fact that the melting point of the reaction mixture $3\text{BaF}_2 + 2\text{NaCl}$ is observed at 780°C contributes to the high yield of the

disordered modification found experimentally. Electron microscopy reveals a remarkable generation of nano-channels along the c-axis upon heating to 850°C, illustrating the expulsion of sodium out of the structure.

Most of the $\text{A}_7\text{B}_{12}\text{X}_2$ crystal structures found in the literature are ordered structures with space group $\text{P}\bar{6}$. It will be interesting to re-examine disordered structures such as $\text{As}_7\text{Ca}_2\text{Co}_{12}$ [13] or $\text{P}_7\text{Zr}_2\text{Mn}_{12}$ [14] for the presence of small, stabilizing impurities.

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