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Thermal analysis and phase diagram of the LiF–BiF_3 system

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ABSTRACT

Differential thermal analysis up to complete melting was thoroughly performed for the pseudobinary system LiF–BiF_3. Melts with high bismuth fluoride concentration suffered from high evaporation; nevertheless even pure BiF_3 could be molten at 655 °C. The system contains one intermediate compound $BiLiF_4$ which melts by peritectic decomposition with the formation of LiF at 450 °C. The eutectic between $BiLiF_4$ and BiF_3 melts at 415 °C. Thermodynamic assessment yielded the following parameters for $BiLiF_4$: $\Delta H = -1,514,900\,\mathrm{J\,mol^{-1}}$, $S = 158.5\,\mathrm{J\,mol^{-1}\,K^{-1}}$, $c_p = 166.173 - 0.01072 \cdot T$ (in $\mathrm{J\,mol^{-1}\,K^{-1}}$). The melt has negative excess Gibbs free energy.

1. Introduction

In 1987 Schultheiss et al. [1] reported Czochralski growth of $BiLiF_4$ single crystals of up to 70 mm in length. These crystals were found to have the scheelite structure, being analogous to the intermediate $RELiF_4$ compounds that were reported to exist in many rare earth fluoride–lithium fluoride systems [2]. $BiLiF_4$ was reported to melt incongruently at 369 °C, but no data about the whole pseudobinary system LiF–BiF_3 are available so far. However, the ternary Li–Bi–F was evaluated theoretically based on elementary electrochemical principles recently [3], and it was concluded that two intermediate ternary compounds exist within the ternary system, namely $BiLiF_4$ and $BiLiF_6$. This is a confirmation that $BiLiF_4$ should be the only intermediary phase in which bismuth is trivalent.

The component LiF is well known and can be handled without special precautions, though some care should of course be taken since all fluorides are more or less susceptible to hydrolysis in the presence of moisture. It is a well-known compound [4,5] which does not undergo polymorphism upon heating, is not hygroscopic and melts congruently at 842 °C.

BiF_3, however, is far less unambiguous and conflicting data can be found in the literature. Some reports [6,7] state that it has an orthorhombic crystal structure (tysonite structure, *Pnma* space symmetry group), though its structure has also been reported as cubic [8] (gananite, pdf 39-345), the latter being in agreement with X-ray spectra that were performed in the framework of the current study. Different reports give melting point temperatures ranging from 725 to 770 °C [6,7], approximately 100 °C higher than the value that was measured in this study. Others state that it melts congruently at about 649 °C without polymorphism; BiF_3 is a stable chemical under ambient conditions, aside from minor hygroscopicity [3,9].

The disparate data on BiF_3 may be explained by contamination by oxygen and humidity, possibly with the formation of the oxyfluoride BiOF [7]. Degradation of samples, crucibles and even thermal sensors employed during measurements are cited by numerous authors [1,9–11], hence affecting reproducibility of data. It should be mentioned that the materials used in those works – vitrified carbon, platinum, nickel – are known for usually being resistant to chemical corrosion by fluorides, which are very aggressive at high temperature [12].

Novikova et al. [11] suggested that the degradation of samples containing BiF_3 is due to the reduction of this compound by the materials of the crucibles and sensors upon heating. Schultheiss et al. [1], however, presented detailed evidence that pure BiF_3 is not responsible for the damage. Instead, the presence of contaminants (oxygen and water related ions) leads to partial hydrolysis of BiF_3 and may result in damage by the formation of Bi_2O_3, bismuth oxyfluorides or metallic bismuth.

$BiLiF_4$ could be potentially interesting for opto-electronic applications, such as laser devices or scintillation detectors for photons. Bi^{3+} should provide a suitable site for doping by lanthanide ions. Furthermore, the wide band-gap that is typical for most fluorides could make $BiLiF_4$ a feasible laser host. Natural bismuth is monoisotopic ^{209}Bi and, due to its large atomic mass, the compound should

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efficiently interact with high energy photons. This paper reports the investigation of the LiF–BiF_3 system by thermal analysis and X-ray diffraction and is considered as a preliminary step for future studies on $BiLiF_4$, particularly due to the significant crystal growth difficulties reported by Schultheiss et al. [1].

2. Experimental

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) measurements were performed in a Netzsch STA Jupiter 449C with vacuum-dense rhodium furnace under dynamic argon atmosphere (99.999% purity, 30 ml/min flow rate). Graphite crucibles with platinum lids and compounds of high purity were used: BiF_3 99.999% (metals basis) from Alfa Aesar and LiF from Aldrich, initially only 99.9% pure. The LiF, however, was refined by zone melting under Ar/HF flow [13]. The "type S" thermocouples of the sample carriers were calibrated at the melting points of Zn and Au, and at the phase transition point of $BaCO_3$, respectively. Degassing of the samples and the chamber was performed under vacuum of approximately 5×10^{-5} mbar for a few hours prior to each experiment, a preventive measure to purge the chamber and samples of oxygen and humidity, which are particularly present in BiF_3.

Little or no damage to the graphite components was observed throughout the many experiments. Platinum parts, however, showed signs of corrosion after prolonged use. Samples in the entire composition range, 0–100% BiF_3, were measured by DTA, in steps of 5%; they were of approximately 50 mg. Most of the measurements were performed with a heating rate of 10 K/min; further measurements with selected samples were performed with 2 K/min in order to resolve overlapping peaks.

X-ray powder diffraction measurements of larger samples (~250 mg) were made in a General Electric XRD 3003TT diffractometer of Bragg–Brentano geometry using Cu Kα radiation.

3. Results

A DSC measurement of pure bismuth fluoride was performed at a rate of 10 K/min. The resulting curve is presented in Fig. 1, together with the thermogravimetry curve. Significant mass loss occurred above 575 °C, which reflects the known high vapor pressure at higher temperatures which amounts to ca. 20 mbar at this temperature [9]. Several minor endothermic peaks are present in the curve in that range, likely related to heat loss due to sublimation. The sharp peak around 655 °C corresponds to melting, which was confirmed by visual inspection of the sample after the measurement. This temperature corroborates some of the literature [9,14], though it differs from the value given by the producer Alfa Aesar, 727 °C. It is remarkable that this value is almost identical with the α-to-δ transition of Bi_2O_3 that has a high transformation heat of 29.8 kJ/mol [14,15]. It seems realistic to assume that the high melting temperature reported by Alfa Aesar and some other references [6] has its origin in partial hydrolysis of BiF_3 to the oxide prior to, or during the measurements. The results of thermoanalytic measurements with LiF were entirely compatible with the literature.

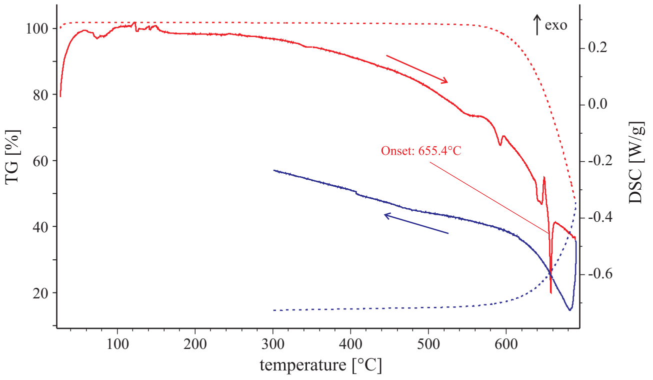

Fig. 1. DSC and TG curves (solid and dashed lines, respectively) of pure BiF_3; heating (red) and cooling (blue) performed at 10 K/min. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

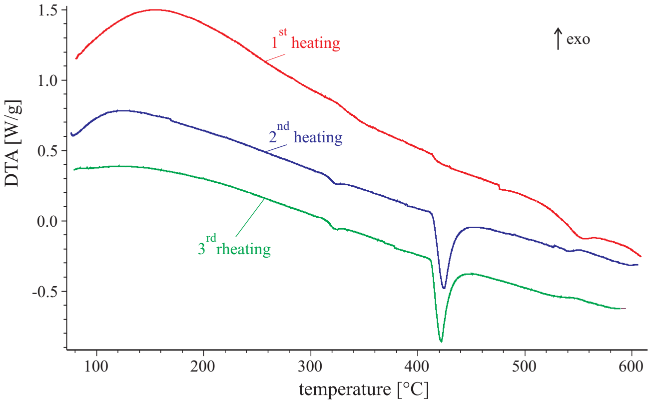

Fig. 2. First (red), second (blue), and third (green) heating runs (10 K/min) of a 65% BiF_3 sample. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

Samples of intermediate composition could not be prepared by mixing them prior to the measurement e.g. in a mortar, because hydrolysis with ambient humidity or close contact with other materials would result in contamination. Instead, the components were weighed directly in the crucibles and were mixed by melting them together in a preliminary DTA heating/cooling cycle. Fig. 2 shows such a first DTA mixing run and subsequent heating cycles for one sample. Due to bismuth fluoride's tendency to sublimate, as observed when the pure compound was measured, heating was usually interrupted as soon as evaporation started to take place in order to avoid significant changes in sample concentration. Maximum temperatures reached in the measurements fluctuated around 600 °C and total mass loss was typically minor – about 1 or 2% of initial mass – despite multiple melting cycles being performed with each sample.

Three thermal events of invariant temperatures were observed for different compositions within the LiF–BiF_3 system. An intense transition was observed at approximately 415 °C in almost all compositions (peak II). By visual inspection of samples that were cooled immediately after being heated just past peak II it became obvious that it is related to melting of a major portion of the sample. Another transition (peak III) was detected at ca. 450 °C. The separation of both peaks II and III was only possible at slower heating rates of 2 K/min; at 10 K/min the peaks overlapped. Peak III was clearly observed only in samples with bismuth content lower than 60%. For higher concentrations of BiF_3 it was either not observed, or almost negligible. The smallest "peak I" occurred in nearly all measurement over the whole concentration range between LiF and BiF_3 at a constant temperature of approximately 315 °C, but was never observed when measuring the pure components. These thermal events are summarized in Table 1. Examples of the three invariant peaks are shown in Fig. 3: peaks II and III are separated in the 2 K/min curve of sample 50% BiF_3, but overlapping hides peak III in the case of the higher heating rate, whereas it does not occur at all in the 90% BiF_3 sample.

Onset temperatures of all three peaks were highly reproducible (~±2K) throughout the measurements; peak areas, however, were not. Peaks II and III displayed a strong tendency to reduce in size

Table 1
Relevant transitions observed in the thermoanalytic measurements.

Transition temperature	Composition range	Remark
842 °C	0%	LiF melting
~315 °C (invariant)	$0 < x < 100\%$ BiF_3	Peak I
~415 °C (invariant)	$0 < x < 100\%$ BiF_3	Peak II
~450 °C (invariant)	$x < 60\%$ BiF_3	Peak III
655 °C	100% BiF_3	BiF_3 melting

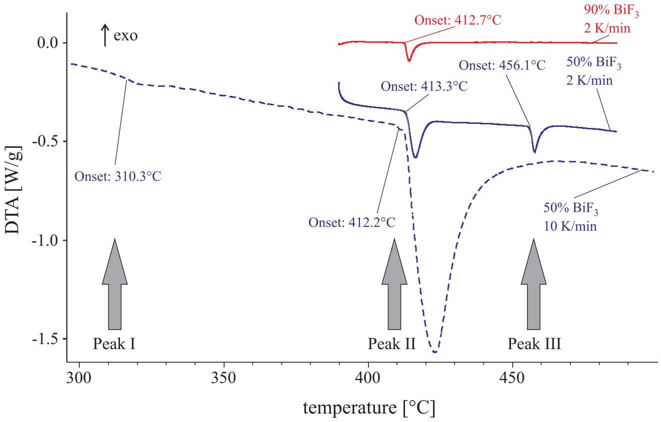

Fig. 3. The three invariant peaks for different compositions and heating rates: 90% BiF_3 at 2 K/min (red line), 50% BiF_3 at 2 K/min (solid blue line) and 50% BiF_3 at 10 K/min (dashed blue line). (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

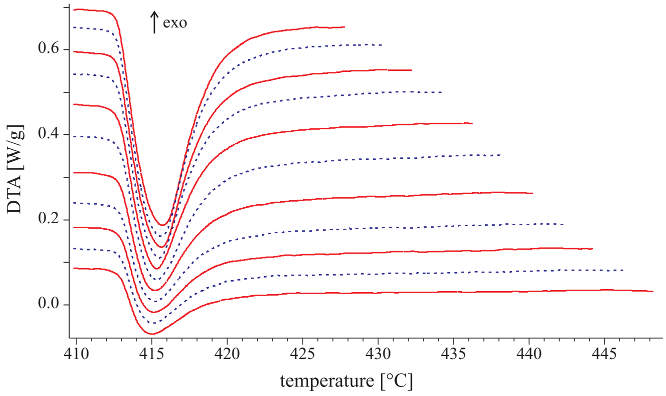

Fig. 4. From top to bottom: 11 subsequent heating cycles (heating/cooling runs with ±2 K/min; sample with 45% BiF_3). For each subsequent cycle the maximum temperature T_{max} is increased by 2 K. The topmost cycle has $T_{max} = 428$ °C, the last cycle shown has $T_{max} = 448$ °C.

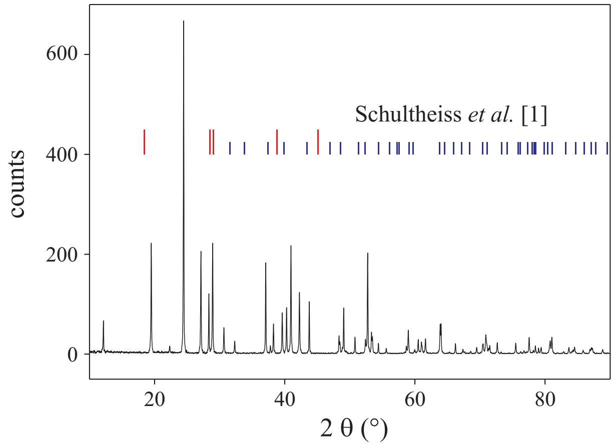

Fig. 5. X-ray powder diffraction pattern of a 40% BiF_3 sample. The vertical bars indicate the positions that would follow from PDF entry 01-085-1491 (scheelite type $BiLiF_4$, [1]). The longer red bars correspond to the 5 strongest scheelite peaks. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

upon repeated heating/cooling cycles after some critical temperature range beyond peak II was reached. This is demonstrated in Fig. 4. In this measurement a 45% BiF_3 sample of 44.27 mg was initially heated at 20 K/min to a temperature of $T_s = 390$ °C. Then a series of 45 heating/cooling cycles with rates of ±2K/min were performed up to a maximum temperature $T_{max} = (400 + 2i)$ °C, where i is the number of the cycle, starting from $i = 0$. Fig. 4 shows the heating curves from $i = 14$ ($T_{max} = 428$ °C) to $i = 24$ ($T_{max} = 448$ °C) and a gradual shrinking of peak II is clearly visible. The heating curves for all previous heating cycles $i < 14$ (not shown in the figure) were almost identical, thus demonstrating that the sample was not affected by hydrolysis or evaporation during the long measurement time exceeding 40 h. Instead, the following mechanism is proposed to be responsible for the shrinking area of peak II.

Bismuth fluoride has a very high density of 8.2–8.3 g cm^{-3}. (This value from the thorough work by Hund and Fricke [8] seems more reliable than other sources claiming lower values around 5.3 g cm^{-3}.) In contrast, the density of LiF is only 2.6 g cm^{-3}. Upon cooling, when one of the components crystallizes from the molten mixed phase it either settles on the bottom (BiF_3) or floats to the surface (LiF) of the crucible. Hence, a part of that substance is removed from equilibrium reactions, hindering formation of $BiLiF_4$. This process progresses with every subsequent heating/cooling cycle and can be observed visually by inhomogeneous coloring of larger samples (see below).

X-ray powder diffraction patterns of two samples of 250 mg with the composition of 40% BiF_3 were taken. Both were prepared in the furnace of the DTA equipment by annealing at 475 °C in argon, because under these conditions contamination by oxygen or humidity could be ruled out. The first sample was cooled from this temperature at a rate of 10 K/min. Its diffraction pattern yielded nothing but the components of the system, LiF and BiF_3, despite obvious signs of melting. Segregation of the components in the sample was visible to the eye, due to differing coloration, with LiF (which is white) concentrated on top, and BiF_3 (grey) on the bottom of the crucible. This was surprising, as the formation of the intermediate compound $BiLiF_4$ was expected.

The second sample was cooled from 475 °C at a considerably slower rate of 2 K/min for better mixing, and yielded an unknown phase. Unexpectedly, the diffraction pattern of this phase is different from the scheelite pattern [1] (Fig. 5). One can conclude that clearly an intermediate phase made of LiF and BiF_3 was formed, that has no scheelite structure. From the current data it was impossible to relate the measured pattern to a crystal structure. Nevertheless, polymorphism of the compound $BiLiF_4$ seems a realistic assumption, because e.g. the scheelites $YLiF_4$ [16] and $LuLiF_4$ [17] become monoclinic at high pressure. Schultheiss et al. [1] performed Czochralski growth with scheelite $YLiF_4$ seeds. Such conditions might compel the crystallization of $BiLiF_4$ in the same crystal structure type of the seed, which is not necessarily the thermodynamic stable one.

4. Phase diagram

The construction of the phase diagram will be described in comparison to the LiF–REF_3 (RE: rare earth element) phase diagrams that were presented e.g. by Thoma [2]. In these systems, the REF_3 are the highest melting compounds with $T_f \approx 1200–1400$ °C, depending on the RE element. LiF melts at 842 °C (Table 1). In the

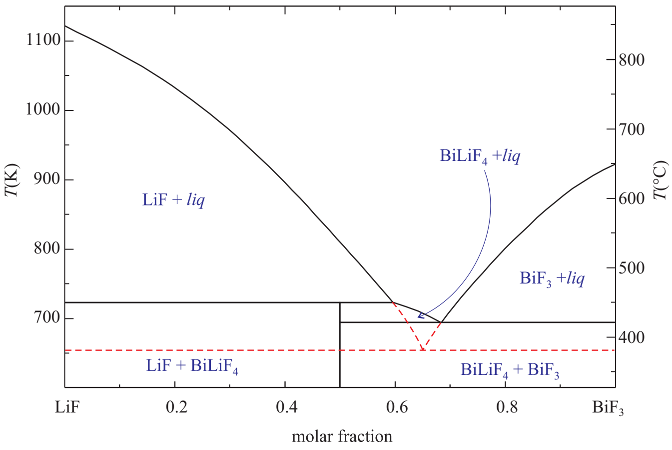

Fig. 6. *Full lines*: The equilibrium phase diagram LiF–BiF_3. *Dashed lines*: Non-equilibrium formation of a LiF/BiF_3 eutectic if $BiLiF_4$ formation is incomplete due to segregation.

case of the elements with smallest RE^{3+} radius (Lu, Yb, Tm, Er), the intermediate scheelite compound $RELiF_4$ melts congruently near 800 °C. T_f grows monotonously with the REF_3 for the subsequent RE (Ho, Dy, Tb, Gd, Eu) and the $RELiF_4$ undergo peritectic melting with the formation of the corresponding REF_3. The peritectic decomposition temperature tends to be lower for the larger RE (799 °C for Ho, only 690 °C for Eu). In the case of the next two RE's the scheelites are even more unstable and undergo a peritectoid decomposition to solid LiF and solid REF_3 at 570 °C ($SmLiF_4$) or 362 °C ($PmLiF_4$), respectively.

For LiF–BiF_3 the situation is reversed, because BiF_3 melts substantially lower than LiF. Incongruent melting of $BiLiF_4$ was already reported [1], but it is reasonable that this process leads to peritectic formation of LiF instead of BiF_3. As the strong thermal event peak II was clearly due to melting it is reasonable to assume that this is the eutectic transition. The somewhat weaker peak III occurring for LiF-rich compositions (Table 1) results from the peritectic decomposition of $BiLiF_4$. Liquidus temperatures could unfortunately be detected only for a few compositions mainly in the LiF-rich part of the diagram, due to the influence of strong evaporation on the DTA signal in BiF_3-rich samples (Fig. 1).

The equilibrium phase diagram in Fig. 6 explains all experimental results. Solid lines result from a thermodynamic assessment of the system performed with the FactSage thermodynamic program and database system [14]. Data for LiF and BiF_3 could be extracted directly from the "Fact53" database. Raw data for $BiLiF_4$ were calculated with the "mixer" module (Neumann–Kopp rule) and then refined to $\Delta H = -1, 514, 900$, $S = 158.5$, $c_p = 166.173 - 0.01072 \cdot T$. The excess Gibbs free energy of the melt was assessed in a polynomial (Kohler/Toop) model to

$$\begin{aligned}\Delta G_{ex} = {} & [x(1-x)(2922 - 12.77\,T - 0.005\,T^2)] \\ & + [x(1-x)^2(-1033 - 4.444\,T - 0.01\,T^2)] \qquad (1)\end{aligned}$$

and is negative for all conditions shown in Fig. 6 (all data in J mol^{-1} or J mol^{-1} K^{-1}, respectively).

The invariant point of lowest temperature (peak I in Table 1) is tentatively interpreted as a metastable eutectic between LiF and BiF_3. The formation of $BiLiF_4$ either by the peritectic reaction or from the solid components is a slow, diffusion controlled process and hence prone to non-equilibrium. Moreover, segregation of LiF (top) and BiF_3 (bottom) due to large density difference means that both components could remain present in the system even if the system resided within the bottom phase fields of Fig. 6, where $BiLiF_4$ is an equilibrium phase. Consequently minor amounts of LiF and BiF_3 can always be simultaneously available inside the crucible as non-equilibrium phases, and form a eutectic. Non-equilibrium conditions and sample inhomogeneity also account for peak II being observed in BiF_3-poor compositions. The position of the metastable eutectic was estimated by the intersection of the LiF and BiF_3 liquidus prolongation which is shown in Fig. 6 in dashed lines. Actually the eutectic temperature (~380 °C) is higher than the experimental peak I (~315 °C, Table 1), but it should be taken into account that this temperature was not subject of the current (equilibrium) assessment. Besides, no liquidus data for BiF_3 rich melts were available and hence the liquidus slope there relies basically on the FactSage data for its heat of fusion ($\Delta H_f = 21.6$ kJ mol^{-1}) [14]. A smaller ΔH_f would shift the eutectic to lower T.

5. Conclusions

It is possible to perform DTA/TG measurements of LiF–BiF_3 mixtures with arbitrary composition up to the melting point within lidded graphite crucibles in dry flowing argon. For BiF_3-rich mixtures (and particularly for pure BiF_3), however, the melting process is accompanied by considerable evaporation. The system contains one intermediate phase $BiLiF_4$, but the X-ray powder diffraction pattern of this phase is different from the scheelite related pattern that was measured by Schultheiss et al. [1] for this compound. This discrepancy could originate from polymorphism, and the actual crystal structure would depend on the growth conditions (seeded growth vs. unseeded solidification in the crucible). $BiLiF_4$ melts incongruently at 450 °C with formation of LiF. This temperature is considerably higher than reported by Schultheiss [1], but their value (369 ± 5 °C) was measured with a Ni-Cr thermocouple that was corroded during the measurement.

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