Journal of Thermal Analysis and Calorimetry, Vol. 57 (1999) 193-202

STUDY OF THE SOLID–LIQUID EQUILIBRIUM IN MIXED ALKALINE EARTH FLUOROHALIDES

H. Hagemann[1], *P. Tissot*[2], *D. Lovy*[1], *F. Kubel*[1] *and H. Bill*[1]

[1]Département de Chimie physique
[2]Département de Chimie minérale, analytique et appliquée, Université de Genève, 30, quai E. Ansermet, CH 1211 Geneva 4 Switzerland

Abstract

We have studied the solid-liquid equilibrium of the system $Sr_{1-y}Ba_yFCl_{1-x}Br_x$ using DTA and X-ray diffraction techniques. The entire composition range in this system yields solid solutions which crystallize in the PbFCl (Matlockite) structure type. The melting points of the entire composition range have been parametrized (within 5°C rms error) using a biquadratic fit of the available data obtained by experiment and from the literature.

Keywords: barium strontium fluorohalides, DTA, X-ray diffraction

Introduction

Layer structure crystals of the PbFCl-type family (Matlockite structure) doped with Sm^{2+} show remarkable photochemical properties under optical hole burning (HB) at room temperature [1, 2] and as a consequence, promising potentiality for optical information storage applications. Additionally, some of these host materials present potential applicability for image storage in X-ray detection systems [e.g. 3, 4]. For these reasons the extension of knowledge about crystallochemical, structural and thermodynamic properties of these compounds is worthwhile. Several publications [5–7] reported experimental melting point temperatures of the binary subsystems SrFCl–BaFCl, SrFCl–SrFBr, BaFCl–BaFBr. These present a minimum melting point, whereas the system SrFBr–BaFBr [6] is reported to have an eutectic. Apparently, there is disagreement between some of the published results [6–8]. For the three former systems the literature gives a quasi-linear variation of the tetragonal lattice parameters a and c [6, 7]. In previous papers [9–11] we presented experimental results showing that the compounds $Sr_{1-y}Ba_yFCl_{1-x}Br_x$ form solid solutions over the entire x,y composition range.

The present paper gives results on the solid-liquid equilibrium of the mixed system $Sr_{1-y}Ba_yFCl_{1-x}Br_x$ over the entire composition range obtained from our DTA and X-ray diffraction studies. Raman and luminescence experiments were also performed. It further gives an approximate parametrization of the melting point temperatures of the set. The formula used is based on thermodynamical arguments and allows to determine approximate values of this quantity within the whole phase diagram.

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

Samples

Starting compounds were BaFCl, BaFBr, SrFBr and SrFCl. They were prepared by slowly cooling the melt of a stoechiometric mixture of BaF_2 (or SrF_2) and the corresponding chloride or bromide under 0.2 bar of ultrapure argon (5N5), often slightly fluorinated. Carefully dried materials of high purity were used. Precautions were applied to avoid any oxygen contamination. The mixed compounds were obtained by mingling the starting compounds in the appropriate ratios, heating the batch to 1100°C (above the melting point) and cooling it within 3 h to 800°C (below the melting point). A typical batch size was ca 400 mg for X-ray and luminescence studies and approximately 100 mg for the DTA experiments.

System $Sr_{1-y}Ba_yFBr$

Mixtures with nominal mole fractions y=0.99, 0.75, 0.7, 0.65, 0.6, 0.55, 0.5, 0.45, 0.3, 0.15 and 0.01 were grown under extremely controlled conditions, in particular with respect to maintaining as closely as feasible thermodynamic equilibrium conditions. In particular, one batch close to the minimum melting composition (y=0.3) as well as another with y=0.6 was molten and cooled with a rate of 9°C h^{-1} from ca 50°C above the melting point to ca 40°C below the melting point, this latter temperature being kept constant for within 88 h before cooling to room temperature.

SrFBr and $Sr_{1-y}Ba_yFBr$ with $y\leq 0.4$ are rather moisture sensitive. If kept in air for some time, one observes the formation of $SrBr_2\cdot 6H_2O$ and $BaBr_2\cdot 2H_2O$ (and $(Sr,Ba)F_2$), as demonstrated by X-ray analysis.

Measurements

All DTA experiments were performed as follows. Each sample was subjected to 3 heating and cooling cycles in an argon atmosphere, between 700 and 1100°C, at a rate of 4°C min^{-1}. The data of the third cycle were used. The absolute temperature calibration of the apparatus was obtained by melting NaCl in the same graphite crucible under otherwise identical conditions. The melting temperature was obtained as the intercept of the interpolated baseline and the linearly extrapolated sloped part preceding the last occurring pronounced relative maximum of the corresponding DTA signal, recorded with increasing temperature. The procedure was applied in a similar manner to each maximum when the signal presented multiple peaks. The apparatus is described in [12].

X-ray and optical measurements were performed with the instruments described before.

Experimental results

System $Sr_{1-y}Ba_yFBr$

No eutectic was found in this system by X-ray powder diffraction on the different compounds prepared. Our single crystal structure data for four different members of this system are summarized in Table 1. The complete crystallographic data of our new structure determinations are transferred to the ICSD data base. This table further contains structural data from the literature of the pure matlockites and other mixed crystals of the family $Sr_{1-y}Ba_yFCl_{1-x}Br_x$.

DTA measurements

Figure 1 presents typical DTA traces ($\Delta T=f(T(t))$) obtained from our samples. These signals exhibit genuine complex shape indicative of a complicated fusion mechanism in the layer compounds. Only one simple fusion peak was observed for the NaCl calibration sample. The simple binaries SrFCl, SrFBr, BaFCl, BaFBr all exhibit two fusion temperatures separated by 5 to 9°C (Fig. 1). The mixed compounds either present several resolved melting temperatures (typically at intervals of 6 to 15°C) or one broad DTA signal (Fig. 1). The results obtained for the pure binaries as well as those of the mixed compounds are summarized in Table 2. Two melting point data sets for the system SrFCl–BaFCl are reported in the literature [5, 7]. Our reproducibly observed melting point of 929°C for the nominal composition $Sr_{0.64}Ba_{0.36}FCl$ is quite far from the value of 906°C given in the old investigation by Bergman and Bukhalova [5]. We retain for this reason only the more recent values [7].

Table 3 compares the observed melting point temperatures of the pure compounds BaFCl, BaFBr, SrFBr and SrFCl with literature data. BaFCl and SrFCl were measured twice. Good agreement is found for BaFCl and BaFBr. The one of SrFCl agrees with one of the values published. The melting temperature for SrFBr is in the range of values estimated from literature information [6]. We thus conclude that the data set given in Tables 2 and 3 is a reliable basis for the analysis of the results presented below.

X-ray measurements

X-ray powder diffraction measurements were realized on 5 samples with varying chloride content and a Sr mole fraction $1-y=0.65\pm0.05$. Sharp diffraction peaks characteristic of the PbFCl structure with a well-defined composition were obtained for all of them. Other nominal compositions were already earlier studied by this technique and these results are already published. For instance, samples with a Sr mole fraction $1-y=0.3$ (discussed in [10]) presented the complex diffraction patterns characteristic of several compositions being simultaneously present. This situation is met with when fractional crystallization occurs. The compound $Sr_{0.67}Ba_{0.33}FCl_{0.33}Br_{0.67}$ (close to the minimum melting point composition) was studied in some detail. The powder diagrams of two different batches were identical. The second of these batches was prepared with a total amount of ca 20 gr. Three samples taken at different locations of this batch gave mutually identically X-ray powder diffraction patterns. A single crystal from the first (ca 400 mg) batch was chosen for single crystal X-ray diffraction. The refinement of the tetragonal PbFCl-type structure (with $R=0.034$) yielded the population of Sr (0.60, standard deviation 0.03) and of Cl (0.40, standard deviation 0.03). This composition corresponds within 2 standard de-

Table 1 Single crystal structure data for $Sr_{1-y}Ba_yFCl_{1-x}Br_x$ compounds
Space Group P4/nmm, F on site (–0.25,0.25,0.0), (Sr, Ba) and (Cl, Br) on site (0.25,0.25,*z*)

A. Literature data

x	*y*		*a*/pm	*c*/pm	$V/10^6$ pm^3	*z*/Sr, Ba	*z*/Cl, Br
0	0	SrFCl[16]	412.59(8)	695.79(13)	118.445	0.2015(2)	0.6429(5)
0	1	BaFCl[16]	439.39(6)	722.48(9)	139.48	0.2049(1)	0.6472(7)
1	0	SrFBr[13]	421.8(2)	733.7(5)	130.54	0.18594(12)	0.64791(13)
1	1	BaFBr[14]	450.8(4)	744.1(15)	151.22	0.1911(4)	0.6497(5)
1	1	BaFBr[13]	450.3(2)	743.5(4)	150.8	0.1923(1)	0.6495(3)
1	1	BaFBr[15]	451.0(1)	744.1(3)	151.3	0.1927(2)	0.6495(3)

B. Our results

x	*y*	a/pm	*c*/pm	$V/10^6$ pm^3	*z*/Sr, Ba	*z*/Cl, Br
1	0.301(5)	431.10(2)	737.45(5)	137.055(12)	0.18860(3)	0.64877(5)
1	0.432(8)	434.40(3)	738.18(12)	139.30(3)	0.18956(5)	0.64886(7)
1	0.602(9)	439.10(4)	740.24(14)	142.72(4)	0.19040(4)	0.64907(7)
1	0.883(8)	447.33(3)	742.02(9)	148.48(3)	0.19141(4)	0.64954(7)
0.429(8)	1.	444.90(3)	732.21(16)	144.93(4)	0.19854(4)	0.6483 (1)
0.70(2)	0.40(3)[11]	428.61(3)	719.22(10)	126.43(3)	0.19367(3)	0.64537(6)
0	0.806(6)[10]	433.76(3)	715.75(6)	134.667(22)	0.20476(1)	0.64768(5)
0.3	0.7[10]	436.66(2)	722.13(6)	137.690(17)	0.20120(2)	0.64683(6)

viations to the nominal one. This composition is probably a good choice for the growth of well-defined good quality single crystals from the melt. First attempts yielded optically very transparent, but small samples.

Discussion

Melting temperatures from the DTA results

Pure alkaline earth fluorohalides

Each one presents two nearby fusion temperatures (Fig. l). This fact has to be corroborated with the following results. Published [19, 20] ionic conductivity studies of several pure alkaline earth fluorohalides systematically show that their conductivity is anisotropic with a maximum perpendicular to the tetragonal crystal axis. But no solid-solid structural phase transition was found. Then, it is well known that alkaline earth fluorohalides can be prepared by solid state reaction. Several laboratories report sample preparation by this approach [8, 21]. Thereby mixtures of the alkaline earth fluoride and halide (e.g. SrF_2 and $SrCl_2$) are reacted between 600 and 850°C. All this indicates that premelting of the halide (chloride or bromide) lattices may take place prior to the melting of the metal-fluoride backbone in the pure Matlockite compounds. For these reasons the higher values of the two temperatures read from the corresponding DTA curves was taken as the final fusion temperature of the compound.

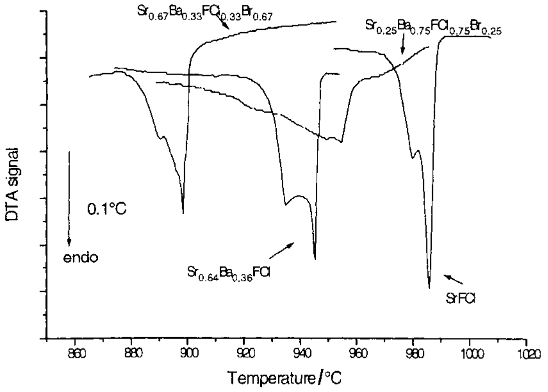

Fig. 1 Typical DTA heating traces for 4 different samples (see text)

Mixed compounds

Part of the mixed alkaline earth fluorohalides show complex structure of the DTA traces (Fig. 1). This one is related to the possibility of fractional crystallization of these systems. This effect depends on the gradient of the melting point temperature with respect to compositional changes. It is almost absent in composition regions with a small gradient, as for instance around a Sr mole fraction of 1–*y*=ca 0.65. At approximately this same mole fraction one finds not only the absolute minimum

Table 2 Results of the DTA experiments

No.	Run/Nominal composition	T_f (heat)/	T_f (cool.)/	ΔT/	Comments
		°C			
1	SrFCl	974	963	9	
2	BaFBr	931	912.5	18.5	
3	BaFCl	1006.5	1005	1.5	
4	BaFBr	992	977	15	
5	$Sr_{0.51}Ba_{0.49}FCl_{0.51}Br_{0.49}$	895	872	23	
6	$Sr_{0.66}Ba_{0.34}FCl_{0.66}Br_{0.34}$	897	888	9	
7	$Sr_{0.64}Ba_{0.36}FCl$	929	921.5	7.5	
8	$Sr_{0.70}Ba_{0.30}FBr$	892	883	9	
9	$Sr_{0.67}Ba_{0.33}FCl_{0.33}Br_{0.67}$	883	869	14	
10	$Sr_{0.63}Ba_{0.37}FCl_{0.58}Br_{0.42}$	892	884	8	
11	$Sr_{0.61}Ba_{0.39}FCl_{0.53}Br_{0.47}$	892	888	4	
12	$Sr_{0.60}Ba_{0.40}FCl_{0.40}Br_{0.60}$	884	868	16	
13	$Sr_{0.76}Ba_{0.24}FCl_{0.24}Br_{0.76}$	888	871	17	
14	$Sr_{0.68}Ba_{0.32}FBr$	894	878	16	
15	$SrFCl_{0.30}Br_{0.70}$	921	910.5	10.5	
16	$Sr_{0.80}Ba_{0.20}FCl_{0.80}Br_{0.20}$	896.5	912	–15.5	broad transition
17	$Sr_{0.24}Ba_{0.76}FCl_{0.24}Br_{0.76}$	ca 920	928.5	–8.5	broad transition
18	$Sr_{0.25}Ba_{0.75}FCl_{0.75}Br_{0.25}$	ca 925	950	–25	broad transition

melting point, but also the one of the two binary systems SrFCl–BaFCl and SrFBr–BaFBr. The occurrence of sharp X-ray powder diffraction patterns observed for these systems further indicates a small liquidus-solidus separation. In the opposite situation as for instance for $y \cong 0.7$ there are clearly several compounds of neighboring fractional composition simultaneously present. Three other samples (runs no 16 to 18 in Table 2) investigated by DTA produced a comparatively broad melting curve with solidification occurring at higher temperature than melting. These three samples correspond to areas in the composition-temperature diagram where the temperature gradient as a function of composition has a rather important value and there is probably a comparatively large difference between the solidus and the liquidus curve. This results in more pronounced fractional crystallization upon cooling and, as a consequence, in remelting that spreads over a certain temperature range. In an earlier publication [10] we showed, however, that crystals of defined composition can be synthesized.

Interpolation of the available melting temperature data

Binaries

The melting point temperatures of the binary systems were determined as follows. The literature data of the binary systems had to be read from figures in references [6, 7]. This is unfortunate because an estimated error of ±10°C results. The data were first corrected by shifting uniformly all the melting temperatures of a given binary set such that in the corresponding composition-temperature diagram best agreement with the melting points of the pure alkaline earth fluorohalides (Table 3) resulted. The temperature shifts used were: SrFCl–SrFBr [6]: –4°C; BaFCl–BaFBr [6]: –7°C; SrFCl–BaFCl [7]: –12°C; SrFBr–BaFBr [6]: –12°C. The obtained results show that the pairs BaFCl–BaFBr, SrFCl–SrFBr present a minimum melting temperature as a function of x. The system SrFBr–BaFBr indicates a more complex melting behavior and the couple BaFCl–SrFCl is well described by a quadratic dependence of T_m on x_i. But none seem to have an eutectic.

Doubly mixed systems

All the melting temperature points form a surface in the phase diagram. None of the doubly mixed systems we investigated allowed to confirm the presence of a eutectic. By extrapolating this finding to the whole phase diagram one may approximate the surface by a truncated power series expansion in the mole fractions. This was performed by fitting equation 1 below to obtain a satisfactory description of the experimental melting temperatures of Tables 2, 3. It is clear that this is an approximation, but in practice the errors between the temperatures predicted by Eq. (1) and the experimental values were found to be small. In detail the fit is based on the following additional considerations. A total of 44 data points were obtained from the adjusted binary diagrams. Our results No. 5 to 15 of Table 2 were then added, each weighted by a factor of 4. Finally temperatures No. 1–4 (Table 2) were included by weighting them by a factor of 2. This smaller factor was chosen because these data were already taken into account for the fit of the literature data. A total of 96 experimental input values are thus available for the interpolation, thereby insuring reasonably good balance between data points originating from binary and fully mixed compounds. Interpolation of this data set with the aid of Eq. (1) yields predicted melting points for any given composition in the complete system $Sr_{1-y}Ba_yFCl_{1-x}Br_x$.

$$T = [x^2, x, 1]\begin{bmatrix} -88.8 & 53.4 & 105.0 \\ 96.2 & -24.0 & -152.6 \\ 229.3 & -198.8 & 976.3 \end{bmatrix}\begin{bmatrix} y^2 \\ y \\ 1 \end{bmatrix} \quad \text{in } ^{\circ}\text{C} \tag{1}$$

The results of the interpolation are presented Fig. 2 for the binaries and isohypses of this approximate melting tempature surface are drawn in the composition-temperature diagram Fig. 3. The residual error between the experimental and calculated values (4.2°C rms) is remarkably small. This is illustrated for instance in Fig. 2 where the analytical results are compared with the shifted literature values.

Table 3 Melting point of the pure alkaline earth fluorohalides

Compound	Literature data/	This work/
	°C	
SrFCl	960[5], 974[17]	974, 973
SrFBr	ca 940[6]*	931
BaFCl	1008[5, 17]	1006.5, 1007
BaFBr	994±5[18]	992

* value estimated from the figures in Ref. [6]

We tried to extend the model by fitting the data with a bicubic polynomial (16 parameters). The residual error decreased only marginally (to 3.8°C rms) and yields also a flat minimum melting point region. The calculated minimum melting point composition at 885°C by the biquadratic model is predicted at the composition $Sr_{0.623}Ba_{0.377}FCl_{0.342}Br_{0.658}$, while it is shifted to the composition $Sr_{0.7}Ba_{0.3}FCl_{0.31}Br_{0.69}$ in the bicubic fit. These compositions deviate slightly from the experimental one as our lowest observed melting temperature amounting to 883°C was observed for the composition $Sr_{0.67}Ba_{0.33}FCl_{0.33}Br_{0.67}$. The 'true' location of the absolute experimental minimum is probably within the range of the three above values. This model implies that crystals of well-defined composition are available (see above).

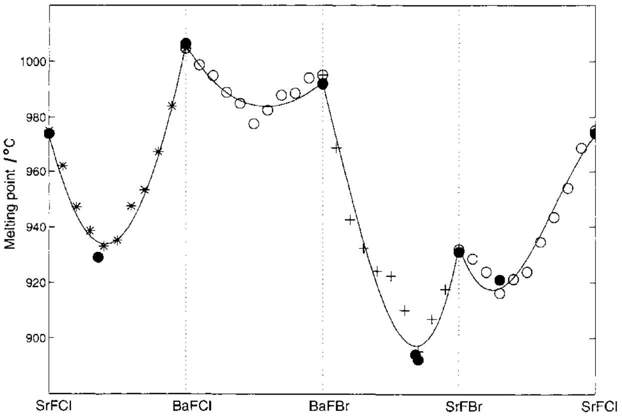

Fig. 2 Projection of the shifted (see text) literature melting point data for the pseudo-binary subsystems (SrFCl–BaFCl, etc.) on the calculated curves from the biquadratic fit Our DTA data (Table 2) are superimposed for comparison (black filled circles)

If a sample of a given fixed overall composition is molten and solidified several times, then the solidus-liquidus curves come into play. The two surfaces meet at the positions of the pure Matlockite compounds and at around $x \cong 0.66$ and $y \cong 0.38$ in the composition-temperature diagram of Fig. 3. They further meet at the minima of the binary diagrams (Fig. 2) beginning at the absolute minimum (x, y) position of the

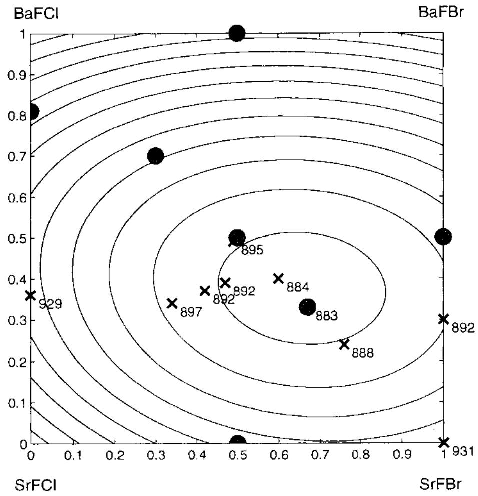

Fig. 3 Contour plot of the calculated (biquadratic fit) melting point in °C as a function of composition in the $Sr_{1-y}Ba_yFCl_{1-x}Br_x$ system. Successive lines correspond to 10°C increments. The values labelled '*x*' correspond to the present DTA results (Table 2). The open circles refer to samples subject to single crystal lattice parameter measurements ($SrFCl_{0.5}Br_{0.5}$ and $Sr_{0.5}Ba_{0.5}FCl_{0.5}Br_{0.5}$) and to single crystal structure determinations ([10, 11 and this work])

diagram in Fig. 3. Therefore the most simple possibility is to assume a star of minimum tenperature lines betwen each of the four binary minima and the central one.

Conclusions

We determined an extended set of melting temperatures for the family of the title compounds and critically reviewed published data. Estimates of melting point temperatures were obtained for any composition of the systems $Sr_{1-y}Ba_yFCl_{1-x}Br_x$ by an interpolation formula. The results of this investigation allowed to grow good quality single crystals of various but well-defined compositions within this family of compounds.

* * *

Thanks are due to Mrs. H. Lartigue for the DTA measurements and to Mr D. Frauchiger for help with the preparation of the samples.

This work was supported by the Swiss National Science Foundation and the Swiss Priority Project Optique 1.

References

1 R. Jaaniso and H. Bill, Europhys. Lett., 16 (1991) 569.
2 H. Bill, R. Jaaniso, H. Hagemann, D. Lovy, A. Monnier and M. Schnieper, Opt. Eng., 34 (1995) 2333.

3 K. Takahasi, J. Miyahara and Y. Sibahara, J. Electrochem. Soc., 132 (1985) 1492.
4 A. R. Lakshamanam, Phys. Stat. Sol., (a) 153 (1996) 3.
5 A. G. Bergman and G. A. Bukhalova, Zhur. Obshei Khim., 19 (1949) 603; J. Gen. Chem. U.S.S.R., 19 (1949) 553 (Engl. translation).
6 L. Jianhua and S. Mianzeng, Gaodeng Xuexiao Huaxue Xuebao, 6 (1985) 957.
7 S. Ruan, M. Gong, Z. Jie and S. Mianzeng, Zhongguo Xitu Xuebao, 3 (1985) 47.
8 S. A. Hodorowicz, E. Hodorowicz and H. Eick, J. Solid State Chem., 50 (1983) 180.
9 R. Jaaniso, H. Hagemann, F. Kubel and H. Bill, Chimia, 46 (1992) 133.
10 H. Hagemann, F. Kubel and H. Bill, Mat. Res. Bull., 28 (1993) 353.
11 H. Hagemann, F. Kubel and H. Bill, Mat. Res. Bull., 30 (1995) 405.
12 F. Licci, H. J. Scheel and P. Tissot, J. Crystal Growth, 112 (1991) 600.
13 H. P. Beck, Z. anorg. allg. Chem., 451 (1979) 73.
14 W. Liebich and D. Nicollin, Acta Cryst., B33 (1977) 2790.
15 T. N. Bhat, H. L. Bhat, A. H. R. Rao, M. R. Srinivasan and P. S. Narayanan, Curr. Sci., 47 (1978) 204.
16 M. Sauvage, Acta Cryst., B30 (1974) 2786.
17 G. A. Bukhalova, N. N. Mirsoyanova and E. S. Yagub'yan, Zh. Neorg. Kiim., 31 (1986) 2164.
18 D. Nicollin and H. Bill, J. Phys. C Solid State Phys., 11 (1978) 4803.
19 G. P. M. van der Heuvel, G. Blasse and J. Schoonman, Solid State Commun., 28 (1978) 689.
20 D. Ayachour, M. Sieskind and P. Geist, Phys. Stat. Sol., (b) 166 (1991) 43.
21 H. P. Beck, J. Solid State Chem., 17 (1976) 275.