A study of the $LiYF_4$-$LiErF_4$ psuedo-binary system

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The constitution and structure of compounds represented by the general formula $LiY_{1-x}Er_xF_4$ $(0 < x < 1)$ have been studied by X-ray diffraction, magnetic susceptibility and differential thermal analysis (DTA). X-ray diffraction shows that the b c t Scheelite structure is retained across the system with only a very slight change in the lattice parameters. Large changes in room temperature magnetic susceptibilities as a function of x have been observed and these have been used to provide a very sensitive composition check on the compounds. DTA profile analysis shows that, for samples prepared in a carefully purified environment, the solidus—liquidus separation is so small that an approximation to congruent melting can be made for all the compounds in the system. A comparison with material prepared under unpurified conditions provides information on the effects of contamination upon the melting behaviour.

1. Introduction

During an investigation into the phase relationships within the $LiF-YF_3-ErF_3$ system, we have shown that the iso-structural compounds $LiYF_4$ (LYF) and $LiErF_4$ (LEF) are both congruently melting provided that oxygen and water vapour are rigorously excluded from the preparative environment [1]. Other workers have shown that congruently melting behaviour can also be induced by the presence of HF [2]. Previous reports [3, 4], that LYF was a peritectic phase are, therefore, incorrect, and substantial evidence now exists to show that the apparent peritectic behaviour can be attributed to the effect of contamination [1, 2].

The results presented here represent an investigation of the phase relationships existing in the pseudo-binary section LYF—LEF and of the effects of contamination on the observed melting behaviour. Materials within this phase field can be used as host lattices for laser ions such as Nd^{3+} [5] and Ho^{3+} [6]. For this application, the materials are prepared in single crystal form using melt growth procedures [7, 8] where a knowledge of the factors influencing melting behaviour can have an important bearing upon the resultant crystal quality.

2. Material preparation

Melts with compositions covering the range from LYF to LEF were prepared by the technique described below from two forms of material; (a) the "standard" melts used the component fluorides LiF, YF_3 and ErF_3 received as commercially produced powders from BDH Ltd, and (b) the "Z-R melts" were prepared from transparent, crystalline, zone-refined LYF and LEF [1]. These were compared with material obtained from Czochralski [7] or Stockbarger [8] grown single crystals.

1 g samples of the melts were induction melted under 1 atm gettered argon in a closed vitreous carbon boat which acted as the susceptor. The sample and boat were outgassed at $\sim 600^\circ$ C to 10^{-6} Torr prior to admitting the argon, and after melting, the samples were homogenized for several hours at $\sim 750^\circ$ C. The standard melts prepared from powders were often found to be covered with a black deposit, which usually could be brushed off or ultrasonically removed in acetone. Occasionally the deposit melted into the surface of

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the material, but the bulk of the material was always free from this contamination. Melts performed in a closed platinum crucible produced the same deposit, thus suggesting that it was not associated with the crucible. The weight loss recorded during melt preparation was typically 2 to 3%.

The melts prepared from zone-refined material used an improved argon atmosphere in which the gas was first passed through a molecular sieve. Details of the zone-refining procedure have been given elsewhere [1]. Samples prepared in this way were, in general, found to be free from the black deposit.

The single crystal samples used were from transparent material cut directly from either Czochralski or Stockbarger boules. The Stockbarger material contained small additions of the respective lasing and sensitising ions Ho^{3+} and Tm^{3+} (total ~ 2 mol%).

3. Material analysis

Melting reactions of these compounds were studied by differential thermal analysis (DTA). A detailed description of the equipment technique, and profile analysis has been given elsewhere [1, 9]. X-ray powder diffraction patterns were recorded on a standard 114 mm diameter Debye–Scherrer Camera using filtered $CrK\alpha$ radiation.

Magnetic susceptibilities were measured by the Faraday method using a Sartorius vacuum microbalance in conjunction with a Newport electromagnet. The sample (~ 0.05 g) was suspended between the magnet poles in a silicon spiral or bucket on the end of a silica suspension of sufficient length to avoid interference of the balance head from the applied fields. The system, capable of evacuation to 10^{-5} Torr, allows the apparent weight change in different applied fields to be measured to a resolution of $< 1 \mu$g giving a susceptibility sensitivity of $\pm 0.005 \mu$emu g^{-1}. All samples were checked for ferromagnetic impurities and in no case was any field dependence observed.

4. Results

X-ray powder photographs of all the samples prepared showed a pattern characteristic of the reported body-centred tetragonal Scheelite structure [10]. Hence this structure is retained throughout the $LiY_{1-x}Er_xF_4$ system. The associated lattice parameter changes are very small as seen in Table I, which also compares present and previously published data for the two end components. No significant difference in the parameters was measured on the three types of specimen prepared.

Diffraction patterns of the black deposit formed on melts prepared directly from the individual fluorides revealed lines which corresponded exactly to the strongest lines of the tetragonal phase. Many of the weaker lines were missing, due to the difficulty in collecting enough material for recording a complete powder pattern.

It is clear from Table I that the substition of Er for Y in these compounds produces little change in lattice spacing, thus precluding this measurement from use as a simple composition reference on both melts and crystals. However, due to the large localized magnetic moment of erbium, measurement of the magnetic susceptibility should provide a composition check for one of the components. Fig. 1 shows the variation of room temperature magnetic susceptibilities with composition across the LYF–LEF section. The large change in susceptibility, from a very low value for LYF ($< 10^{-5}$) to 3.75×10^{-2} emu mol^{-1} for LEF, provides a very sensitive means of checking any composition variation in these fluoride materials. It is seen that the measured values lie on, or close to, the expected straight line joining the two ends of the system with the exception of the doped Stockbarger crystal which had a significantly higher

TABLE I Comparison of lattice parameters for the tetragonal fluorides $LiYF_4$ and $LiErF_4$

| Reference | Lattice parameters (Å) | | | | | |
| | $LiYF_4$ | | | $LiErF_4$ | | |
	a	c	c/a	a	c	c/a
R. E. Thoma et al. [4]	5.26	10.94	2.08	—	—	–
Keller and Schmutz [10]	5.175	10.74	2.077	5.162	10 70	2.073
Present work	5.168	10.728	2.076	5.162	10.706	2.074

There was no detectable difference in the parameters measured on the three types of specimens in the present work. The discrepancy in the LYF parameters between the present and previous work, which is not apparent in LEF, may be attributable to the greater susceptibility to contamination observed in LYF, suggesting that the contamination levels were significantly higher in the earlier work.
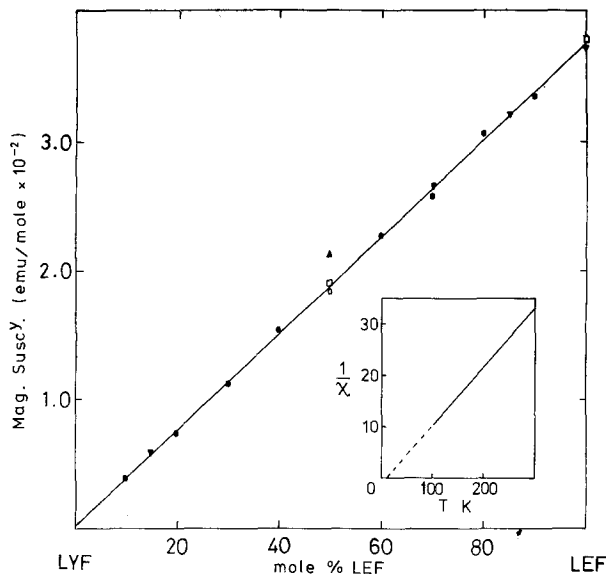
Figure 1 Room temperature mangetic suscepti-bilities as a function of composition across the LYF–LEF system. ● Melts (standard), ▼ Melts (Z–R), □ Czochralski crystal, ○ Stockbarger crystal (undoped), ▲ Stockbarger crystal (doped). Inset shows variation of inverse susceptibility with temperature for a sample with composition $LiY_{0.2}Er_{0.8}F_4$.

value attributable to the contribution from the Ho^{3+} and Tm^{3+} dopants. (Note that the undoped value exhibits good agreement with the general linear variation.) No significant difference was observed in the values of susceptibility measured on the three different types of sample.

The variation of the magnetic susceptibility with temperature was determined for two samples ($LiEr_{0.2}Y_{0.8}F_4$ and $LiEr_{0.8}Y_{0.2}F_4$) and both exhibited a Curie–Weiss behaviour (see inset in Fig. 1) with $\theta \simeq 10$ K and $\mu_{Er} = 9.25 \pm 0.05$ which is close to the theoretical value of $9.6\,\mu_B$. All the room temperature magnetic susceptibility data are consistent with the maintenance of these values of θ and μ_{Er} across the whole composition range. The atomic fraction of Er(x) can be obtained from the

room temperature molar susceptibility (X_m) by the expression:

$$x = \frac{X_m}{3.753} \times 10^2.$$

The parameters, peak height, half-peak breadth and temperature derived from the DTA analysis of the endotherms recorded on 22 samples are plotted in Fig. 2. The most striking feature is the significantly lower melting temperature of samples prepared from the individual fluorides under un-purified argon compared to those from zone-refined material under purified argon. This difference, varying from 13° for LYF to 8° for LEF, is well outside the experimental error ($\pm 2°$) and is
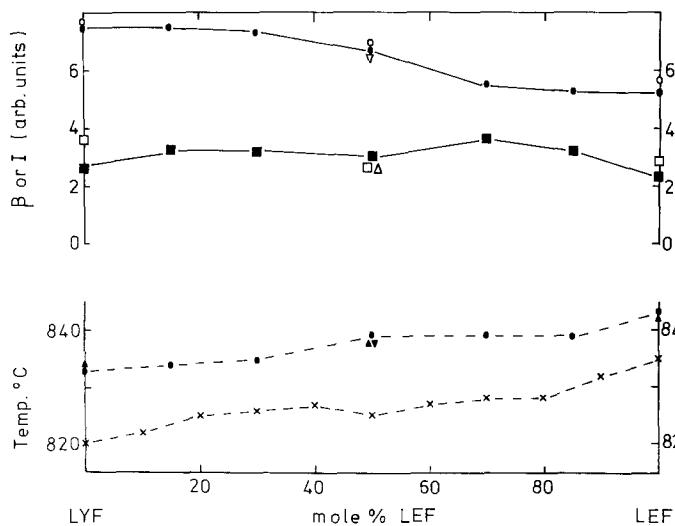

Figure 2 The parameter, peak height, half-peak breadth and temperature derived from the endotherms recorded on various samples in the LYF–LEF system. Estimated errors on intensity and breadth measurements are ± 0.05.

Sample	Intensity	Breadth	Temperature
Melts (standard)			X — — X
Melts (Z–R)	●——●	■—■	●--●
Czochralski crystal	○	□	△
Stockbarger crystal	▼	▲	▽

consistently maintained across the system. The melting temperature recorded for the four single crystal samples agreed with those for the zone-refined melts.

The difference in melting temperature is associated with a change in the form of the reaction profiles. The Z-R samples gave essentially single peak reactions across the entire system; the breadth and peak heights derived from those profiles are plotted in the upper part of Fig. 2. The peak breadth remained approximately constant across the system although there is some evidence for a very small increase in breadth in the intermediate melts when compared with the two end components. A typical endotherm of a zone-refined melt recorded for the intermediate composition $LiY_{0.5}Er_{0.5}F_4$ is shown in Fig. 3a.

In contrast to the Z-R melts, the endotherms recorded on the standard melts were predominantly double peak profiles typified by that shown in Fig. 3b for a sample having the same nominal composition as that in Fig. 3a. In general, this profile difference was more marked for the Y-rich compounds than for the Er-rich compositions, in keeping with the previous observation that LYF is more susceptible to contamination than LEF [1]. Because of the nature of the profiles typified by Fig. 3b, meaningful half-peak breadths and peak heights cannot be measured to compare with those shown in Fig. 2.

The breadth and intensity parameters of the single crystal samples again showed excellent agreement with the Z-R melts. The data for the Stockbarger $LiY_{0.5}Er_{0.5}F_4$ crystal containing Ho and Tm dopants is taken from a previous paper [11] and is shown for comparison. There was no detectable difference between the endotherms recorded on the two types of single crystal.

5. Discussion

The congruent melting behaviour of LYF and LEF establishes that a finite solidus–liquidus separation must exist across the intervening pseudo-binary system. However, the data presented in Fig. 2 show that the extent of this separation is very small, no significant broadening of the melting endotherm being detected. These data are consistent with the behaviour of an intra-rare earth system where the nature of the species being exchanged is so similar. (Here we can regard the alloying behaviour of yttrium as typical of the heavy rare earth elements.) This result is clearly important in the single crystal growth of these materials since it establishes that segregation between the rare earth components is minimal and that the distribution coefficients approximate closely to unity. Furthermore, the close approximation to congruent melting behaviour means that single crystal growth should be possible across the entire system. The addition of the small amounts of Ho and Tm necessary for laser action might have been expected to modify the phase relationships slightly but the similarity in melting behaviour of the Stockbarger crystal doped with these ions and the undoped materials suggests that doping is not a serious problem in the single crystal growth of these complex fluorides.

These arguments, however, only apply provided contamination of the melt and/or constituent losses are kept to a minimum. It has already been shown that these compounds are very susceptible to contamination from oxygen and/or OH^- ions [1, 2] and the present work further emphasizes this point The standard melts prepared from the powdered individual fluorides show broadened or double peak profiles which can be attributed to contamination. Our earlier work showed that the congruent phase
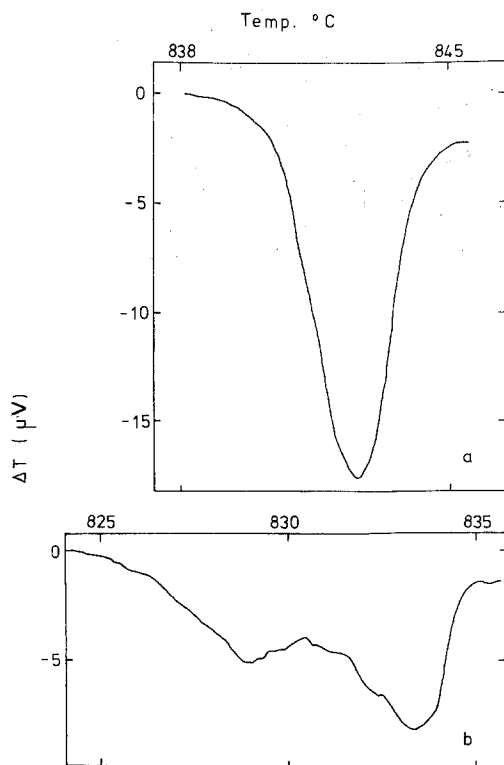

Figure 3 Typical endotherms recorded on (a) a $LiY_{0.5}Er_{0.5}F_4$ zone-refined melt and (b) a standard melt of the same composition.

has a range of stability and that contamination moves the composition off the congruent point producing broadened melting endotherms [1]. Constituent loss or compositional changes within the homogeneity range due to segregation can also cause peak broadening but the resultant composition shift is insufficient to significantly lower the melting temperature [1, 11]. However, the extensive peak broadening and, in particular, the double peak profiles of the standard melts observed in the present work represent a significant solidus–liquidus separation and are associated with a marked reduction in melting temperature. This indicates, therefore, quite a large shift in composition away from the pseudo-binary section demonstrating that the level of contamination in these melts is relatively high. Prior to the establishment of congruency for these compounds by eliminating such contamination, observations such as these were erroneously interpreted in terms of a peritectic melting behaviour [3, 4].

The black deposit found on these melts also suggests a high degree of contamination. The discrete nature of this deposit implies either that it floats to the surface when the sample is molten or that it volatilizes and is subsequently deposited on the sample surface on cooling. The X-ray patterns show that this material is composed essentially of the appropriate fluoride, and the black colouration can be attributed to contamination which could be from the starting material or from the environment.

The DTA measurements indicate that the melts prepared using zone-refined material show no evidence of contamination demonstrating once again that purified argon is a satisfactory environment in which to prepare melts and crystals of these fluorides. The similarity in the endotherms of these melts and those for the single crystal samples confirms this point.

It is apparent from the present work and the author's previous studies [1, 11] that DTA is a very effective way of characterising contamination effects in these materials. Lattice parameter variations are too small to be detected by standard powder techniques and recourse to high accuracy ïngle crystal X-ray techniques would be necessary in order to determine any parameter variation with contamination. Magnetic susceptibility is not sensitive to the levels of contamination encountered here, involving non-magnetic species, but this measurement does provide a sensitive constituent check. This is extremely useful in systems such as these, where the species being exchanged possess very similar ionic radii giving rise to very small changes in lattice parameters, and may prove particularly helpful in monitoring the levels and distribution of dopants in laser crystals of these materials.

Acknowledgements

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