

Cesium Fluoride–Bromine Intercalation Compounds

Abstract: CsF reacts with Br₂ to form the two intercalation compounds CsF·Br₂ and 2CsF·Br₂. The former consists of layers of CsF squares separated by layers of Br₂ molecules oriented perpendicular to the CsF layers. 2CsF·Br₂ is a second-stage compound, composed of two layers of CsF followed by one layer of bromine molecules. Iodine cannot replace bromine; instead, it reacts with CsF to form Cs₂I₈, and probably CsIF₆ between 0° and 120 °C. Chlorine does not react at all with CsF. Bromine reacts with RbF only superficially, and after a long time some RbBr₃ is observed; RbF and I₂ give RbI₃.

Keywords

bromine compounds · cesium compounds · crystal structure · fluorides · intercalation compounds

Introduction

Intercalation is a classical phenomenon in layered compounds that have strong intralayer forces but weak interlayer ones. The best-known examples are the graphite intercalation compounds, where both electropositive and electronegative atoms or molecules are intercalated, resulting in characteristic changes of the physical properties of the host graphite material. A typical characteristic for intercalation compounds is the existence of different stages, which means that only some layers are filled, often in a regular way (every second or third). Graphite intercalation compounds are again the best-known examples of this behavior, but by no means the only ones.

Following the observation that reactivity of elemental bromine is enhanced in the presence of CsF,^[1–3] we succeeded in growing single crystals of CsF·Br₂ by allowing both compounds to stand for many weeks at 70 °C in sealed glass or Teflon FEP tubes. We presented the crystal structure in a short communication.^[4] Calling the material an intercalation compound was controversial, since the CsF (NaCl-type) lattice is not normally considered a layered but rather a uniform three-dimensional structure. In this paper we will discuss the evidence that the CsF structure is indeed energetically very close to a layered structure. We will also describe the second-stage structure of 2CsF·Br₂, and show the limits of existence of this new class of compounds.

A theoretical work on such compounds has recently appeared.^[5] Ruiz and Alvarez calculated the energetics of such compounds with sophisticated ab initio methods including electron correlation. As we will demonstrate, these calculations reproduce the experimental data well, but are over-optimistic about the range of existing alkali-halide intercalation compounds.

Results and Discussion

The compound CsF·Br₂ can be grown as single crystals,^[4] the results of the structure determination are shown in Figure 1 and Tables 1 and 2. The following features are noteworthy:

- 1) The Cs···F layers are similar to the *ab*0 planes in cubic CsF, except that the cesium–fluorine distances of 295.3(1) pm are now shorter than in CsF (300.1 pm), even if the lower measuring temperature is taken into account. This means that the transition from octahedral coordination of Cs and F in CsF to square planar coordination in CsF·Br₂ increases the attractive forces between the reduced number of components.
- 2) The fact that the Cs···F layers are eclipsed is also important. Cs⁺ is positioned above Cs⁺ and F[−] above F[−], but the interlayer distance of 736.4(2) pm is quite large.

Whatever the driving force of the bromine intercalation is, repulsive forces between the layers ought to be small.

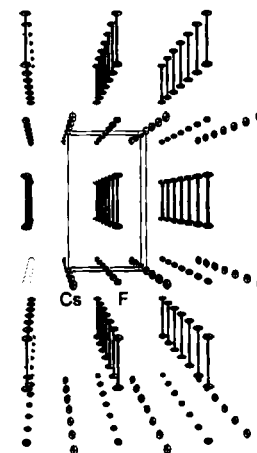


Fig. 1. View into the CsF·Br₂ layered structure: ORTEP plot, 50% probability.

Table 1. Atomic coordinates and temperature factors for CsF·Br₂. First entry: nondisordered model; second entry: Cs⁺ disordered model.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> ₁₁ [pm ²]	<i>U</i> ₃₃
Br	0.5	0.5	0.3422(1)	127(2)	44(3)
	0.5	0.5	0.3422(1)	127(2)	44(3)
F	0.5	0.5	0	103(12)	63(12)
	0.5	0.5	0	103(12)	60(22)

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Table 2. Experimental details of the CsF·Br₂ single crystal structure determination; values in brackets are for the Cs⁺ disordered model.

size [mm]	0.1 × 0.1 × 0.2	
a [pm]	417.7(2)	
c [pm]	763.4(2)	
V [10 ⁶ pm ³]	127.8	
space group	P4/mmm (no. 123)	
z	1	
2θ _{max} [°]	80	
T [°C]	-153	
measured reflns	886	
independent reflns	287	
I ≥ 3σ(I)	264	
parameters	8	(8)
R	0.0315	(0.0310)
R _w	0.0262	(0.0258)
residual electron density	2.5	(2.5)
[112 pm from Br, 10 ⁻⁶ e pm ⁻³]		

- 3) The stacked bromine molecules are positioned between the fluorine atoms. A bromine–bromine bond length of 231.3(1) pm is found, compared with 227(1) pm in solid Br₂^[6] or 228.108 pm in gaseous Br₂,^[7] but also with 215(1) in Br₂⁺Sb₃F₁₆⁻.^[8] The bond lengthening with respect to elemental Br₂ indicates a small but not negligible charge transfer from F⁻ to Br₂. A similar qualitative picture is obtained from the Raman spectra of Br₂ (ν = 317 cm⁻¹), Br₂⁺ (360),^[9] Br₂⁻ (160, 177),^[10] and CsF·Br₂ (287). We hesitate to give a quantitative number for the charge transfer in CsF·Br₂ by interpolation of these numbers, because only Br₂ and CsF·Br₂ have the same (singlet) electronic state. The atomic charges calculated for CsF·Br₂ by the Hartree–Fock/MP2 calculation^[5] are Cs^{0.937}, F^{-0.859}, and Br^{-0.037}.
- 4) The structure determination is precise enough (-153 °C, data parameter ratio 33:1, R_w = 0.026) to discuss the shape of the vibrational ellipsoids. The atoms in the chain F⁻···Br–Br···F⁻··· have larger vibrational amplitudes perpendicular to the chain, as expected. The Cs ions, however, seem to be expanded, although only a little, in the z direction. This may be a consequence of the fact that the Cs ions have no negative counterparts directly above and below. But replacing the two vibrational parameters U₁₁ and U₃₃ of Cs by an isotropic vibrational parameter and a z value ≠ 0 gives marginally better R values. The Cs ion now lies at 8.8(1) pm above (or below) the fluorine atoms in a disordered manner, less than but comparable to the out-of-plane positioning in the 2CsF·Br₂ structure (see below). There is, however, no indication of an enlarged unit cell or a lowering of the crystal symmetry to account for the Cs ion positioning z ≠ 0 in an ordered manner.

Abstract in German: CsF reagiert mit Br₂ unter Bildung zweier Intercalationsverbindungen, CsF·Br₂ und 2CsF·Br₂. CsF·Br₂ ist aus quadratischen CsF Schichten aufgebaut, die durch Brommolekülschichten getrennt sind. Die Brommoleküle stehen senkrecht zu den CsF Schichten. 2CsF·Br₂ ist eine Einlagerungsverbindung 2. Stufe, aufgebaut aus zwei Schichten CsF und einer Schicht Brommolekülen. Brom kann nicht durch Iod ersetzt werden; es reagiert mit CsF zu Cs₂I₈ und vermutlich CsIF₆ zwischen 0° und 120 °C. Chlor reagiert gar nicht mit CsF. Br₂ reagiert nur oberflächlich mit RbF, und nach langer Reaktionszeit wird RbBr₃ beobachtet; RbF und I₂ ergeben RbI₃.

The central question is: Can the cubic CsF lattice be considered a layered structure from the energetic viewpoint? To answer this question we have calculated the Madelung part of the lattice energy^[11] for CsF as a function of one crystallographic axis to be expanded (Fig. 2). Lattice energy is lost by expansion, but soon a plateau is reached where further expansion does not change the energetics any more. The interlayer distance of CsF·Br₂ lies in the plateau, as indicated by an arrow in Figure 2.

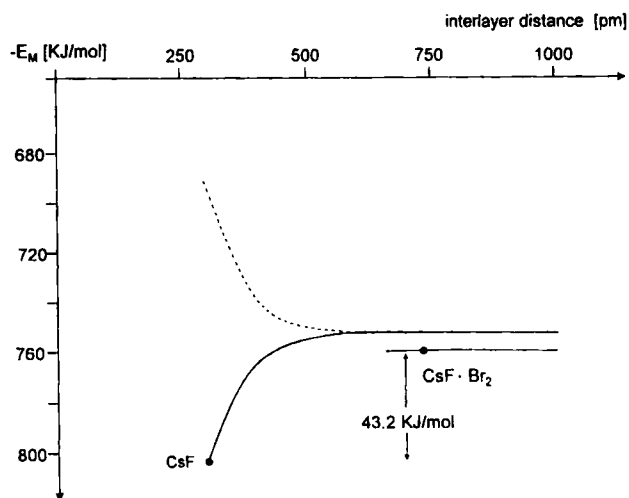


Fig. 2. Madelung part of the lattice energy calculation. Starting with CsF (●), expansion of layers gives the lattice energy as shown by the solid line, if intralayer Cs···F distances are held constant. Expansion beyond twice the Cs···F distance in CsF does not change the lattice energy any further. The broken line shows the lattice energy for the actual stack variant in CsF·Br₂, that is, Cs⁺ above Cs⁺ and F⁻ above F⁻. Only at small interlayer distance would repulsion be important. The second solid line represents the lattice energy at the experimentally found Cs···F intralayer distance, which is smaller than in CsF. The energy loss from CsF (cubic, *Fm* $\bar{3}$ *m*) to the observed CsF layered structure is 43.2 kcal mol⁻¹ or 5.4%.

Readjustment of the original orientation (Cs above F) to Cs above Cs, F above F orientation costs very little lattice energy at large interlayer distances, but would of course cost a lot at shorter distances because of increasing repulsion forces (Fig. 2). Relaxation of the Cs–F distance in CsF (300.2 pm) to the experimental intralayer distance in CsF·Br₂ (295.3 pm) gives a small gain in energy, so that finally only 43.2 kJ mol⁻¹ or 5.4% of the entire lattice energy is lost. In the ab initio calculation this energy loss comes out to 53.3 kJ mol⁻¹ (12.75 kcal/mol).^[5] This energy loss must be covered by the Br₂ intercalation, the energy of which cannot be properly addressed by the purely electrostatic model.

The second-stage 2CsF·Br₂ compound: It was clear that our success in growing single crystals could not be repeated with compounds of lower bromine content, because pumping off bromine inevitably resulted in formation of a powder. By weight balance it was established that at room temperature and under a vacuum of 10⁻² mbar the powder composition was 2CsF·Br₂. Qualitatively the structure can be predicted, if every second bromine layer is assumed to be empty, and if neighboring CsF layers without bromine intercalation are assumed to be stacked as in pure CsF (that is, Cs above F and vice versa). Such a model would result in a very elongated, body-centered tetragonal unit cell, if otherwise highest symmetry is retained (Fig. 3).

X-ray and neutron powder diffraction data could easily be indexed for a body-centered tetragonal cell with a = 425.81(6), c = 2031.9(4) pm. No other extinctions were observed except

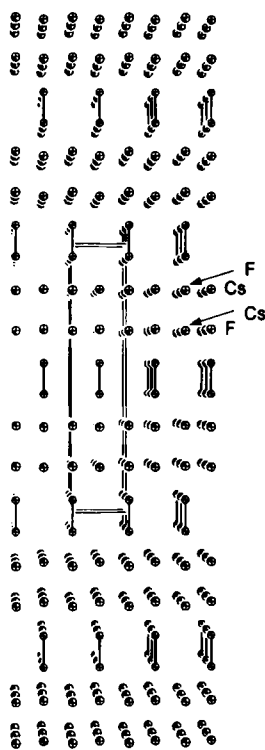


Fig. 3. ORTEP plot of the $2\text{CsF}\cdot\text{Br}_2$ structure. Several unit cells are depicted to show the layer principle.

$h + k + l \neq 2n$, leaving only space group $I4/mmm$ (no. 139), assuming centrosymmetry. Solution of the structure with the Rietvelt method was simple because only three positional parameters needed to be refined ($\text{Cs } 00z$, $\text{F } 00z$, $\text{Br } 00z$) besides the vibrational parameters; see Table 3 and Figure 4. Considering that only powder data are available, the agreement between X-ray and neutron diffraction data is good. The Br–Br distance again proves to be a little elongated (232.5(12) X-ray, 238.9(16) pm neutron data), similar to $\text{CsF}\cdot\text{Br}_2$, indicating the same sign of charge transfer, which is also shown by the bromine–bromine stretching vibration at 287.0 cm^{-1} in the Raman spectrum.

Again, one important question concerning the features of this compound is whether the CsF layers are planar or not. They should be completely planar if no bonding interaction of whatever character to the intercalated bromine molecule exists, since points with +1 and –1 charge

are interchangeable in the purely electrostatic model. The experiment shows a small elevation of the cesium ions toward the bromine molecules, 15 pm in the X ray data, 24 pm in the neutron data. From the assumption that there is a weak bond of the kind $\text{F}^- \cdots \text{Br}-\text{Br} \cdots \text{F}^-$, one might assume that the fluorine ions should be displaced toward the bromine atoms. However, the contrary is the case. The electrostatic model can even explain this paradox: The above-mentioned weak bond between F^- and Br_2 will inevitably yield in some charge transfer from F^- to Br_2 , resulting in movement of the positive cesium ions slightly toward the bromine atoms.

Table 3. Atomic coordinates and isotropic temperature factors for $2\text{CsF}\cdot\text{Br}_2$. X-ray powder data: first entry; neutron powder data: second entry.

Atom	x/a	y/b	z/c	U [pm^2]
Cs	0	0	0.3274(2)	408(20)
	0	0	0.3288(3)	303(28)
Br	0	0	0.0572(3)	312(27)
	0	0	0.0588(4)	346(29)
F	0	0	0.1803(16)	451(75)
	0	0	0.1831(4)	237(29)

The ab initio calculation for $2\text{CsF}\cdot\text{Br}_2$ was performed qualitatively on a similar model, but a very different c axis of 2705.7 pm instead of the experimental value 2033.5 pm was obtained. This was a consequence of a wrong interlayer distance between the unfilled CsF layers of about 589 pm instead of the experimental 298.9 pm in the starting model. Starting with a more reasonable estimate, the following structure parameters were obtained: $a = 428.4$, $c = 21.135$, $\text{Cs } z/c = 0.32039$, $\text{Br } z/c = 0.05592$, $\text{F } z/c = 0.17961$. Cs and F were held exactly in

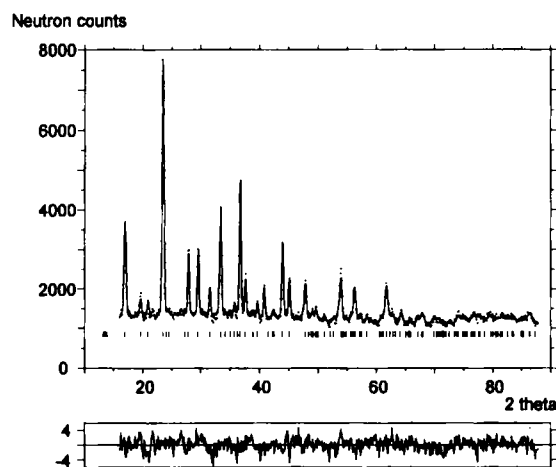
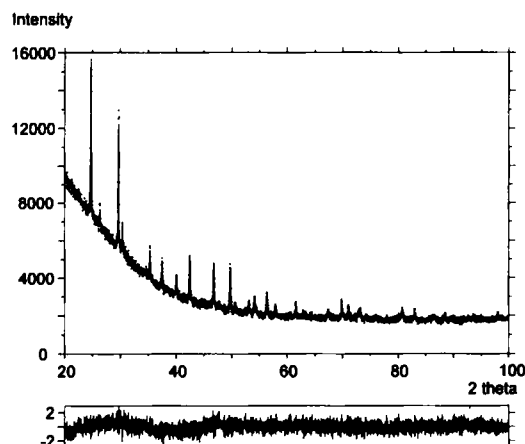


Fig. 4. Powder X-ray (above) and neutron diffraction data (below) of $2\text{CsF}\cdot\text{Br}_2$. The dots represent measured data and the lines represent the best fit of the model.

plane. This structure is calculated to be 14.8 kJ mol^{-1} more stable than $2\text{CsF} + \text{Br}_2$ and has the same energy, within 0.8 kJ mol^{-1} , as the system $\text{CsF}\cdot\text{Br}_2 + \text{CsF}$.^{11,21}

On lowering the pressure around $2\text{CsF}\cdot\text{Br}_2$, no sign of any further compounds (e.g., $4\text{CsF}\cdot\text{Br}_2$) was observed. the only product obtained is CsF, as was established by X-ray powder diffraction.

The CsF–I₂ and CsF–Cl₂ systems: It has previously been stated that iodine's intercalation behavior is similar to that of bromine.^{11,31} This, however, is not the case. We have shown by X-ray powder data for the system CsF/I_2 , obtained at temperatures between 0°C and 100°C , as well as by ^{19}F and ^{133}Cs NMR spectra of CsF in molten I_2 , that immediate reaction occurs according to Equation (1). The major product could



be indexed as known Cs_2I_8 .^{11,41} Also the chemical shift of the ^{19}F NMR spectrum of the CsF/I_2 solution shows a considerable shift to higher field, as is expected for iodine-bonded fluorine atoms. Finally, FT-Raman spectra of I_2 -free samples show clearly several intense lines attributed to I_8^{2-} , and a weak line at 448.3 cm^{-1} indicative of an I–F stretching vibration. Cl_2 , on the other hand, does not react at all with CsF, even if held at -78° and after a long period of ultrasound treatment.

The RbF–Br₂ and RbF–I₂ systems. The ab initio work predicted that KF (but not LiF) may also be a good host for intercalation, and indeed DesMarteau et al. have described a very small absorption of Br₂ by KF. We were more conservative and tried RbF. There is certainly a superficial reaction between RbF and Br₂ since the RbF turns yellow, but even at different temperatures and after ultrasound treatment no measurable weight increase is observed and therefore no intercalation compound is formed. Very long reaction times result in the formation of brown crystals of Rb⁺Br₃⁻, which were identified by a single-crystal structure determination.^[15] This is possibly a product of a disproportionation reaction [Eq. (2)]. I₂ does not



intercalate into RbF either; again the only compound that can be identified is Rb⁺I₃⁻.

Conclusion

The CsF lattice is energetically very close to a layered structure. Intercalation can be observed if a number of other conditions are met, most importantly, that no chemical reaction occurs. It remains to be seen whether other compounds can be intercalated.

There are similarities between the behavior of CsF and that of graphite. Graphite intercalates bromine readily, chlorine only under pressure, and iodine not at all. The phase richest in bromine is C₁₆Br₂, a second-stage compound like 2CsF·Br₂. The bromine molecules lie flat between the graphite sheets; the bromine–bromine distance is not established with certainty.^[16] Generally it is assumed that it too acts towards graphite as an electron acceptor.

Experimental Procedure

General: NMR spectra: Jeol FX 90Q spectrometer, CFCI₃ (¹⁹F) and CsNO₃H₂O (¹³³Cs) external standard; Raman spectra: Spex Industries, type 1403, argon and neon gas laser excitation; X-ray crystal structure determination: Enraf–Nonius CAD 4 four-circle diffractometer, MoK_α irradiation, graphite monochromator, and Stoe powder diffractometer; neutron diffraction: flat cone and powder diffractometer E2 at the BER II reactor, Berlin. CsF, CsF·Br₂, and 2CsF·Br₂ are very air-sensitive materials and were handled in a drybox with less than 0.1 ppm of H₂O. Elemental analyses were performed by Beller, Göttingen. CsF and RbF were melted in a platinum crucible and ground to very fine powders by a steel ball mill under exclusion of moisture. Bromine and iodine were purified according to standard procedures.

CsF·Br₂: Weighed amounts of CsF and Br₂ (excess) were placed in a thoroughly dried glass ampule under vacuum, which was then sealed. The ampule was kept at +70 °C for 8 weeks. On the glass wall near the surface of the liquid bromine, orange crystals formed slowly, while the majority of the CsFBr₂ remained in the bottom of the ampule as orange powder. Bulk CsFBr₂ was obtained by quick evaporation of excess bromine. Raman spectrum: 292.5 cm⁻¹. A suitable crystal was mounted on the diffractometer under cooling and in an inert atmosphere. Lattice constants were obtained by refining 25 reflections with 20° ≤ θ ≤ 25°. Intensities were measured with the *w*2θ scan mode with max. 80 s for each reflection, allowing 25% of this time for background measurements. Absorption correction was done by the *ψ* scan method; no extinction correction was applied. The structure was solved by the SHELXS 86 and SHELXS 76 procedures (see Table 2 for details). Further details of the single-crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-405184.

2CsF·Br₂: A weighed amount of CsF·Br₂ was maintained in a dynamic vacuum of 20⁻² mbar at room temperature. Pumping was stopped when the weight loss was less than 1 mg 3 h⁻¹. The weight loss corresponded to 2CsF·Br₂. Elemental analysis: 463.6, calcd Cs 57.3, F 8.2, Br 34.5, found Cs 56.8, F 8.1, Br 34.61; Raman spectrum: *v* = 287.0 cm⁻¹. X-ray powder data were obtained by means of the Guinier–Simon method in 0.2 mm o.d. glass capillaries and also from a thin powder layer protected by polyethylene foil (Table 4). Neutron powder data were obtained from a 2 g sample in a vanadium can of 0.7 cm diameter (Table 4). Following unit cell indexing by hand with all powder lines, the crystal structure was solved by the Rietveld method of profile refinement with the program Fullprof [17]. A pseudo-Voigtian type peak shape was applied to account for Gaussian and Lorentzian contributions to the line widths; background was removed by applying a polynomial

Table 4. Experimental details of the X-ray and neutron powder diffraction measurements for 2CsF·Br₂.

	X-ray diffraction	Neutron diffraction
instrument	Stoe X-ray powder diffractometer STADI/P	flat cone and powder diffractometer
monochromator	Ge	Ge
plane of reflection	(111)	(311)
collimator in front of monochromator	–	10°
detector	position-sensitive linear multiscaler	curved multidetector with 400 detection elements covering a 2θ range of 80°
wavelength [pm]	154.06	121.8
2θ range [°]	20–100	16–88
step size [°]	0.02	0.1
counting time [h]	8	1
<i>μ</i> _r	3.0	0.04
phase 1	(2CsF·Br ₂)	2CsF·Br ₂
space group	<i>I4/mmm</i> , no. 139	<i>I4/mmm</i> , no. 139
<i>z</i>	2	2
<i>a</i> [pm]	425.79 (2)	425.81 (6)
<i>c</i> [pm]	2032.5 (1)	2031.9 (4)
<i>V</i> [10 ⁶ pm ³]	368.5 (1)	368.4 (1)
number of reflections	79	113
number of refined structural parameters	7	7
number of refined profile parameters	15	15
<i>R</i> ₁	14.7	9.3
<i>R</i> _{wp}	3.8	4.3
<i>R</i> _e	5.7	2.6
phase 2	–	CsBr
space group	–	<i>Pm3m</i> , no. 221
<i>z</i>	–	1
<i>a</i> [pm]	–	429.1 (1)
number of reflections	–	23
number of refined structural parameters	–	2
number of refined profile parameters	–	4
<i>R</i> ₁	–	8.6

al function. A cylindrical sample absorption correction was performed both on the X-ray and neutron data. Assuming a centrosymmetric structure, all space groups other than $I4/mmm$ (no. 139) could be excluded because necessary conditions (besides $h+k+l \neq 2n$) were definitely not observed. A starting model was deduced from the structure of $\text{CsF} \cdot \text{Br}_2$ by setting all atoms in $00z$ positions. Only small shifts of z were necessary to arrive at the final positions. An inspection of the fitted profile showed that the sample used for the neutron experiment was impure. It turned out to contain a small amount of CsBr , which was accounted for in a multiphase refinement.

CsF/I₂ system: CsF was dissolved in iodine in a sealed ampule at 120 °C, and NMR spectra were recorded: ^{133}Cs : $\delta = 73.2$, 12 Hz line width; ^{19}F : $\delta = -117$, 3500 Hz line width. After pumping off all iodine at room temperature a dark brown powder was obtained. Raman spectrum: 448.3 (w), 170.4 (s), 146.9 (s), 105.2 (s), 73.9 (m), 50.1 (m), 44.0 (m) cm^{-1} . X-ray powder diffraction data showed the presence of three phases (stronger reflections only). The stronger reflections correspond with a calculated powder diagram based on the single-crystal structure determination of Cs_2I_8 [13]. The weaker reflections could be attributed to CsF and CsF_6 . The same results were obtained if CsF and I_2 were treated at 20 °C and 0 °C with ultrasound.

RbF/Br₂ system: Treatment for 3 days with ultrasound and pumping off all bromine gave no measurable weight increase, although a yellow coloration of the RbF remained. Powder data showed pure RbF. After weeks at 80 °C, brown crystals were formed that were identified as $\text{Rb}^+ \text{Br}_3^-$ [14].

RbF/I₂ system: X-ray powder data of RbF/I₂ mixtures treated with ultrasound showed lines for RbI_3 .

CsF/Cl₂ system: No weight increase or even coloration was obtained under any conditions.

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