Studies on the reaction of ammonium fluoride with lithium carbonate and yttrium oxide

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Abstract

The reaction of Y_2O_3 and Li_2CO_3 with NH_4F to produce $LiYF_4$ was studied by thermogravimetric and X-ray diffraction methods. NH_4F reacts easily with Li_2CO_3 in a one-step exothermic process. Fluorination of yttrium oxide gives first $YF_3 \cdot 1.5NH_3$ which decomposes at 300–380°C to $YF_3 + NH_3$. This process is exothermic. In the absence of excess NH_4F, an amount of YOF is produced, in addition to YF_3, as a product of the reaction of YF_3 and unreacted Y_2O_3. This reaction is endothermic. In the ternary system $NH_4F–Li_2CO_3–Y_2O_3$, the first reacts separately with each of the other two and the resulting mixture of simple yttrium and lithium fluorides is converted into $LiYF_4$ at high temperatures.

1. Introduction

The development of laser technology has resulted in the need for increasingly efficient laser materials. One of the most promising is monocrystalline lithium-yttrium fluoride (abbreviated as YLF) doped with rare earth elements [1,2].

An essential condition of obtaining a proper YLF crystal is the appropriate chemical and phase purity of the polycrystalline stock material used for the single crystal growth. In our studies, lithium-yttrium fluoride of good quality was obtained [3] by the reaction of NH_4F with lithium carbonate and yttrium oxide.

The process proceeds in two stages. In the first step, a mixture of lithium carbonate, yttrium oxide, and ammonium fluoride is heated at a temperature below 400°C until volatile reaction products and excess NH_4F are removed. The temperature is then raised and the product melted at 850–900°C to obtain polycrystalline $LiYF_4$. The material is doped with 0.5–2.0 mol% of rare earth elements by partial substitution of Y_2O_3 with oxides of appropriate lanthanides which, like yttrium oxide, also react with NH_4F to give corresponding fluorides.

The aim of this work was to investigate the course of the reaction of ammonium fluoride with Li_2CO_3 and Y_2O_3 by means of thermal and thermogravimetric analysis and X-ray diffraction. The literature information on this subject is rather scarce and limited to the binary systems: Li_2CO_3–NH_4F [4] and Y_2O_3–NH_4F [5–8].

2. Experimental

All the reagents used in this study were of high purity grade. Lithium carbonate and yttrium oxide, both of 4N purity, were supplied by the Institute of Electronic Materials Technology (Poland) and ABCR (Germany). Ammonium fluoride of analytical grade was supplied by Riedel-de Haën.

Measurements of thermal effects and mass losses during calcination of the reaction mixtures were performed using a MOM Q-Derivatograph, which enabled simultaneous registration of T, and TG, DTG, and DTA curves. Samples of the mixtures, generally 300 or 900 mg in mass, were placed in a platinum crucible and heated, at a rate of 2.5 or 5.0 K min^{-1} up to 500 or 1000°C in air atmosphere. The reference material was α-Al_2O_3.

The phase composition of the reaction products was studied by means of a Siemens X-ray diffractometer (D500) equipped with a high-stability generator type K-800. The diffractometer was equipped with an Si(Li) semiconductor detector, which enabled monochromatization of the dispersed beam and good statistics for the measurements due to its high spectral resolution. Chromium $K_\alpha = 0.229$ nm radiation was used, with selection of appropriate 2θ angles. The diffraction data were transmitted to an IBM PC and the phase analysis was carried out using a computer program.

The X-ray diffraction patterns were taken from samples obtained by calcination of mixtures of ammonium fluoride with lithium carbonate, yttrium oxide, or both in a 1:1 ratio according to the stoichiometry of the final compound, i.e. $LiYF_4$. The variable parameters of the experiments were the temperature and the relation of NH_4F to the other reagents.

3. Results and discussion

Fig. 1 shows the TG, DTG, and DTA curves recorded for the reaction of ammonium fluoride with lithium carbonate. The reaction was carried out at the molar ratio NH_4F:$Li_2CO_3 = 3:1$, i.e. with 50% excess of NH_4F. In the mixture of the reagents, the reaction starts even at room temperature, as evidenced by the smell of ammonia
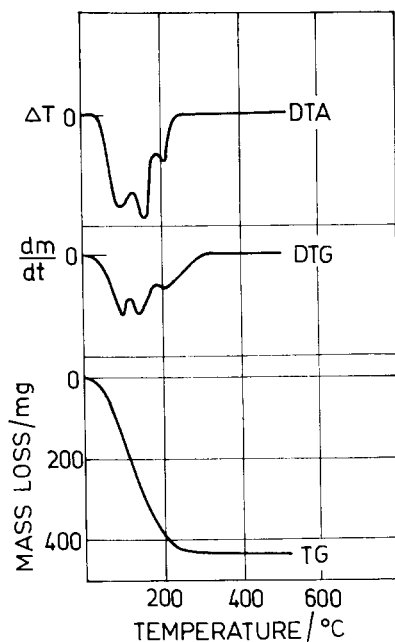
Fig. 1. TG, DTG and DTA curves for the reaction of ammonium fluoride with lithium carbonate $(NH_4F:Li_2CO_3 = 3:1)$.

liberated as a reaction product. The first minimum on the DTG curve is observed at about 100°C. This signal is accompanied by a negative peak on the DTA curve, confirming the endothermic nature of the LiF synthesis. The two other thermal effects on the DTA curve are also endothermic. They appear at about 165 and 225°C and are connected with transformations of NH_4F that take place during heating [9]. The relationships observed with samples containing higher amounts of NH_4F were analogous to those shown above and for this reason they are not been in detail.

The phase analysis of the products, obtained after heating the $Li_2CO_3–NH_4F$ mixture at 400°C for 4 h, showed that the small excess of ammonium fluoride (in relation to the stoichiometric mixture) provides complete conversion of Li_2CO_3 to LiF. The results presented conform fully with the results obtained for a similar system by Ikram and Rakhimov [4].

Figs. 2 and 3 summarize the results of the thermogravimetric studies of the fluorination of yttrium oxide. The reaction was carried out at various molar ratios of $NH_4F:Y_2O_3$ varying from 6:1 (stoichiometric relation) to 9:1 (50% excess of NH_4F). As for the fluorination of lithium carbonate, this reaction begins at room temperature and is more intense in mixtures containing an excess of NH_4F. It is manifested by the presence of a small but quite distinct signal on the DTG curve at 60–70°C (Fig. 3) which is absent in the case of the stoichiometric mixture (Fig. 2). That signal is accompanied by an endothermic effect on the DTA curve. Two other endothermic effects present on the DTA curves are due to transformations of NH_4F.
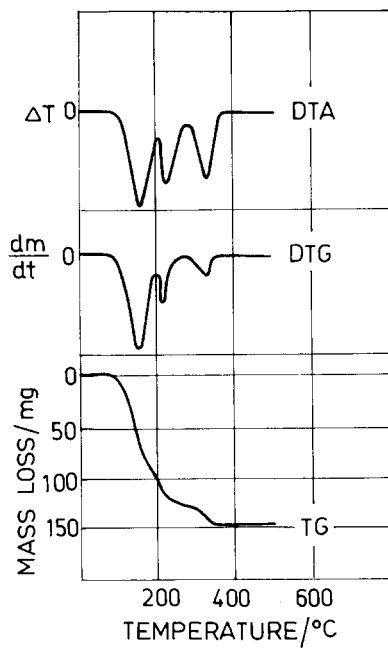
Fig. 2. TG, DTG and DTA curves for the reaction of ammonium fluoride with yttrium oxide $(NH_4F:Y_2O_3 = 6:1)$.

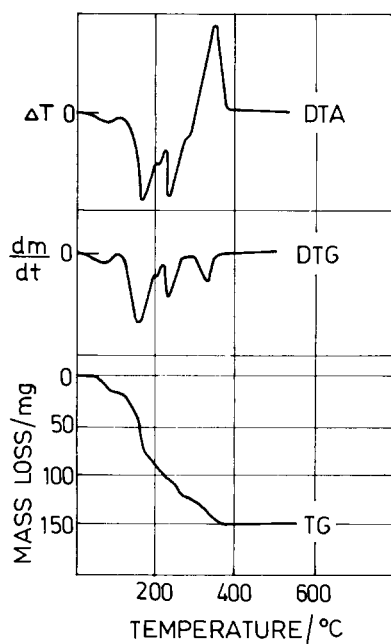Fig. 3. TG, DTG and DTA curves for the reaction of ammonium fluoride with yttrium oxide $(NH_4F:Y_2O_3 = 9:1)$.

An essential difference between the two systems represented by the thermogravimetric curves shown in Figs. 2 and 3, consists of the different nature of the thermal effect observed in the higher temperature region, 300–380°C. For the stoichiometric mixtures represented in Fig. 2, an endothermic effect is observed, whereas for those containing 50% excess (as well as 100% and 200% excess, not shown in Fig. 3), the effect is exothermic.

To elucidate the causes of the observed differences, we have studied the phase composition of the products of the reaction between NH_4F and Y_2O_3 carried out, successively, for 18 h at 200°C, for 5 h at 270°C, and for 5 h at 400°C. It has been found that, with a large excess of NH_4F ($\geq 50\%$), the only product of the reaction carried out at 200°C and at 270°C is the complex $YF_3 \cdot 1.5 NH_3$, but at 400°C only simple YF_3 is produced. No indication was detected, however, of other, more complex forms of yttrium fluoride, e.g. $NH_4Y_2F_7 \cdot NH_4F$, as suggested by Mikhailov [6], or $YF_3 \cdot 3NH_3$ [5].

Another situation is observed, however, when the initial ratio of the reagents corresponds with the stoichiometry of the reaction, or when NH_4F is slightly deficient. Such a mixture heated at 270°C contains yttrium fluoride and unreacted yttrium oxide. Further heating of the sample at 400°C resulted in a substantial decrease in the YF_3 phase and the appearance of a new phase, YOF, to the detriment of Y_2O_3.

Analysis of the results of thermogravimetric and XRD studies shows that the formation of the $YF_3 \cdot 1.5 NH_3$ complex is associated with an endothermic effect, well seen in the temperature range 70–100°C (DTA curve in Fig. 3). At higher temperatures, the thermal effects characteristic for NH_4F (at 165 and 225°C) might have been superimposed with the effects due to formation of the complex [10].

The decomposition of $YF_3 \cdot 1.5 NH_3$ to form yttrium fluoride and gaseous ammonia takes place above 280–300°C (TG curve in Fig. 3) and is exothermic, as evidenced by the positive signal on the DTA curve with a maximum at about 340°C (Fig. 3). It should be pointed out that in published works [5,7,8], the decomposition of the complex is considered to be endothermic. It seems to be probable that the overall thermal effect at 340°C is due to a superposition of two partial effects: an endothermic one due to decomposition of the complex, and an exothermic one connected with structure rearrangement of the yttrium fluoride formed.

When considering the course of the reaction carried out with stoichiometric mixtures of NH_4F and Y_2O_3 or with a small excess of Y_2O_3, one can see that the amount of NH_4F escaping from the system becomes significant and competitive with the fluorination reaction and, just as important, that the YOF phase is formed by reaction of yttrium oxide with the yttrium fluoride previously formed in the process (XRD results). The endothermic effect on the DTA curve (Fig. 2) at 300–380°C would be due, therefore, to the reaction of yttrium oxide with yttrium fluoride, and not to the decomposition of the ammonia complex.

Fig. 4 represents TG, DTG, and DTA curves obtained for the ternary mixture lithium carbonate–yttrium oxide–ammonium fluoride with $Li_2CO_3:Y_2O_3 = 1:1$. The thermogravimetric curves were recorded in a wider range of temperature (up to 1000°C) for a mixture with 50% excess of NH_4F. As can easily be seen, at temperatures below 500°C the TG, DTG, and DTA curves of the ternary system correspond to a superposition of the curves obtained for the binary systems as shown in Figs. 1 and 3.
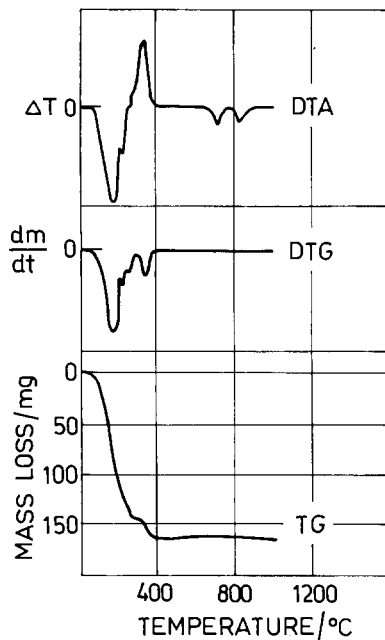
Fig. 4. TG, DTG and DTA curves for the reaction of ammonium fluoride with lithium carbonate and yttrium oxide ($NH_4F:Li_2CO_3:Y_2O_3 = 12:1:1$).

In the temperature region 500–1000°C, the DTA curve has two more endothermic effects not accompanied by changes in sample mass.

The X-ray diffraction patterns of samples obtained by fluorination of the stoichiometric mixture ($NH_4F:Li_2CO_3:Y_2O_3 = 15:1:1$) are shown in Fig. 5. The process was carried out in two stages: the reagent mixture was first heated for 5 h at 400°C in air (Fig. 5a); then the temperature was raised to 850°C (slightly above the melting temperature of $LiYF_4$) and the heating was continued for 1 h in dry argon (Fig. 5b). It is seen that the main products of the first reaction step are simple lithium and yttrium fluorides (Fig. 5a). As late as after melting the charge, one obtains pure lithium-yttrium fluoride free of both LiF and YF_3 (Fig. 5b).

The reaction in the ternary system needs no special discussion. As long as NH_4F or its product $NH_4F \cdot HF$ is present in the system, it reacts separately with each of the two starting materials to form LiF and $YF_3 \cdot 1.5NH_3$ which is then transformed into YF_3. Hence the curves obtained in thermal analysis (Fig. 4) are a superposition of the thermal effects characteristic for the simple binary systems, i.e. $Li_2CO_3 + NH_4F$ (Fig. 1) and $Y_2O_3 + NH_4F$ (Fig. 3). The difference appears at high temperatures, in the range 700–850°C. The two endothermic signals observed on the DTA curve in that tempera-ture range (Fig. 4) are due to the eutectic transition $LiF/LiYF_4$ (about 700–710°C) and the melting of $LiYF_4$ (about 820°C) [11–13].
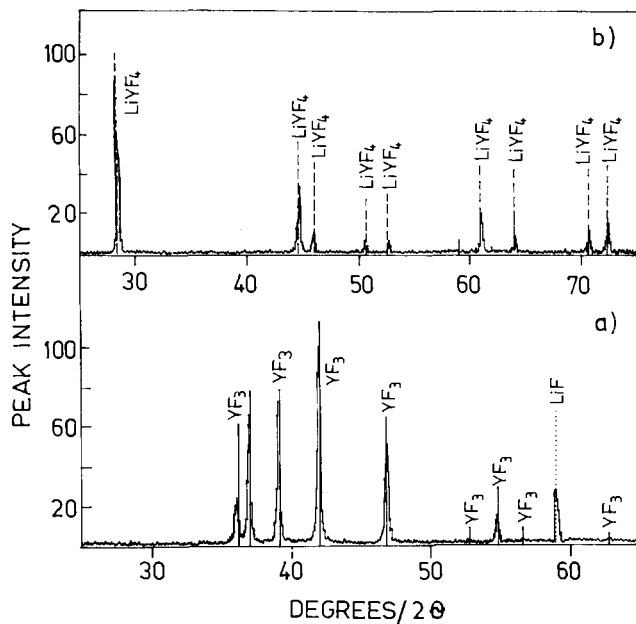
Fig. 5. XRD patterns for the reaction products in the $NH_4F-Li_2CO_3-Y_2O_3$ system; $NH_4F:Li_2CO_3:Y_2O_3$ = 15:1:1: (a) 400°C; (b) 850°C.

References

[1] T.M. Pollak, W.F. Wing and R.I. Grosso, IEEE J. Quantum Electron., 18 (1982) 159.
[2] W. Koechner, Solid-State Laser Engineering, Springer, Berlin, 2nd edn., 1988, p. 60.
[3] E. Kowalczyk, J. Radomski, R. Diduszko, I. Iwanejko, Z. Kowalczyk and K. Grasza, Pol. J. Appl. Chem., 38 (1994) 583.
[4] D.D. Ikram and M. Rakhimov, Zh. Neorg. Chimii., 29 (1984) 1924.
[5] J. Hölsä and L. Niinistö, Thermochim. Acta, 37 (1980) 155.
[6] M.A. Mikhajlov, Zh. Nieorg. Chimii., 8 (1973) 1508.
[7] L. Markovskij, Zh. Nieorg. Chimii., 15 (1970) 5.
[8] L. Markovskij, Zh. Nieorg. Chimii., 16 (1971) 330.
[9] Atlas of Thermoanalytical Curves, G. Liptay (Ed.) Vol. 2, Akademiai Kiado, Budapest, 1973, p. 101, 102.
[10] G. Rakov and I. Melnitshenko, Usp., 53 (1984) 1463.
[11] R.E. Thoma and C.F. Weaver, J. Phys. Chem., 65 (1961) 1096.
[12] I.R. Harris and B. Cockayne, J. Mater. Sci., 18 (1983) 1235.
[13] I.R. Harris, J.S. Abell, B. Cockayne and J.G. Plant, J. Mater. Sci., 11 (1976) 1807.