

## PROBLEMS IN THE THERMAL INVESTIGATION OF THE $\text{BaF}_2$ - $\text{YF}_3$ SYSTEM

G. H. G. Nakamura<sup>1</sup>, S. L. Baldochi<sup>1,\*</sup>, V. L. Mazzocchi<sup>1</sup>, C. B. R. Parente<sup>1</sup>, M. E. G. Valério<sup>2</sup> and D. Klimm<sup>3</sup>

<sup>1</sup>IPEN-CNEN/SP, CP 11049, 05422-970, São Paulo, SP, Brazil

<sup>2</sup>Federal University of Sergipe, Physics Department, Campus Universitário, São Cristóvão, Brazil

<sup>3</sup>Institute for Crystal Growth, Max-Born-Str. 2, 12489 Berlin, Germany

The  $\text{BaF}_2$ - $\text{YF}_3$  system was partially investigated, with focus given to the  $\text{BaY}_2\text{F}_8$  compound and its neighboring phases. In this report, various difficulties that hinder the thermal analysis investigation of this binary fluoride system are described in detail. Samples of various compositions ranging from 58 to 79%  $\text{YF}_3$  were prepared and subjected to thermal analysis (DTA, TG and DSC) and X-ray diffraction. Diffraction patterns were analyzed through the Rietveld method for the calculation of phase concentrations in samples and determination of the lattice parameters of monoclinic  $\text{BaY}_2\text{F}_8$ . Thermal results were compared with data from the literature and discrepancies were found.

**Keywords:**  $\text{BaY}_2\text{F}_8$ , DSC, DTA, fluorides, phase diagrams, TG, XRD

### Introduction

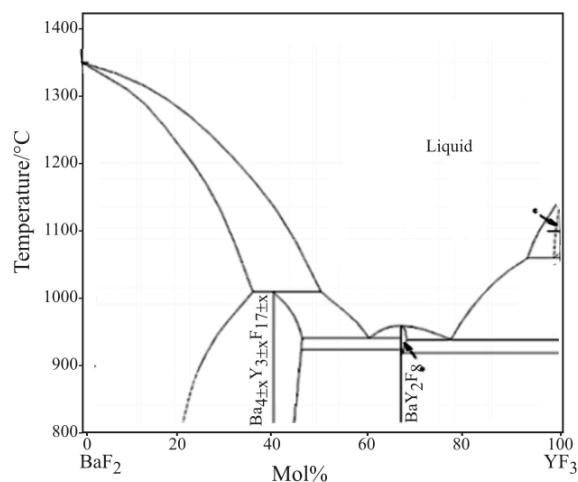
The compound  $\text{BaY}_2\text{F}_8$  (BAYF) possesses great potential for use in solid-state lasers. Crystals of this material have been the focus of numerous studies regarding its spectroscopy and laser applications when doped with rare-earth (RE) elements [1–4]. Nevertheless, the thermal behavior of this compound has yet to be fully understood, which significantly hinders the process of growing BAYF single crystals.

In the 1970s and 1980s, the  $\text{BaF}_2$ - $\text{YF}_3$  binary system was investigated by various authors such as Ippolitov *et al.* [5], Tkachenko *et al.* [6], Sobolev *et al.* [7] among others. These works resulted in detailed phase diagrams for the system and the proposal of Sobolev *et al.* [7] is shown in Fig. 1.

Thermal investigation of this system is reportedly non-trivial. Obstacles include huge supercooling effects and remarkable vulnerability to oxygen contamination, which is particularly damaging since it leads to the formation of rare-earth oxifluorides. In the composition range surrounding BAYF, interpretation of thermal analysis results is additionally complicated by the overlapping of thermal events, all of which occur at similar temperatures, making the identification of individual events difficult.

According to Sobolev and Tkachenko [7], the thermal character of BAYF is marked by a polymorphic transition from the monoclinic ‘*m*-phase’ to possibly an orthorhombic ‘*o*-phase’ and the formation of solid

solutions of up to 1% excess of  $\text{YF}_3$ . The transition temperature differs in each side of the compound: it is 928°C on the  $\text{BaF}_2$  rich side and drops to 920°C for the  $\text{YF}_3$  rich solid solutions. An  $\text{YF}_3$ -rich eutectic at 940°C, a  $\text{BaF}_2$ -rich eutectic at 946°C and the congruent melting of the compound at  $T_f=960^\circ\text{C}$  are also reported. In the same report, however, the authors remark about the difficulty of experimentally splitting the broad thermal event observed in the melting of  $\text{Ba}(\text{Y,Ln})_2\text{F}_8$  compounds, which is attributed to the closeness of the polymorphic transformation to the melting point of these compounds. They do not discard, therefore, the possibility that further studies might reach different interpretations for the phase equilibria in the region in which these compounds are formed.



**Fig. 1** Reproduction of the  $\text{BaF}_2$ - $\text{YF}_3$  phase diagram [7]

\* Author for correspondence: baldochi@ipen.br

The disputed existence of the  $\text{BaYF}_5$  compound is another feature of the  $\text{BaF}_2\text{--YF}_3$  system that is not completely conclusive. Though none of the studies regarding phase equilibria describe this compound, growth of  $\text{BaYF}_5$  crystals has been reported in the literature [8, 9].

With our present work we hope to clarify some discrepancies about this system, as well as contribute to the study of fluoride compounds through thermal analysis methods. This first report stands as a preliminary step in that direction. The  $\text{BaF}_2\text{--YF}_3$  system was partially investigated, with focus given to the  $\text{BaY}_2\text{F}_8$  compound and its neighboring phases; we relate the difficulties that arose during our thermal investigation of this system.

## Experimental

Several samples were prepared for this study. Compositions vary within the range of 58–79 mol%  $\text{YF}_3$ , which includes the stoichiometric composition for BAYF and the two eutectics (60%  $\text{YF}_3$  and 77%  $\text{YF}_3$ ) described by the phase diagram from Fig. 1.

The starting fluoride materials for the samples were obtained through fluorination under HF flow of high-purity  $\text{BaCO}_3$  (>99.99%) and  $\text{Y}_2\text{O}_3$  (>99.99%), both obtained commercially. This procedure is described in detail in [10]. Samples were initially prepared by weighing out appropriate quantities of  $\text{YF}_3$  and  $\text{BaF}_2$  and mixing them mechanically. In order to enhance homogeneity, the samples were individually melted (heated to the temperature of 985°C) in Pt boats under a constant flow of HF and the obtained ingots were subsequently pulverized in a mortar. Resulting powders were used for thermal analysis and X-ray diffraction (XRD) experiments.

XRD measurements were performed at room temperature in a Rigaku DMAX 2000/PC diffractometer. The diffraction patterns were taken in the  $2\theta$  range from 14 to 80° in step scan mode, with steps of 0.02°, 2 s per point, using  $\text{CuK}\alpha$  radiation. Resulting patterns were used for quantitative calculation of phase concentrations through the Rietveld method; the analyses were performed using program DBWS-9807a [11].

Thermogravimetry (TG) and differential thermal analysis (DTA) measurements were simultaneously performed on each sample using a TA Instruments SDT 2960, under constant helium flow (99.999% purity, 100 cc min<sup>-1</sup>). Unlidded Pt–Au crucibles containing approximately 50 mg of the samples were used. Two sets of experiments were performed using heating and cooling rates of 10 and 40 K min<sup>-1</sup> up to the temperature of 1200°C. The DTA apparatus was previously calibrated for temperature at the melting points of LiF, NaI, NaF,  $\text{MgF}_2$  and KCl.

Differential scanning calorimetry (DSC) and thermogravimetry experiments were simultaneously performed on samples on a Netzsch STA 449C/Jupiter system. A standard DSC/TG sample carrier was used. Sample powders were placed in lidded Pt DSC crucibles. Two sets of experiments were performed; the first using heating rates of 10 and the second with 5 K min<sup>-1</sup>; 50 and 10 mg of the samples were employed, respectively, in each set. Maximum temperature was around 1100–1150°C. Prior to each experiment the furnace was evacuated to  $6 \cdot 10^{-2}$  Pa. A first heating run above the melting point was always performed for sample homogenization and then followed by a second consecutive heating run using the same leftover material. The first and second runs were always identical in terms of maximum temperature and thermal rates. Other consecutive runs were performed for samples with the (1:2) composition (related to the stoichiometric BAYF phase), using 2 and 1 K min<sup>-1</sup> heating rates. All runs were performed under a constant flow of argon (99.999% purity). The DSC apparatus was previously calibrated for temperature and sensitivity at the melting points of Zn, Au, Ni and at the phase transformation point of  $\text{BaCO}_3$ .

## Results and discussion

### X-ray diffraction

Calculated phase concentrations of several samples are presented in Table 1. Observed concentrations show some deviation; for example, according to the lever principle [15], the sample with starting composition 22%  $\text{BaF}_2$ :78%  $\text{YF}_3$  should contain approximately 66% of BAYF and 34% of  $\text{YF}_3$ , but a greater quantity of the latter compound is observed. Nonetheless, the observed phases in each sample mostly agree with what should be expected after the synthesis process (which involves its melting and subsequent solidification), in accordance with the phase diagram (Fig. 1). The sample with the (1:2) composition, however, should be composed solely by the  $\text{BaY}_2\text{F}_8$  phase, though a measurable quantity of  $\text{YF}_3$  was detected. It should be noted that three different samples were synthesized from a mixture of 33.33% molar fraction of  $\text{BaF}_2$  plus a molar fraction of 66.66%  $\text{YF}_3$  (1:2 composition) and all presented a small amount of  $\text{YF}_3$  in the X-ray diffraction data. Only crystalline samples obtained from crystal growth processes presented pure  $\text{BaY}_2\text{F}_8$  in the X-ray diffraction pattern. Two possible explanations may be either the existence of a non-stoichiometric range of  $\text{BaY}_2\text{F}_8$  that would accept  $\text{BaF}_2$ , resulting in an  $\text{YF}_3$  excess in the synthesized samples, or that the excess is the result of incomplete mixing during the synthesis process.

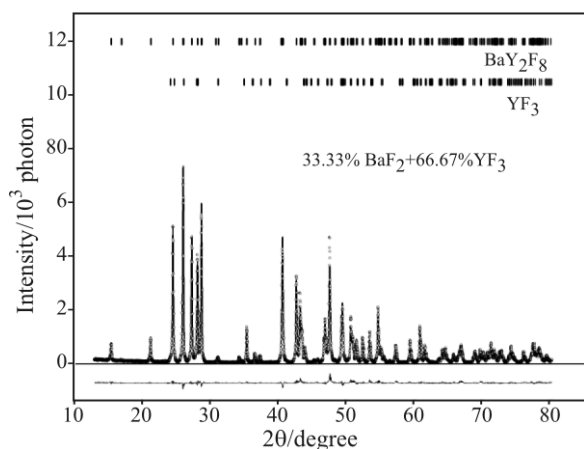
**Table 1** Phase concentrations calculated through the Rietveld method

| Sample YF <sub>3</sub> | BaY <sub>2</sub> F <sub>8</sub> [12]/<br>mol% | YF <sub>3</sub> [13]/<br>mol% | Ba <sub>4±x</sub> Y <sub>3±x</sub> F <sub>17±x</sub> [14]/<br>mol% | R <sub>p</sub> | R <sub>WP</sub> | R <sub>e</sub> | S    |
|------------------------|-----------------------------------------------|-------------------------------|--------------------------------------------------------------------|----------------|-----------------|----------------|------|
| 78                     | 36.5                                          | 63.5                          |                                                                    | 9.11           | 12.73           | 5.21           | 2.44 |
| 77                     | 41.2                                          | 58.8                          |                                                                    | 8.72           | 11.38           | 4.93           | 2.30 |
| 67.7                   | 81.2                                          | 18.8                          |                                                                    | 8.03           | 10.58           | 5.24           | 2.02 |
| 66.7                   | 87.6                                          | 12.4                          |                                                                    | 9.65           | 12.42           | 5.38           | 2.30 |
| 65.7                   | 98.3                                          |                               | 1.7                                                                | 14.43          | 18.77           | 9.29           | 2.02 |
| 61                     | 83.0                                          |                               | 17.0                                                               | 7.38           | 9.85            | 5.68           | 1.73 |
| 60                     | 82.0                                          |                               | 18.0                                                               | 8.59           | 11.65           | 5.87           | 1.98 |
| 59                     | 70.6                                          |                               | 29.4                                                               | 11.40          | 15.15           | 6.27           | 2.41 |

R<sub>p</sub>='R-pattern', R<sub>WP</sub>='R-weighted pattern', R<sub>e</sub>='R-expected', S='Goodness-of-fit' [11]

**Table 2** BaY<sub>2</sub>F<sub>8</sub> lattice parameters

| Sample                | a/Å         | b/Å          | c/Å          | β/°        |
|-----------------------|-------------|--------------|--------------|------------|
| 67.7% YF <sub>3</sub> | 6.97257(13) | 10.50262(19) | 4.257180(79) | 99.6696(4) |
| 66.7% YF <sub>3</sub> | 6.97347(21) | 10.50479(32) | 4.25780(13)  | 99.6699(5) |
| 65.7% YF <sub>3</sub> | 6.97334(22) | 10.50453(34) | 4.25779(14)  | 99.6719(6) |
| [15]                  | 6.9781(5)   | 10.5099(7)   | 4.2603(3)    | 99.682(8)  |
| [16]                  | 6.9829(5)   | 10.519(1)    | 4.2644(4)    | 99.678(8)  |

**Fig. 2** Diffraction pattern and its corresponding fitted curve; sample 66.7% YF<sub>3</sub>

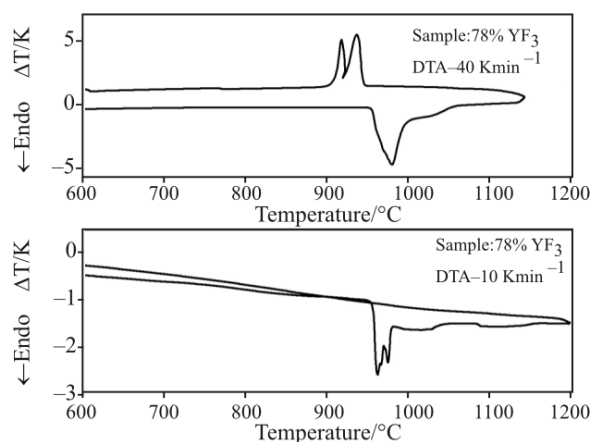
One of the diffraction patterns obtained is presented in Fig. 2, along with the Rietveld fitted theoretical curve and the difference pattern. It should be noted that the compound Ba<sub>4±x</sub>Y<sub>3±x</sub>F<sub>17±x</sub> was detected in the samples with excess BaF<sub>2</sub>, whereas BaYF<sub>5</sub> was detected in none; however, none of the prepared samples has the exact stoichiometric composition of this compound.

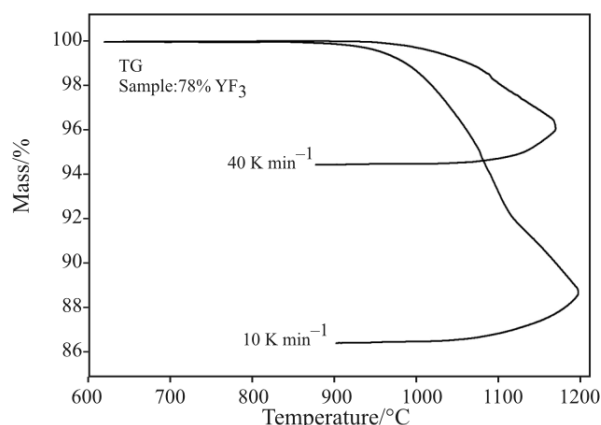
Diffraction patterns of three samples were used for obtaining the lattice parameters of monoclinic BaYF<sub>5</sub>; results are presented in Table 2, along with two values found in the literature [12, 16].

### Thermal analysis

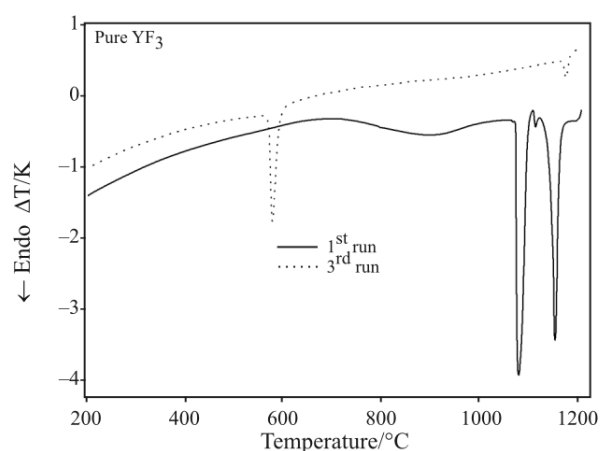
DTA results obtained in the first set of experiments, performed with 10 K min<sup>-1</sup> rates, were found to be unreliable; even though thermal events were observed during heating, upon cooling none of the curves presented any peaks whatsoever. An example of this can be seen in Fig. 3.

Experiments performed with the higher heating/cooling rate (40 K min<sup>-1</sup>) produced DTA curves which did present exothermic peaks upon cooling, as expected for this material. The remarkably different results were a serious indication that, during the experiments

**Fig. 3** DTA curves from experiments performed with differing rates; sample composition 78% YF<sub>3</sub>



**Fig. 4** TG curves obtained simultaneously with the DTA curves from Fig. 3



**Fig. 5** DTA curves of the first and third heating runs of pure  $\text{YF}_3$

performed with the  $10 \text{ K min}^{-1}$  rate, samples underwent some process which led to a complete change in character. In the experiments performed with the  $40 \text{ K min}^{-1}$  rate, four times faster than the previous ones, samples were clearly less affected.

Indeed, TG curves from the first set of experiments show a steep loss of mass: total loss varied from 8 to 14% of initial masses. In the second set of experiments, total mass loss was smaller, though still significant: 2–6% of initial masses. A comparative example is shown in Fig. 4.

Evaporation and oxygen contamination account for the observed loss of mass. Formation of oxyfluoride phases is likely the cause of the anomalous results from the first set of DTA experiments. It is well known that heating rare-earth fluorides under a non-fluorinating atmosphere may produce oxyfluoride phases due to reaction with even trace amounts of oxygen and moisture [17]. Figure 5 shows the DTA curves of two heating runs of pure  $\text{YF}_3$ . The curve obtained from the first heating of the compound shows two large thermal events corresponding to the polymorphic transition and melting of  $\text{YF}_3$  and a smaller event in-between probably related to contami-

nation by oxygen, as suggested by the partial  $\text{YF}_3\text{--Y}_2\text{O}_3$  phase diagram from [17]. The presence of a hint of contamination as early as the first heating run demonstrates how really vulnerable to oxygen the compound  $\text{YF}_3$  is. The curve obtained from a third consecutive heating, vastly different from the previous curve, shows that the sample has changed almost completely. The transformation of  $\text{YF}_3$  into one or more oxyfluorides throughout of the experiment is evidenced by the thermal event at  $568^\circ\text{C}$  (onset). This event likely corresponds to the rhombohedral  $\rightarrow$  cubic polymorphic transition of YOF, reported to occur at  $571^\circ\text{C}$  by [18] and at  $560^\circ\text{C}$  by [19].

Hence, the absence of thermal events upon cooling in the experiments performed with  $10 \text{ K min}^{-1}$  may be explained by the formation of oxyfluoride compounds that do not present transitions in the temperature range explored. It is also possible that composition variations caused by differential evaporation of compounds within the samples coupled with massive oxygen contamination may have caused the samples to undergo a glass transition.

The use of a much faster rate of heating and cooling certainly reduced, but did not eliminate the contamination problem in the second set of DTA experiments. Moreover, peak overlap was unduly exacerbated. Results were found to be entirely unreliable for accurate identification of phase transitions and precise determination of the temperatures in which they occur.

The DSC system used in this work allowed for a much better controlled atmosphere. Vacuum treatment of the furnace and samples prior to the measurement led to much smaller loss of mass during experiments, despite the use of lower thermal rates: typically less than 1% per heating/cooling run. This indicates that oxyfluoride formation was negligible. Evaporation accounts for the remaining loss and was also small since crucibles lids were used.

The diminutive loss of mass made possible a second consecutive heating/cooling run during each experiment. This is desirable, since the sample homogeneity problem detected through XRD is reduced, in the second run.

Overlapping of peaks remained a problem in all thermal analysis curves; even for those DSC curves obtained with  $5 \text{ K min}^{-1}$  rates. Curiously, very little variation was observed between the onset temperatures of the very first event in each thermal analysis curve. In all DSC curves, the first thermal event always occurred at the temperature of  $954^\circ\text{C}$  (onset); the same was observed in all DTA curves as well, with slightly larger temperature variation. This can be observed in the example given in Fig. 6.

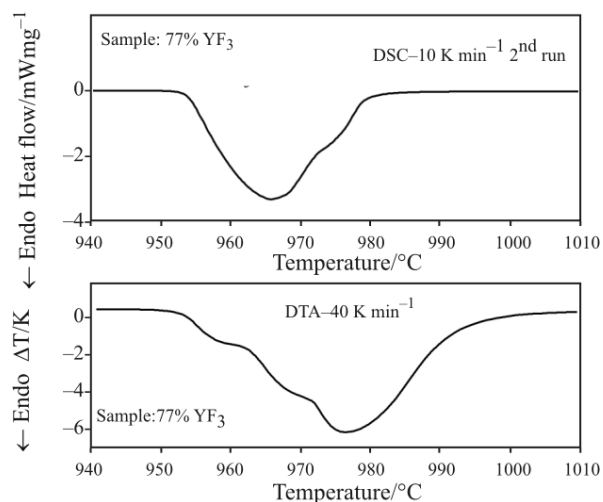


Fig. 6 DSC and DTA heating curves of sample 77%  $\text{YF}_3$

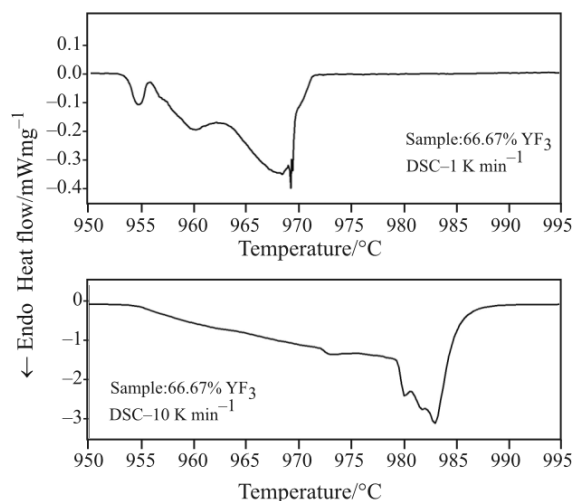


Fig. 7 Two DSC curves obtained consecutively for samples with 1:2 compositions (BAYF phase)

Partial separation of peaks was achieved in the DSC curve of the  $1 \text{ K min}^{-1}$  heating run of sample 66.7%  $\text{YF}_3$ . The relevant portions of this curve and the one obtained with  $10 \text{ K min}^{-1}$  can be seen in Fig. 7. The first peak was identified as corresponding to the polymorphic phase transition of BAYF reported by [6, 7]. This transition must be the one responsible for the invariant first onset ( $954^\circ\text{C}$ ) observed in all samples. Results disagree with the phase diagram in Fig. 1, since no difference in the temperature of this transition in each side of the stoichiometric BAYF line in the diagram was observed. Moreover, peaks in all thermal curves occur at temperatures systematically higher than what the phase diagram would allow: according to the diagram BAYF melts at  $960^\circ\text{C}$  and its phase transition occur at  $920^\circ\text{C}$  (eutectoid phase transition at  $928^\circ\text{C}$ ).

Remaining thermal events in the curve from Fig. 7 ( $1 \text{ K min}^{-1}$ ) were attributed to melting. The elongated profile of the melting suggests the possibility that

BAYF may be actually very slightly incongruent: it may decompose before reaching complete melt.

## Conclusions

Samples with varying concentrations of  $\text{BaF}_2$  and  $\text{YF}_3$  were synthesized under reactive atmosphere. X-ray diffraction patterns of the samples were obtained and quantitative phase calculations of their final composition and the determination of the lattice parameters of BAYF phase were performed through the Rietveld method.

Thermal analysis was performed under different conditions in order to study the influence of experimental settings in thermal measurements of the binary fluoride system  $\text{BaF}_2\text{-YF}_3$ . Contamination of the samples with traces of oxygen and moisture during thermal analysis experiments was determined to be a very relevant hindrance to the thermal investigation of the system. It must be mitigated through the use of a well controlled atmosphere, preferably with vacuum treatment of the furnace and the sample previously to the each experiment. Overlapping of thermal peaks remains a problem even if low thermal rates are used. Interpretation of resulting thermal curves was found to be further complicated by intense supercooling effects, as described in the literature. Cooling curves are unreliable for determination of phase transition temperatures.

Experimental data mostly corroborate the phase diagram from the literature at low temperatures, but some deviation was observed at higher temperatures, at least in the composition range surrounding the BAYF compound. Thermal analysis curves show no variation in the polymorphic transition temperature of BAYF in each side of the compound. Conclusive evidence of the presence of the solid solution range of BAYF mentioned in previous literature has not been found. All thermal peaks were observed to occur at temperatures much higher than described by the diagram. DSC results suggest the possibility that BAYF may actually be incongruent. The observed discrepancies are under further investigation and will be the subject of a next publication.

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