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# Members of the PbFCl-Type Family: Possible Candidates for Room-Temperature Photochemical Hole Burning

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**Abstract.** We report on crystal growth and about physico-chemical studies on  $\text{Sr}_y\text{Ba}_{1-y}\text{FCl}_x\text{Br}_{1-x}$  ( $y = 0, 0.5, \text{ and } 1$ ) compounds doped with Sm. Persistent spectral hole burning at 300 K is further reported on  $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{FCl}_{0.5}\text{Br}_{0.5}:\text{Sm}$  single crystals.

## Introduction

Recent successful photochemical hole burning experiments realized in our laboratory with  $\text{SrFCl}_{0.5}\text{Br}_{0.5}:\text{Sm}^{2+}$  crystals [1] at room temperature produced evidence of new useful properties of the PbFCl family.

Among the large number of members contained in this family, the alkaline-earth or rare-earth double halides MeFX with  $\text{Me} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Eu}, \text{Sm}$  etc. and  $\text{X} = \text{Cl}, \text{Br}, \text{I}$  are of particular interest to us.

These compounds have since as far as 1894 been the subject of crystallochemical studies [2]. They all crystallize in the tetragonal  $P4/nmm$  (no 129) *Matlockit* structure  $D_{4h}^7$  (Fig. 1). Crystallographic data including all coordinates of the atoms in the unit cell are now available for most of them [3].

It is further known for some time already that mixed crystals can be grown from equimolar mixtures of SrFCl and SrFBr and also of BaFCl and BaFBr. From our EPR experiments performed on  $\text{Gd}^{3+}$ -doped mixed crystals of this composition, we concluded that neither the chloride nor the bromide enters into a fluoride lattice position [4]. Instead, they are located in

the double halogen layers between the Me–F–Me sheets. In other words, part of the basic structure is unaffected by the mixing process in these systems.

Recent systematic crystallochemical studies of the miscibility range give for several mixtures the phase diagrams and global crystal structure [5], when applicable.

In particular, it is known now [5a, b] that  $\text{SrFCl}_x\text{Br}_{1-x}$  and  $\text{BaFCl}_x\text{Br}_{1-x}$  exist and are miscible for all values of  $x$  between 0 and 1.

According to [5a], a tetragonal structure persists through this range of  $x$  values, and the lattice parameters  $a$  and  $c$  are given by  $a = 421.8 - 9.2x$  [pm] and  $c = 733.7 - 37.9x$  [pm] for  $\text{SrFCl}_x\text{Br}_{1-x}$ , and  $a = 450.8 - 11.4x$  [pm] and  $c = 741.1 - 18.6x$  [pm] for  $\text{BaFCl}_x\text{Br}_{1-x}$ .

All of the rare earth ions are easily dissolved into these compounds at an impurity concentration level. This is in particular true for the MeFX subset which will be considered in the following ( $\text{Me} = \text{Sr}, \text{Ba}$ ).

The burning of persistent spectral holes into the inhomogeneously broadened impurity bands is now widely used in the low-temperature high-resolution optical studies [6]. The need to use liquid He temperatures in hole burning experiments (as a rule) is caused by the broadening (and weakening) of the impurity zero phonon lines and by the decrease in stability of the product states with increasing temperature.

The main potential applications of the spectral hole-burning method allow to increase considerably the density of optical-data storage [6] or to increase the parallelism of processing [7]. This is made possible by the introduction of the spectral dimension in addition to the spatial coordinates. For this reason, there is an increasing interest to find materials which can be utilized at higher temperatures.

In the PbFCl family, hole-burning experiments were performed first on the ordered systems  $\text{BaFCl}:\text{Sm}^{2+}$  [8a] and in  $\text{CaFCl}:\text{Sm}^{2+}$  [8b]. Part of the BaFCl crystals (class I in [8a]), showed that spectral holes, burnt at 2 K, survived partly after cycling to room temperature and back again to 2 K.

Hole burning above liquid  $\text{N}_2$  temperature (at 80 K) was first reported on a polymer matrix, doped with a derivative of the porphyrine molecule [9]. Although several other molecular systems have been studied now at 80–90 K [10], the extrapolation of these results to room temperature

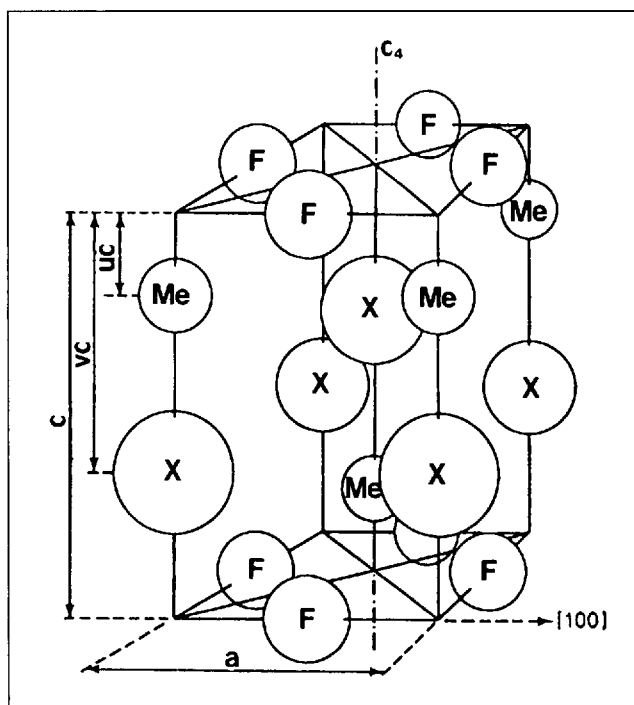


Fig. 1. Unit cell for the MeFX compounds: Me = Ca, Sr, Ba, and X = Cl, Br, I

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shows that the zero phonon lines become considerably weaker, and their (homogeneous) widths achieve the width of the inhomogeneous distribution ( $>100\text{ cm}^{-1}$ ). In 1989, results at 77 K were published for the Sm-doped powders of the composition  $\text{BaFCl}_{0.5}\text{Br}_{0.5}$  [11], where substitutional disorder induces considerable additional inhomogeneous broadening (see also [12] [13]). More detailed hole-burning studies on this compound are published in [14][15].

This investigation was, in part, motivated by the disparity in the experimental data. As already pointed out in [8a], crystals of nominally the same composition give different results. Further, our  $\text{BaFCl}_{0.5}\text{Br}_{0.5}:\text{Sm}^{2+}$  crystal spectra do not agree with those published for powders of the same nominal composition prepared under different conditions [11][13][14].

This paper succinctly presents information about sample preparation and reports the results obtained of an EPR, X-ray, Raman, luminescence and hole-burning study of  $\text{Sr}_y\text{Ba}_{1-y}\text{FCl}_x\text{Br}_{1-x}$  ( $y = 0, 0.5, 1$ ).

### Structure and Crystal Growth

As is easily verified in Fig. 1, the MeFX structure consists of  $(\text{Me}_4\text{F})^{n+}$  tetrahedra which form sheets reminiscent of a truncated  $\text{CaF}_2$  structure (perpendicular to the  $C_4$  axis). Between these sheets, which are separated by one lattice spacing, are sandwiched the double layers of  $X^-$  anions. The two layers are mutually shifted by  $1/2[110]$ . The thickness of the  $(\text{Me}_4\text{F})^{n+}$  sheets is almost independent of X for a given metal, and the Me-F bond lengths are always very close to the sum of the two ionic radii.

The two metal sites of the unit cell have  $C_{4v}$  symmetry. They are related by the inversion operation of the factor group of this non-symmorphic space group.

Crystals were grown either in a Bridgman furnace or in a Kyropoulos-Czochralski setup. The following points are worth of note. Both apparatus are built in such a way that the crystals can be grown either in an atmosphere of ultrapure Ar or under high vacuum. We always doped our crystals with rare-earth fluoride of at least 3N purity (in particular  $\text{SmF}_3$ ). In an unpublished study [16], we have systematically hydrolyzed (typically 8 h, 15 mm Hg  $\text{H}_2\text{O}$  vapor) pure SrFCl crystals and subsequently X-rayed them. EPR results obtained at 4.2-K sample temperature for these crystals allowed to identify an  $\text{O}_2^-$  molecular ion which substitutes for a F<sup>-</sup> ion. Its g values are:

$$g_{[110]} = 2.1719, g_{[110]} = 2.005, g_{[001]} = 2.06.$$

These experimental results were useful in applying EPR as an analytical tool for these substances.

The second point concerns the shape of the crucibles, in particular with respect to the Bridgman technique. We always observed that the crystals grew much faster, when their  $c$  axis is parallel to the solidification isotherm. The reason for this behavior is very likely related to configurational entropy inside a macroscopically small volume comprising the crystallized surface and a thin layer of the melt.

In the event where the growth interface is perpendicular to the  $c$  axis, then within a given short time interval a metal plane (for instance) has to be formed, needing the preferential presence of metal ions in the volume. This process is statistically rather improbable, because the configurational entropy would have to be drastically reduced within the small volume. Near equilibrium, this volume normally contains similar amounts of metal, fluoride, and halogen ions, which will adhere to the crystal with similar probability during solidification. Growth perpendicular to the  $c$  axis is thus much more favorable, and in agreement with a local maximum configurational entropy.

We developed for this reason crucibles of rectangular cross-section which allow to grow even in our Bridgman furnace useable single crystals, in spite of this extremely anisotropic growth pattern.

The mixed compounds  $\text{SrFCl}_x\text{Br}_{1-x}:\text{Sm}$  used in the Raman and X-ray powder study were prepared in graphite boats placed in a sealed quartz ampoule. After introduction of the compound, the ampoule was outgassed at 150–200°, then, 0.2 atm of ultrapure Ar was admitted. Synthesis of the mixed compounds was achieved by melting the mixture of SrFCl and SrFBr at 1100°, and cooling successively to 1000, 900, and 850° before switching the furnace off.

### Spectroscopic Results

#### EPR

An early study in 1972 [16] of  $\text{Gd}^{3+}$  in  $\text{SrFCl}_{0.5}\text{Br}_{0.5}$  allowed to identify, in addition to an axial  $\text{Gd}^{3+}$  EPR spectrum, the signals of a monoclinic variety together with many additional lines.

A systematic EPR study was realized on the pure hosts MeFCl and MeFBr (Me=Ca, Sr, Ba) doped with  $\text{Gd}^{3+}$  and  $\text{Eu}^{2+}$ , respectively. The spectra observed for these systems were always of axial symmetry. The second-order crystal field term was analyzed [17] with the aid of an angular overlap model. This approach, though approximate, allowed to show that the axial  $X^-$  ion and the four other  $X^-$  ions mutually act oppositely onto the ground state [17]. The effect of the fluoride neigh-

bors is remarkably weak. This fact explains qualitatively the very large variations of the  $b_2^0$  crystal field parameter of the ground state multiplet as a function of the nature of X for a given cation [18].

These results permitted to identify the axial  $\text{Gd}^{3+}$  signal in  $\text{SrFCl}_{0.5}\text{Br}_{0.5}$  as arising from an intact  $\text{Cl}^-$  neighborhood, whereas the monoclinic spectrum is probably due to the replacement of one  $\text{Cl}^-$  neighbor by a  $\text{Br}^-$  ion. Work is not yet finished.

#### X-Ray Study

Our powder diffraction measurements on  $\text{SrFCl}_x\text{Br}_{1-x}:\text{Sm}$  (0.1%) confirm [5a] the linear variation, with respect to  $x$ , of the tetragonal lattice parameters. There are additional weak lines on our Guinier-Hägg photographs. They are of two types. Some lines are consistent with the presence of  $\text{SrF}_2$  in the samples. Four additional lines are seen between  $\theta=7^\circ$  and  $\theta=11^\circ$ ; their position varies with the mole fraction  $x$ .

Two single crystals were further studied:  $\text{SrFCl}_{0.5}\text{Br}_{0.5}:\text{Sm}$  (A) and an undoped  $\text{SrFCl}_{0.5}\text{Br}_{0.5}$  (B). Both presented on long exposure precession photographs and from diffractometer measurements (sample A only) an additional tetragonal lattice with  $a = 814.49(36)$  pm and  $c = 697.43(39)$  pm with the same orientation as the parent structure. The normal lattice parameters of these crystals are  $a = 416.08(7)$  pm and  $c = 713.2(2)$  pm. Subsequent polishing of the surfaces of the pure sample B did not eliminate completely this additional lattice. At present, two hypotheses have to be considered.

Either the extra structure arises from epitaxial layers of  $\text{SrCl}_{2-y}\text{Br}_y$  which are intercalated. The simultaneous presence of the  $\text{SrF}_2$  lines suggest indeed minor partial decomposition of the mixed fluorohalide. Raman spectra of a powdered sample of  $\text{SrFCl}_{0.5}\text{Br}_{0.5}:\text{Sm}$  which has been subjected to 4-h exposure to X-rays were identical to those of a virgin sample.

The other less likely hypothesis is that our crystals present an 'out of step' incommensurate phase. We were not yet able to observe the postulated  $\text{SrCl}_{2-y}\text{Br}_y$  phase spectroscopically. Note that an epitaxial layer needs not to have the same orientation and symmetry as the substrate.

#### Raman Results

##### 1. Powder Spectra of the Solid Solutions $\text{SrFCl}_x\text{Br}_{1-x}$ doped with 0.1% Samarium

Fig. 2 shows that the spectra change continuously with  $x$  varying from 0 to 1. No additional lines appear and no lines disappear (with the exception of the  $E_g$

mode around  $100\text{ cm}^{-1}$  at intermediate compositions), indicating that the crystal structure is similar for all. Table 1 collects the Raman shifts observed at 300 K. The two high-frequency bands around  $240$  and  $280\text{ cm}^{-1}$  have been assigned to mainly fluoride vibrations [19a]. Indeed, the width of these bands is not increased significantly in the mixed compounds, while the

lowest frequency bands broaden considerably even for  $x = 0.1$  or  $x = 0.9$ .

A plot of the observed Raman shifts vs. composition yields that the frequency of the two fluoride modes varies linearly with  $x$ . It has been suggested previously [18] that these frequencies should depend on the lattice parameter  $a$ . Indeed, the X-ray data show a linear variation of both

lattice parameters with  $x$ . One may thus use the position of the highest frequency Raman bands to confirm the composition of the compound prepared.

This property is illustrated for the crystal  $\text{BaFCl}_{0.5}\text{Br}_{0.5}\text{:Sm}$ . The lattice parameters of the system  $\text{BaFCl}_x\text{Br}_{1-x}$  are also reported [5a] to vary linearly with  $x$ . The highest frequency Raman band is predicted to be at  $0.5x(251+238) = 244.5\text{ cm}^{-1}$  and observed at  $245\text{ cm}^{-1}$ . Our X-ray powder diffraction data yield the parameters  $a = 444\text{ pm}$  and  $c = 732\text{ pm}$ ; these values are indeed close to the middle of the corresponding values for BaFCl and BaFBr.

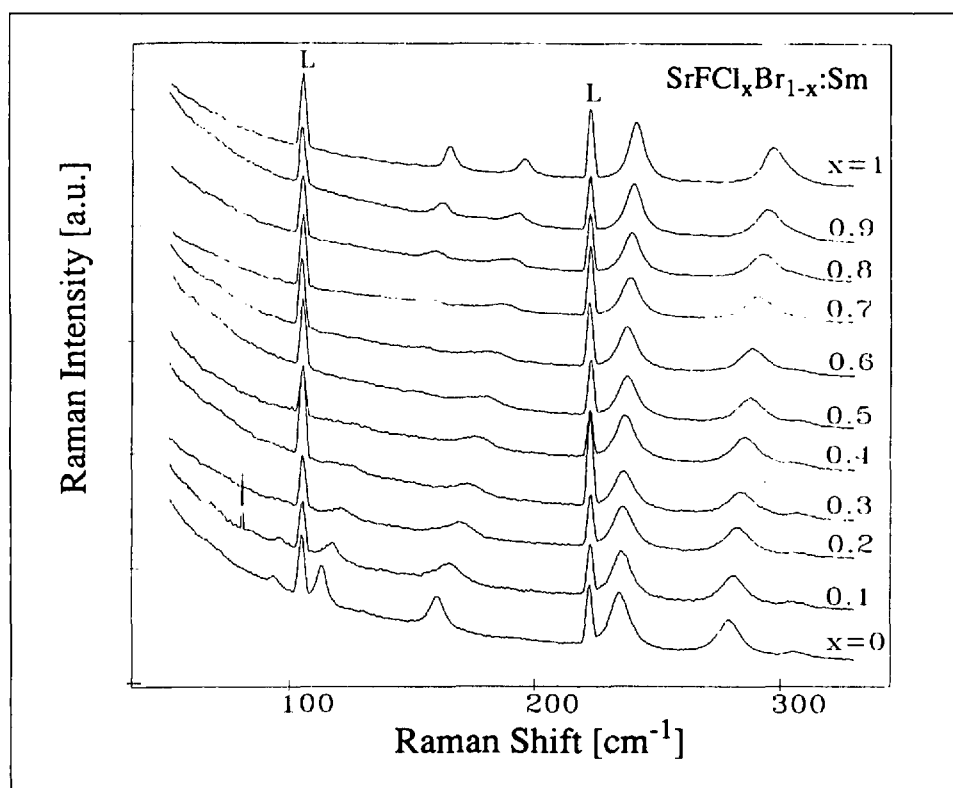


Fig. 2. Raman spectra at 300 K of powdered  $\text{SrFCl}_x\text{Br}_{1-x}\text{:}0.1\%\text{Sm}$ . The sharp lines noted L are laser plasma lines. Slit width  $200\ \mu$ , laser power ca. 100 mW.

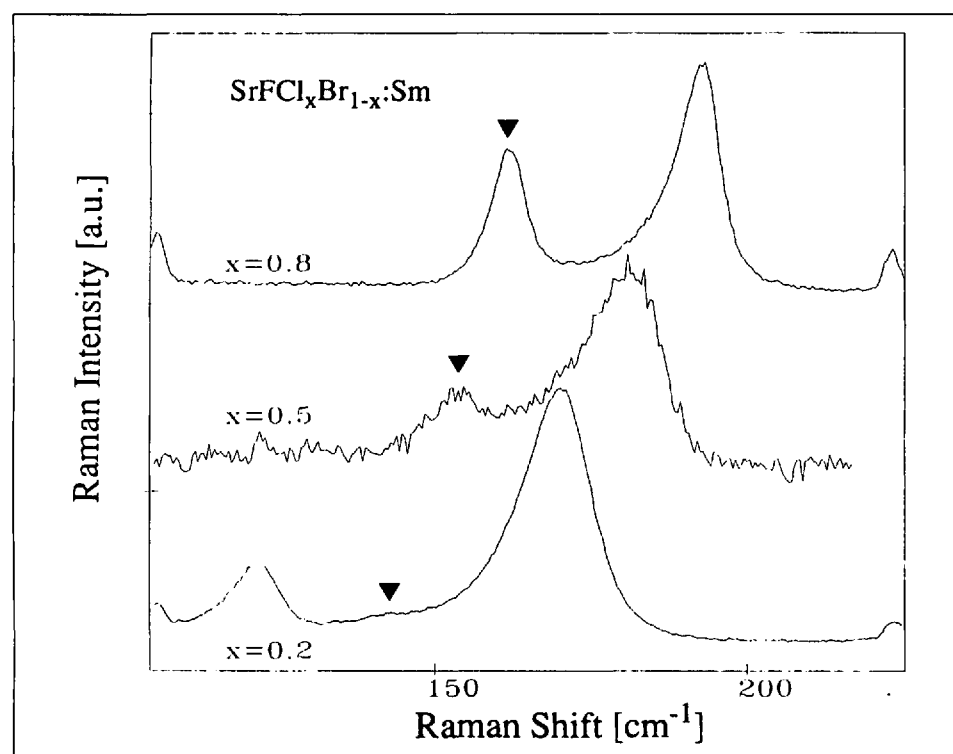


Fig. 3. (cc)+(ca) polarized Raman spectra of crystals  $\text{SrFCl}_x\text{Br}_{1-x}$

### 2. Single-Crystal Measurements

Fig. 3 compares the spectra of three samples between  $110$  and  $220\text{ cm}^{-1}$ . The two strongest bands of the  $x = 0.8$  sample at  $160$  and  $191\text{ cm}^{-1}$  correlate with the mainly Sr-Cl (Sr-Br, respectively) stretching vibrations of the respective pure compounds [19]. In the mixed crystals, an important frequency shift of these bands is observed, as well as a varying and asymmetric line shape. An elementary site-group analysis of the mixed crystals obviously seems thus not to be adequate. It is further interesting to note the significant change of the relative intensity of the  $E_g$  mode (labelled in Fig. 3). Furthermore, a spectrum of a crystal with  $x = 0.5$  was obtained at 77 K. The linewidth of the fluoride modes (above  $200\text{ cm}^{-1}$ ) decreased significantly, while the bands at  $153$  and  $180\text{ cm}^{-1}$  retained essentially their room temperature width and shape.

Another spectrum of a crystal which had been pulled from the melt, with nominal composition  $\text{SrF}_{1/3}\text{Cl}_{1/3}\text{Br}_{1/3}\text{:Sm}$ , yielded the same spectrum as the crystal  $\text{SrFCl}_{0.5}\text{Br}_{0.5}\text{:Sm}$ . This observation, in conjunction with identical Sm luminescence spectra for both crystals, confirms the stabilizing role of the fluoride to form the MeFX compounds: the chloride or bromide ions do not substitute in the fluoride layers. Note that in this case the nominal composition does not correspond to the real one.

The polarized spectra of  $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{FCl}_{0.5}\text{Br}_{0.5}$  are quite similar to those of  $\text{BaFCl}_{0.5}\text{Br}_{0.5}$  and  $\text{SrFCl}_{0.5}\text{Br}_{0.5}$ . The observed Raman shifts are collected in Table 1. Those for the  $\text{Ba}_{0.5}\text{Sr}_{0.5}$  crystal fall between those of the Ba and Sr crystals. These similarities tend to show that the general structure of  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{FCl}_{0.5}\text{Br}_{0.5}$  is also tetragonal or deviates only slightly from this symmetry. No line splittings or additional lines are observed in these spectra, whereas an X-ray study [5b] of mixed compounds of the type (SrFCl-BaFCl) shows that there is a small monoclinic

deviation for some compositions. Thus, Raman spectroscopy seems in this situation not powerful enough to decide between the possible symmetries.

**Hole-Burning Experiments**

Persistent hole burning was first observed at room temperature in SrFCl<sub>0.5</sub>Br<sub>0.5</sub>:Sm<sup>2+</sup> mixed crystals [1]. Two transitions, <sup>5</sup>D<sub>1</sub>-<sup>7</sup>F<sub>0</sub> and <sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>0</sub> of Sm<sup>2+</sup>, were studied and the homogeneous linewidths,  $\Gamma_h$ , equal to 1.75 and 1.3 cm<sup>-1</sup>, respectively, were determined for these transitions. The Br-Cl disorder increases the inhomogeneous linewidth by a factor of 10<sup>2</sup> with respect to the SrFCl lattice (previously also observed for the BaFCl<sub>0.5</sub>Br<sub>0.5</sub> system [11]). This disorder

does not, however, affect the values of  $\Gamma_h$  in SrFCl<sub>0.5</sub>Br<sub>0.5</sub>:Sm<sup>2+</sup> at room temperature. The hole-burning mechanism was found to be two-photon photoionization of Sm<sup>2+</sup> followed by electron trapping, as already observed in BaFCl:Sm<sup>2+</sup> [8a].

Here, we report our preliminary results for the Sr<sub>0.5</sub>Ba<sub>0.5</sub>FCl<sub>0.5</sub>Br<sub>0.5</sub> single crystal host. Fig. 4 illustrates the hole burning in the <sup>5</sup>D<sub>1</sub>-<sup>7</sup>F<sub>0</sub> transition. The fluorescence excitation spectra were measured by scanning the wavelength of a tunable dye laser (DCM dye, 0.15-cm<sup>-1</sup> linewidth) and recording the nonresonant fluorescence via a color filter (RG9).

Hole burning occurred under conditions similar to those for SrFCl<sub>0.5</sub>Br<sub>0.5</sub>: i) pre-irradiation of the sample in an intense Ar<sup>+</sup> laser beam was needed to produce deeper holes; ii) a 50-mW laser beam,

focussed to a diameter of 50-100 μm on the sample, was used, with exposition times ranging from 10 to 100 s (for more details, see [1]).

The holes were fitted with a Lorentzian curve and the minimum holewidth,  $\Gamma_{hole}$ , was determined to be 7 cm<sup>-1</sup>. Using the simple relation  $\Gamma_{hole} = 2\Gamma_h$ , valid for shallow holes [6], one obtains that the value of  $\Gamma_h$  is two times bigger than that determined for the same transition in SrFCl<sub>0.5</sub>Br<sub>0.5</sub>. We note a similar trend for ordered hosts: the room temperature value of  $\Gamma_h$  in BaFCl is ca. 1.5 times the width in SrFCl (see Fig. 5).

To illustrate the occurrence of hole burning, a simple model spectrum consisting of the distribution of frequency-shifted homogeneous zero phonon lines is presented on the top of Fig. 4. Monochromatic irradiation (shown by the arrow) will excite strongly the resonant impurity ions, while the others, with shifted positions of their homogeneous lines, will experience considerably weaker excitation. As a result, mainly the resonant impurities will be photo-ionized (with a certain probability), leaving a hole in the inhomogeneous spectrum of Sm<sup>2+</sup>.

Fig. 5 presents the <sup>5</sup>D<sub>1</sub>-<sup>7</sup>F<sub>0</sub> transition fluorescence spectra for three mixed compounds, Sr<sub>y</sub>Ba<sub>1-y</sub>FCl<sub>0.5</sub>Br<sub>0.5</sub>:Sm<sup>2+</sup> (y = 0, 0.5, 1), measured at room temperature. Table 2 collects spectral data at room temperature for the <sup>5</sup>D<sub>1</sub>-<sup>7</sup>F<sub>0</sub> and the <sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>0</sub> transitions. The fluorescence was excited via the broad f-d transitions at 476.5 nm and, hence, includes the whole inhomogeneous ensemble.

The two maxima for the pure Sr (y = 1) compound (spectrum 1) may be associated with the different nearest neighbor (Cl,Br) ligand configurations [12a][13]. The Ba,Sr mixed compound (y = 0.5) shows a nearly Gaussian spectrum (spectrum 2), an indication of the increased influence of the next configuration sphere(s). The spectrum of the Ba (y = 0) crystal (spectrum 3) is somewhat special, because it has less than half the width of the spectra described in the previous paragraph. More exactly, it consists of the main band and a weak shoulder (less than 10% of the total intensity), shifted by ca. 15 cm<sup>-1</sup> to the higher frequency side. One may assume that in the Ba compound the Sm<sup>2+</sup> preferably stabilizes in one type of the nearest neighbor configuration, whereas for the Sr compound the probabilities to occupy different configurations are more close. This difference may well be related to the cation sizes: the Sr<sup>2+</sup> radius is practically the same as of Sm<sup>2+</sup>, whereas divalent Ba is about 13% bigger. The fact, that the impurity ions in the substitutionally mixed ionic crystals do not occupy the

Table 1. Room-Temperature Raman Shifts [cm<sup>-1</sup>]

SrFCl [18][19a]	107	155	165	195	241	296
SrFCl <sub>0.8</sub> Br <sub>0.2</sub>			160	191	240	294
SrFCl <sub>0.5</sub> Br <sub>0.5</sub>		131	153	180	236	287
SrFCl <sub>0.8</sub> Br <sub>0.2</sub>	97	121	142	169	235	282
SrFBr [19b]	94	113	130	160	234	278
Sr <sub>0.5</sub> Ba <sub>0.5</sub> FCl <sub>0.5</sub> Br <sub>0.5</sub>	79	122	146	162	222	263
BaFCl [18][19a]	82	132	143	165	216	251
BaFCl <sub>0.5</sub> Br <sub>0.5</sub>	79	115	135	151	215	245
BaFBr [18][19a]	76	103	109	123	211	238

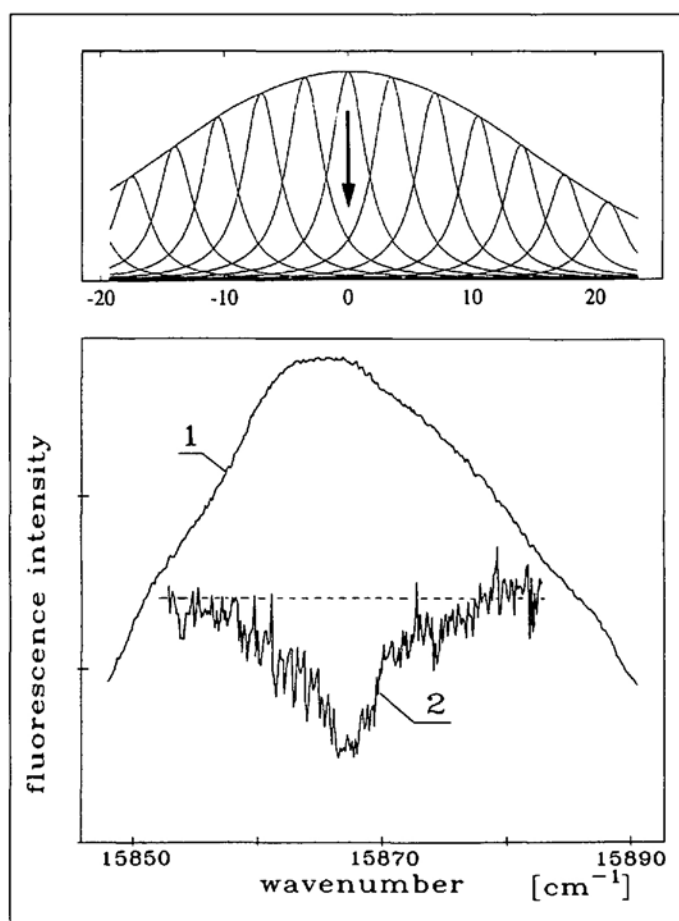


Fig. 4. Sr<sub>0.5</sub>Ba<sub>0.5</sub>FCl<sub>0.5</sub>Br<sub>0.5</sub>:Sm<sup>2+</sup> <sup>5</sup>D<sub>1</sub>-<sup>7</sup>F<sub>0</sub> transition excitation spectrum (1) and the spectral hole (2). The hole is obtained as the difference between the initial spectrum and the spectrum, measured after 100-s exposure with monochromatic light at 15867.4 cm<sup>-1</sup>. Spectrum (2) is shown with 8x magnification and with the zero level at the dotted line. Top-model spectrum of the <sup>5</sup>D<sub>1</sub>-<sup>7</sup>F<sub>0</sub> transition with  $\Gamma_h = 3.5$  cm<sup>-1</sup> and  $\Gamma_{ih} = 35$  cm<sup>-1</sup>.

different ligand configurations with equal probabilities, is known, for example, from the studies of  $Tl^+$  in mixed potassium halides [20] (see also the EPR results above). We note, in addition, that the shape of the spectrum did not depend on the excitation wavelength in the range of 458–514.5 nm, and that the polycrystalline samples (taken from the bottom of the crucible in the Czochralski furnace, *i.e.* made simply by cooling down the melt) showed exactly the same spectra.

The room temperature spectra of  $Sm^{2+}$  in the matrices SrFCl, SrFBr, and BaFCl are shown at the top of Fig. 5 in order to present the correspondence with these systems. These  $Sm^{2+}$  lines are practically homogeneous, and the Lorentzian fit yielded the following values for their widths: 2.07 (SrFCl), 2.38 (SrFBr), and 3.08  $cm^{-1}$  (BaFCl). We estimate the contribution from  $\Gamma_{ih}$  and from instrumental width (0.16  $cm^{-1}$ ) to be 10–20% of these values.

## Conclusion

We have presented a multitude of physico-chemical properties of several members of the family of the title compound. The underlying investigations were motivated by fundamental research issues, but also undertaken in view of the possibility to use these materials for hole burning experiments at elevated temperatures. We have demonstrated the room temperature hole burning in two single crystal materials. The experiments were performed on well-defined and well-characterized samples. We believe that these results induce compelling necessity to continue a full range investigation of intermediate compounds of this family.

Recently, room temperature hole burning was communicated on  $Mg_{0.5}Sr_{0.5}FCl_{0.5}Br_{0.5}:Sm^{2+}$  [21]. This compound could be interesting for (co-)doping with transition metal impurities, which may more easily substitute for the smaller  $Mg^{2+}$  ions. Thereby, it would be useful to extend the comprehensive characterization of the present work to Mg-containing compounds. Their nominal composition should be carefully verified, especially due to the fact that the  $MgF_2$ – $MgCl_2$  system is shown [22] to form only separate phases (*i.e.* no MgFCl can be made).

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Table 2. Room-Temperature Fluorescence Spectra of  $Sm^{2+}$  in Mixed Crystals: Position at Maximum Intensity and Full Width at Half Maximum [ $cm^{-1}$ ]

	$^5D_0-^7F_0$		$^5D_1-^7F_0$	
	Position	Width	Position	Width
SrFCl <sub>0.5</sub> Br <sub>0.5</sub>	14492	30	15827	34
Sr <sub>0.5</sub> Ba <sub>0.5</sub> FCl <sub>0.5</sub> Br <sub>0.5</sub>	14526	30	15866	34
Ba <sub>0.5</sub> FCl <sub>0.5</sub> Br <sub>0.5</sub>	14540	12	15883	13

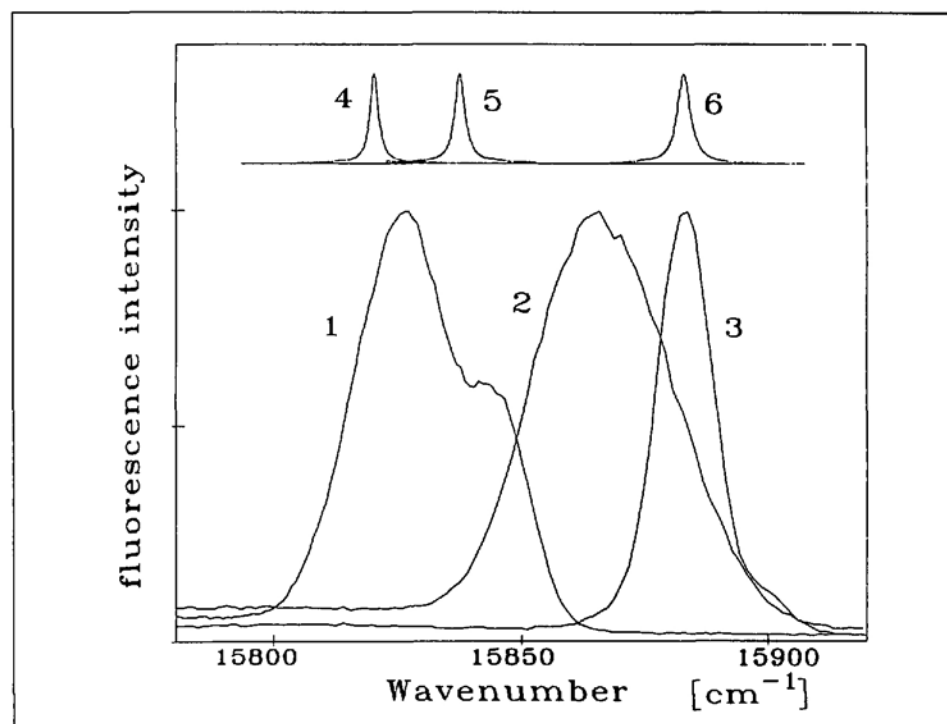


Fig. 5.  $^5D_1-^7F_0$  transition fluorescence spectra of  $Sm^{2+}$  at 300 K in SrFCl<sub>0.5</sub>Br<sub>0.5</sub> (1), Sr<sub>0.5</sub>Ba<sub>0.5</sub>FCl<sub>0.5</sub>Br<sub>0.5</sub> (2), BaFCl<sub>0.5</sub>Br<sub>0.5</sub> (3), SrFCl (4), SrFBr (5), and BaFCl (6)

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