



Zone-melting study of LiSrAlF_6 and $\text{LiSrAlF}_6 : \text{Cr}^{3+}$ by thermal analysis

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Abstract

Pure and Cr^{3+} -doped LiSrAlF_6 compounds were synthesized and purified by the zone-melting technique under HF atmosphere. The preparation process of these compounds was characterized by thermal analysis (TG/DTA), X-ray diffraction, and fluorescence analysis. It was observed that LiSrAlF_6 presents congruent melting but deviations of the initial stoichiometry happen easily due to the high evaporation rate of one of the components. The CrF_3 , used as a dopant, does not maintain chemical stability when heated. In spite of this, the distribution of chromium along the doped refined ingots was approximately uniform. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since the demonstration of their laser properties, $\text{LiSrAlF}_6 : \text{Cr}^{3+}$ (Cr : LiSAF) crystals [1] have attracted considerable attention as a near-infrared laser gain material. In special, there is a great interest in this laser crystal because of its tunability and potential for diode-pumped operation. Cr : LiSAF crystals have brought opportunities for the devel-

opment of diode-pumped all-solid-state lasers for the generation of ultra-short pulses in the near infrared [2].

Optical properties of laser hosts are very important in determining laser performance. Even small crystals, as those required by diode pumping systems (≈ 10 mm long samples), must exhibit good quality, mainly for applications of high-power devices. Several issues can affect the growth of high optical quality fluoride crystals, and studies concerning Cr : LiSAF growth can be found in the literature [3,4]. To the present, the best results have been obtained by the Czochralski technique [3]. However, the preparation of fluoride crystals with high optical quality depends not only on the

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growth procedures but also on the degree of purity and, in some cases, the initial composition of the material used for growth. Detailed studies of the synthesis processes, influence of the degree of purity, and dopant incorporation in Cr:LiSAF crystals are rarely published. We present in this work a detailed study of the conditions of preparation of the Cr:LiSAF compound for crystal growth through the method of zone melting in a HF atmosphere. For characterization of the obtained materials we used X-ray diffraction, X-ray fluorescence analysis and, especially, thermal analysis. Considering the nature of the processes involved, thermal analytical methods [5] are extremely useful tools for evaluation and control of the synthesis and purification process in the preparation of high-purity fluorides for laser crystal growth.

2. Experimental procedures

The starting fluorides SrF_2 and AlF_3 were obtained from the hydrofluorination of commercial SrCO_3 (Johnson Matthey – 99.99%) and Al_2O_3 (Aldrich – 99.8%), respectively; LiF (Aldrich – 99.8%), was previously purified by the method of zone melting under a dynamic atmosphere of HF [6]. The LiSAF compound was obtained by melting the components in a stoichiometric mixture, under a HF flow, in vitreous carbon crucibles. The Cr^{3+} ions were introduced by addition of CrF_3 ($\text{CrF}_3 \cdot 4\text{H}_2\text{O}$ – Aldrich, 99%) after previous dehydration under HF flow. Ingots with molar fractions of 1, 2 and 3 mole% of CrF_3 were prepared to study impurity distribution behavior of Cr^{3+} in LiSAF.

Zone-melting purification of the LiSAF compound was first studied. Experiments with 1–6 thermal cycles were accomplished using a zone speed rate of 4 mm/h. For evaluation of the distribution of the dopant along the refined ingots, zone-melting experiments of Cr^{3+} -doped LiSAF were achieved using only one thermal cycle.

The thermal analysis measurements were accomplished in a simultaneous TG/DTA system from TA Instruments, model SDT 2960. Through the thermogravimetry (TG) it was possible to control the characteristics of the commercial materials as well as the degree of purity of the basic fluorides

obtained by the hydrofluorination reaction. Differential thermal analysis (DTA) was used to demonstrate the influence of impurities on the melting behavior of the pure and doped materials and to observe variations in the initial stoichiometry.

3. Experimental results

3.1. Zone melting of pure LiSAF

The thermal behavior of the synthesized pure compound was previously verified [7]. The LiSAF ingots obtained by the zone melting of the synthesized compound were characterized by thermal analysis by the use of three samples of each ingot: sample A (initial region), sample B (middle region) and sample C (final region). For all measurements we used solid samples with about 15 mg, platinum crucibles, heating rate of $10^\circ\text{C}/\text{min}$ and Argon flow of 100 cc/min.

Fig. 1a shows the DTA curves of sample B of zone refined ingots with 1–3 thermal cycles and the Fig. 1b, DTA curves of ingots refined with 4–6 cycles. It is observed that DTA curves of the samples 1-B and 2-B, present enlarged endothermic peaks with shoulders, evidencing the melting in two stages, which indicates the presence of impurities that were not totally segregated. In the DTA curve of the sample 3-B a decrease of the shoulders is observed, but the base of the peak is slightly enlarged. Sample 4-B presents an endothermic peak well defined and sharp, characteristic of a material free from impurities, showing a good purification of the ingot in this thermal cycle. Finally, it is interesting to note that samples 5-B and 6-B present DTA curves with enlarged peaks. This effect cannot be attributed to the presence of impurities, since the sample 4-B showed characteristics of an already purified material. It is reasonable to suppose that this result is due to the deviation of the initial stoichiometry of the compound, because of evaporation of one or more components during the zone-melting process (probably the AlF_3 and/or LiF). The effect becomes more evident as the number of thermal cycles (passages) increases. In fact, the evaporation effect can be observed in the LiSAF – TG curve presented in Fig. 2. Evaporation is

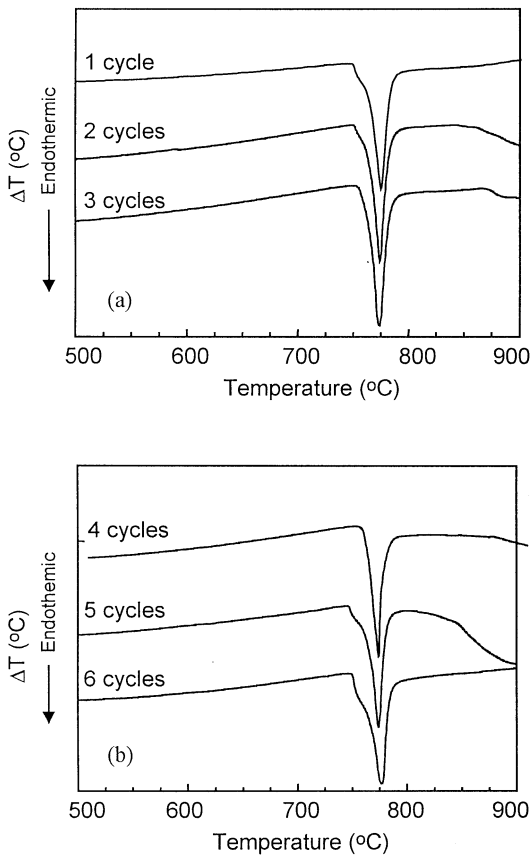


Fig. 1. DTA curves of sample B of pure LiSAF after zone refine: (a) with 1–3 thermal cycles; (b) with 4–6 thermal cycles.

noted just after the melting of the compound, shown in the DTA curve at the onset temperature of 760°C. The resulting endothermic peak has a narrow base and is well defined characterizing the LiSAF congruent melting.

Experimental X-ray diffraction data of sample 4-B are shown in Table 1. Considering the lattice parameters $a = 5.071 \text{ \AA}$ and $c = 10.189 \text{ \AA}$, and the structure of LiSAF [8], we have calculated the values of d , the distance between adjacent planes, in each set (hkl) [9]. These data are also shown in Table 1. The good agreement of the experimental and calculated values confirm the thermal analysis results, that is, sample 4-B is composed of one phase: pure LiSAF.

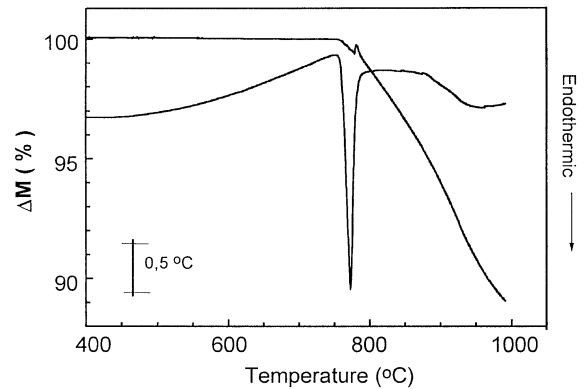


Fig. 2. TG and DTA curves of sample B of pure LiSAF after zone refine with four thermal cycles.

Table 1

X-ray diffraction results of the central region of purified LiSAF ingot and calculated interplanar distances

Experimental data			Theoretical data	
2θ	I/I_0 (%)	d_{exp} (Å)	d_{theor} (Å)	(hkl)
17.575	0.6	5.0422	5.0945	0 0 2
20.385	22.0	4.3531	4.3922	1 0 0
22.155	13.4	4.0091	4.0334	1 0 1
26.910	100.0	3.3105	3.3266	1 0 2
33.445	1.0	2.6771	2.6868	1 0 3
35.555	7.8	2.5229	2.5473	0 0 4
39.745	36.4	2.2661	2.2701	1 1 2
40.990	19.4	2.2001	2.2035	1 0 4
41.125	22.6	2.1932	2.1961	2 0 0
44.980	16.7	2.0137	2.0167	2 0 2
50.815	30.7	1.7953	1.7971	1 1 4
53.955	2.3	1.6980	1.6982	0 0 6
55.305	5.4	1.6597	1.6601	1 2 0
56.175	0.5	1.6361	1.6385	2 1 1
58.200	8.0	1.5839	1.5839	1 0 6
58.455	18.1	1.5776	1.5784	2 1 2
62.195	1.8	1.4914	1.4938	2 0 5
63.530	8.5	1.4632	1.4641	3 0 0
66.150	1.0	1.4115	1.4110	1 1 6
67.255	4.6	1.3910	1.3908	2 1 4
69.915	4.4	1.3444	1.3434	2 0 6
73.455	0.6	1.2881	1.2871	2 1 5
74.360	1.2	1.2747	1.2736	0 0 8
74.820	2.3	1.2680	1.2679	2 2 0

3.2. Cr^{3+} -doped LiSAF

The doped synthesized ingots melted under HF flux presented a dark green coloration layer in their

inferior part. This dark region was identified by X-ray diffraction as Cr_2O_3 phase. The color became more intense as the nominal concentration of CrF_3 increased. In fact, X-ray diffraction analysis of the used CrF_3 showed small contamination with Cr_2O_3 and Cr_2F_5 phases. Wanklyn [10] remarks that CrF_3 presents thermal decomposition when heated above 600°C , according to the reaction:



We could not confirm by X-ray diffraction analysis the presence of CrF_5 or CrF_2 in the used CrF_3 ; however, the formation of the observed phases (Cr_2O_3 and Cr_2F_5) could result from secondary reactions in the dehydration and thermal decomposition process. To clarify these results we checked

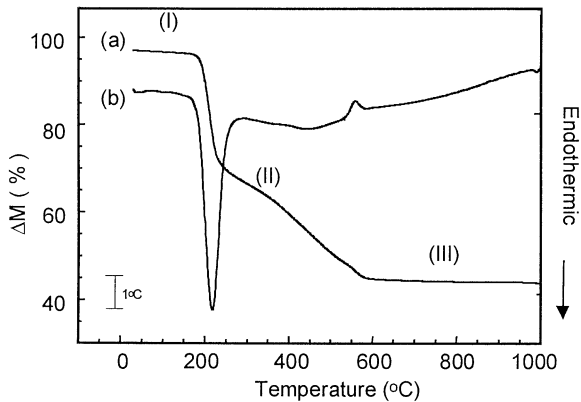


Fig. 3. Thermal analysis curves of the commercial CrF_3 : (a) TG and (b) DTA.

the thermal behavior of the CrF_3 used in the synthesis of $\text{Cr}:\text{LiSAF}$ compound. The thermal analysis curves of the commercial chromium fluoride are shown in Fig. 3. The part I of the TG curve (curve (a)) corresponds to the hydrated material ($\text{CrF}_3 \cdot 4\text{H}_2\text{O}$). Analysis of the DTA curve (curve (b)) indicates that the water molecules are strongly bound; the onset temperature of this first stage of dehydration is 192°C . By the mass balance, it is possible to say that three molecules of water are eliminated in this stage. In the part II, corresponding to the temperature interval from 300 to 600°C , simultaneous events happen. These effects, probably, are: elimination of the last molecule of bound water, thermal decomposition, and oxidation. This last effect can be confirmed by the exothermic peak in the DTA curve, at the onset temperature of 560°C . The oxidation may occur because of the reaction between the last molecule of bound water and one of the products of the thermal decomposition. The final part III, should contain a mixture of CrF_3 , products of the thermal decomposition and Cr_2O_3 .

The above results must be carefully addressed. It is possible that the HF flow used in the dehydration process was not completely effective in eliminating spurious reactions of oxidation of CrF_3 . However, the DTA curve in Fig. 3 indicates that oxidation happens after (or during) the thermal decomposition of CrF_3 , that is, probably with one of the reaction products of Eq. (1). In such a case the oxidation occurs only because of the thermal decomposition.

Table 2
X-ray fluorescence analysis of zone melted $\text{Cr}:\text{LiSAF}$ ingots ($L = 294$ mm)

Nominal concentration			1 mole%	2 mole%	3 mole%
Sample	Distance x_i (mm)	Solidified fraction x_i/L	C_s (mol %)	C_s (mol %)	C_s (mol %)
1	42	0.14	0.8258	1.5672	2.1644
2	84	0.29	0.8635	1.6281	2.1776
3	126	0.43	0.9044	1.6569	2.1799
4	168	0.57	0.8878	1.6246	2.0858
5	210	0.71	0.8788	1.7007	2.1475
6	252	0.86	0.9676	1.7409	2.7827
7	294	1.00	1.0568	1.7299	2.7571

The zone melted ingots doped with 1 and 2 mole% did not present color variation as observed in the synthesized ingots. The 3 mole% doped ingot showed segregation of the dark green phase to the final region. Table 2 shows the X-ray fluorescence analyses of samples from the refined ingots. For the determination of the chromium content, each ingot (total length, $L = 294$ mm) was divided into seven parts of equal size. The measurements showed almost uniform chromium distribution, but the measured Cr^{3+} concentration was always lower than the nominal concentration.

4. Conclusions

A methodology was developed for the preparation of pure and Cr^{3+} -doped LiSAF for laser crystals growth. This process involved the hydrofluorination of the raw materials and their purification by the zone melting process followed by its characterization. It is important to note that thermal analysis is an efficient method to characterize the effects of contamination and deviations of composition of the processed materials.

It was observed that LiSAF presents congruent melting but deviations of the initial stoichiometry happen easily due to high evaporation of one of the components in the melting compound. There was also great difficulty in controlling the synthesis process of $\text{Cr} : \text{LiSAF}$. The dopant CrF_3 does not maintain chemical stability when heated and the chromium can assume different valences. In spite of the above problems observed in the synthesis, the zone melted, doped ingots were transparent and homogeneous in appearance, without color vari-

ation in the stoichiometric part of the ingot. The Cr^{3+} distribution measured along the ingots was approximately uniform, indicating that the coefficient of segregation of the chromium in this matrix is close to unity.

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