Growth and optical characteristics of Ce-doped and Ce : Na-codoped $BaLiF_3$ single crystals

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Abstract

Ce-doped and Ce : Na-codoped $BaLiF_3$ single crystals were grown by the Czochralski technique under reactive atmosphere. Na^+-ions, used as a charge-compensating impurity, compete with Ce^{3+}-ions for Ba^{2+} sites in the host, reducing the Ce^{3+} incorporation and degrading the mechanical integrity of crystals. Ce-doped $BaLiF_3$ showed potential for UV tunable lasers. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Recently, several research groups have been examining the potential of Ce-doped fluoride crystals for lasers in the UV region. In particular, crystals of $LiCaAlF_6$ and $LiSrAlF_6$ doped with Ce^{3+}-ions [1–3], have been receiving a great deal of attention because of their potential capacity for lasing with wide UV tunability using solid-state direct UV pumping. Very few UV laser materials suitable for direct pumping are known, and the search for new

materials is an interesting task. Dubinski et al. [4] have reported studies of Ce : $BaLiF_3$ as a candidate material for a tunable UV laser with direct pumping. $BaLiF_3$ is an inverse perovskite material with cubic structure (space group O_h^1 - Pm3m), where the monovalent Li^+ ion is at the center of a F_6 octahedron and the Ba^{2+} divalent ion is in the 12-fold environment site, resulting in a different field interaction from the classic perovskite structure. The compound $BaLiF_3$ melts incongruently and a single crystal must be grown from a non-stoichiometric melt to avoid precipitation of other phases. Good optical quality crystals of pure $BaLiF_3$ were obtained by Czochralski pulling under a CF_4 reactive atmosphere [5,6].

From spectroscopic features of Ce : $BaLiF_3$, Dubinski et al. [4] predicted laser emission close to 350 nm with pumping by a frequency-quadrupled

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Nd-laser. The estimated pumping threshold, calculated assuming a single site-activation, was found to be about 90 mJ/cm^2. However, taking into account the lattice sites of BaLiF$_3$ crystals, the probability of Ce^{3+}-occupancy of different sites and the formation of charge-compensating defects could not be ignored for concentrations suitable for laser action. The occurrence of heterovalent activation could result in the decrease of the absorption suitable for direct pumping (around 266 nm).

In this study we report on the growth of large, transparent Ce : BaLiF$_3$ and Ce : Na : BaLiF$_3$ single crystals by the Czochralski technique for UV laser tests. The use of a second dopant, Na$^+$, in the growth of Ce-doped BaLiF$_3$ had as objective to increase the dopant concentration without charge-compensating defects. We report the results of compound preparation, Ce^{3+} and Na$^+$-ion incorporation in the host crystal, and optical characterization of the single crystals grown.

2. Experimental procedure

High purity commercial fluorides (99.999% grade) were used as starting materials. The crystals were grown in a vacuum-tight Czochralski system equipped with a graphite heater and automatic diameter control. After weighing and mixing in the appropriate composition (43% BaF$_2$: 57% LiF) [5], the compounds were melted and treated in the furnace for a period of 5–6 h under a reactive atmosphere of CF$_4$ [5,7]. The crystals were grown in the $\langle 1\,0\,0 \rangle$ direction at a pulling rate of 1 mm/h and rotation rate of 15 rpm. After growth, crystals were cooled at a rate of 30°C/h.

Concentrations in the range of 0.5–1 mol% of CeF$_3$ and NaF were used in the preparation of the initial growth charges. The final dopant concentrations were evaluated by the inductively coupled plasma technique (ICP). The dopant concentrations were always measured in the initial (1) and final (2) parts of the boules. The DTA curves were obtained in a TAS100/TG8110 Thermal Analysis Station from Rigaku.

The samples for spectroscopic measurements were cut perpendicular to the growth direction ($\langle 1\,0\,0 \rangle$) and polished manually. The IR spectrum was taken in an FTIR-8200PC spectrophotometer from Shimadzu.

3. Results and discussion

Fig. 1 shows a 1 mol% Ce-doped BaLiF$_3$ single crystal grown under a CF$_4$ atmosphere. The melting of the BaF$_2$ and LiF mixture, under an inert Ar atmosphere, after careful pre-treatment in vacuum, resulted in the formation of a black film on the melt surface (occasionally black spot regions). When the BaLiF$_3$ compound was doped with CeF$_3$, the amount of black substance on the melt surface increased. This film could sometimes be eliminated, after cooling of the material, by grating the solidified surface and subsequently re-melting the compound. Although this procedure enables the growth process, it does not eliminate contamination from the bulk charge. We suppose that this film is formed basically because of oxygen contamination of the raw materials, especially BaF$_2$, which leads to the formation of oxyfluoride complexes after melting. Oxyfluoride compounds have, in general, higher melting points than fluorides, and consequently do not mix with the BaLiF$_3$ liquid phase.

A similar behavior was observed when the material was initially melted under a CF$_4$ atmosphere. However, after some hours of treatment, this black film was completely eliminated by the reaction with
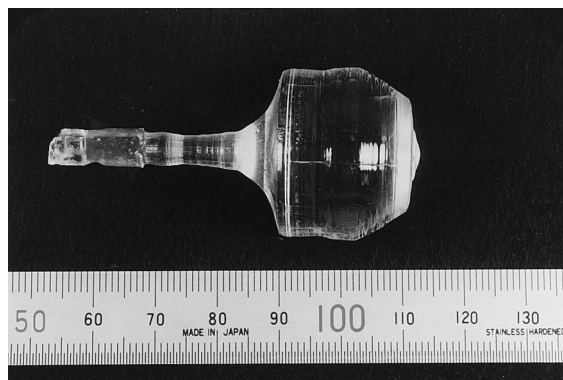

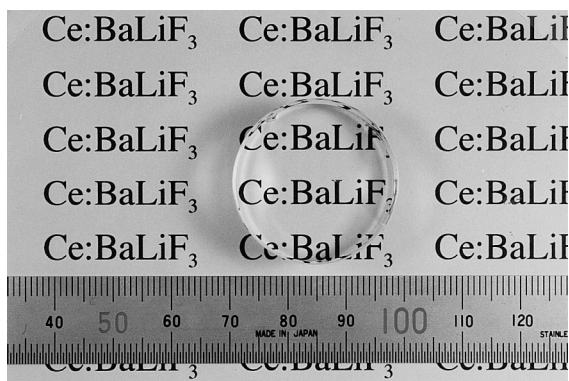Fig. 1. Single crystal of Ce : BaLiF$_3$ as-grown.

Fig. 2. Sample of Ce : BaLiF$_3$ prepared from crystal #2.

the fluorinating agent, allowing the growth of transparent single crystals such as the one shown in Fig. 1. Pastor et al. [7] have shown that CF$_4$ reacts with the water present in the environment, resulting in HF and CO$_2$. This reaction yields a double effect of purification by elimination of water-related impurities and generation of a slightly fluorinating atmosphere that acts on oxygen-derived impurities. A completely transparent and mixed melt is obtained after 5–6 h of melting under CF$_4$. Fig. 2 shows a 10 mm size sample obtained from the crystal shown in Fig. 1. It is transparent and without inclusions in the interior.

Table 1 shows the initial and final composition of the single crystals grown. The measured Ce^{3+} concentration at the final part of crystal #2 was equal to 0.016 mol%. The low incorporation of Ce^{3+}-

ions in the BaLiF$_3$ host is probably influenced by the different valence state of these ions and the available substitutional sites in the crystal. Considering the effective ionic radius and coordination numbers [8], the natural site for Ce^{3+} occupancy in BaLiF$_3$ is the Ba^{2+} site (Table 2). Theoretically, Ce^{3+}-ions can be introduced into the crystal in more than one valence state, with formation of compensating defects, such as vacancies, in the host lattice. This could result in the reduction of the number density of the desired valence state and/or reduction of the incorporation of ions in the host.

Since this is a relatively new system, the site occupancy has not yet been studied in detail. However, a very simple measure to stabilize the valence state is to co-dope the crystal with a second impurity or a charge-compensating additive. We have grown Na$^+$ and Ce^{3+} co-doped crystals to try to improve the Ce incorporation in the BaLiF$_3$ host.

A treatment similar to the one used for Ce-doped crystals was applied to the raw material in the preparation of Ce : Na-codoped crystals. We initially supposed that a higher concentration of sodium in the melt would enhance the Ce^{3+} incorporation in the host crystal. In our first attempt, we used a 1 mol% NaF : 0.5 mol% CeF$_3$ concentration. The crystal grown with this composition, was completely broken during the cooling process. A nonstoichiometric phase formed in the seeding resulted in the crystal cracking. As already mentioned, BaLiF$_3$ melts incongruently, and a single crystal must be grown from a nonstoichiometric melt to avoid other phase precipitation. Fig. 3 shows a DTA cooling curve of a BaF$_2$: LiF : CeF$_3$: NaF sample prepared with the same composition as the grown crystal. We note three

Table 1
Dopant concentration of the grown crystals, in the initial (1) and final (2) parts of the boules

Crystal	Melt concentration C_m (mol%)	Measured concentration C_s (mol%)	
		(1)	(2)
#1	Undoped	–	–
#2	1.0-Ce^{3+}	0.004	0.016
#3	0.5-Ce^{3+}	0.004	0.004
	1.0-Na$^+$	0.096	0.088
#4	0.5-Ce^{3+}	0.004	0.003
	0.75-Na$^+$	0.091	0.070

Table 2
Coordination number and ionic radius [8]

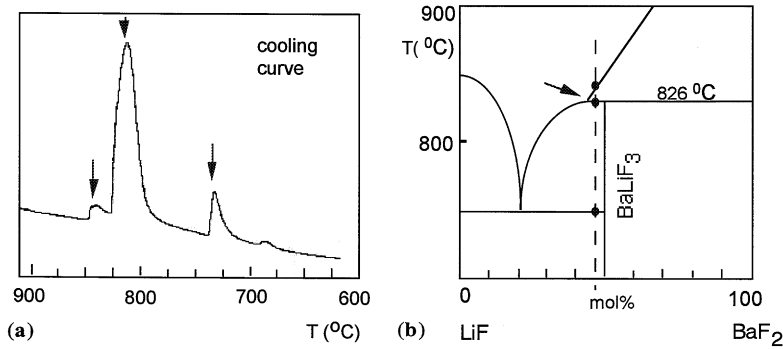| Ion	Coordination number	Ionic radius
Li$^+$	6	0.76
Ba^{2+}	12	1.61
Ce^{3+}	6	1.01
Ce^{3+}	12	1.34

Fig. 3. (a) DTA cooling curve of a $BaF_2 : LiF : CeF_3 : NaF$ sample prepared by mechanical mixing of the compounds; (b) schematic phase diagram of the $LiF–BaF_2$ system.

endothermic peaks, with onset temperatures of 841, 822 and 744°C. These peaks show clearly the occurrence of a deviation from the ideal composition for growth of $BaLiF_3$. As can be visualized from the schematic phase diagram shown in Fig. 3b, the first peak corresponds to the crystallization of a BaF_2-rich phase, the second peak corresponds to $BaLiF_3$ stoichiometric phase, and the third one to eutectic solidification. This variation of the ideal growth composition is related to the introduction of the two dopants in this system.

Fig. 4 shows a $Ce : Na : BaLiF_3$ grown with a lower concentration of Na in the melt (0.75 mol%). The boule is transparent, without macroscopic inclusions on the surface or inside. However, this crystal presented very low mechanical resistance compared to pure or Ce-doped $BaLiF_3$. It cracked easily during the cutting and polishing process. The sodium addition clearly degrades the mechanical integrity of the $BaLiF_3$ host.

The dopant concentrations were measured in the initial and final part of each crystal (Table 1). Because of the low Ce incorporation in the co-doped crystals, it was not possible to determine with high precision the effective dopant concentration. In the case of Na, we observed a slight decrease in concentration along the crystal. In any case, it was possible to observe in final part (2), in the two co-doped crystals, a lower Ce^{3+}-ion incorporation than in the singly doped one. We suppose that Na^+-ions,
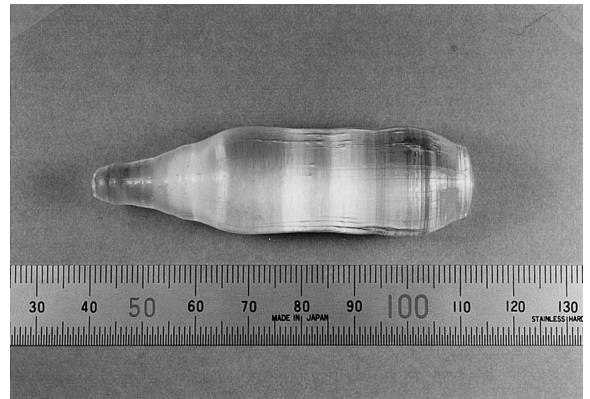

Fig. 4. $Ce : Na$-codoped $BaLiF_3$ single crystal (#4) as grown.

used as a charge-compensating impurity, probably compete with Ce^{3+}-ions for Ba^{2+} site occupancy in the host, reducing the total cerium incorporation.

Fig. 5 shows the absorption spectra in the IR and UV regions for pure and Ce^{3+} doped crystals. The IR measurement was performed with a 10 mm sample and the UV measurements with 1 mm samples. As with other fluorides, undoped $BaLiF_3$ presents a large transparency range (200–5000 nm). In the ultraviolet absorption spectra of $BaLiF_3 : Ce^{3+}$ we observed two absorption bands, the first centered at 238 nm and the other at 249 nm, in accord with previously reported results [4]. In fluoride crystals, free OH^- radicals present absorption bands in the region of 4000–3500 cm^{-1}; from
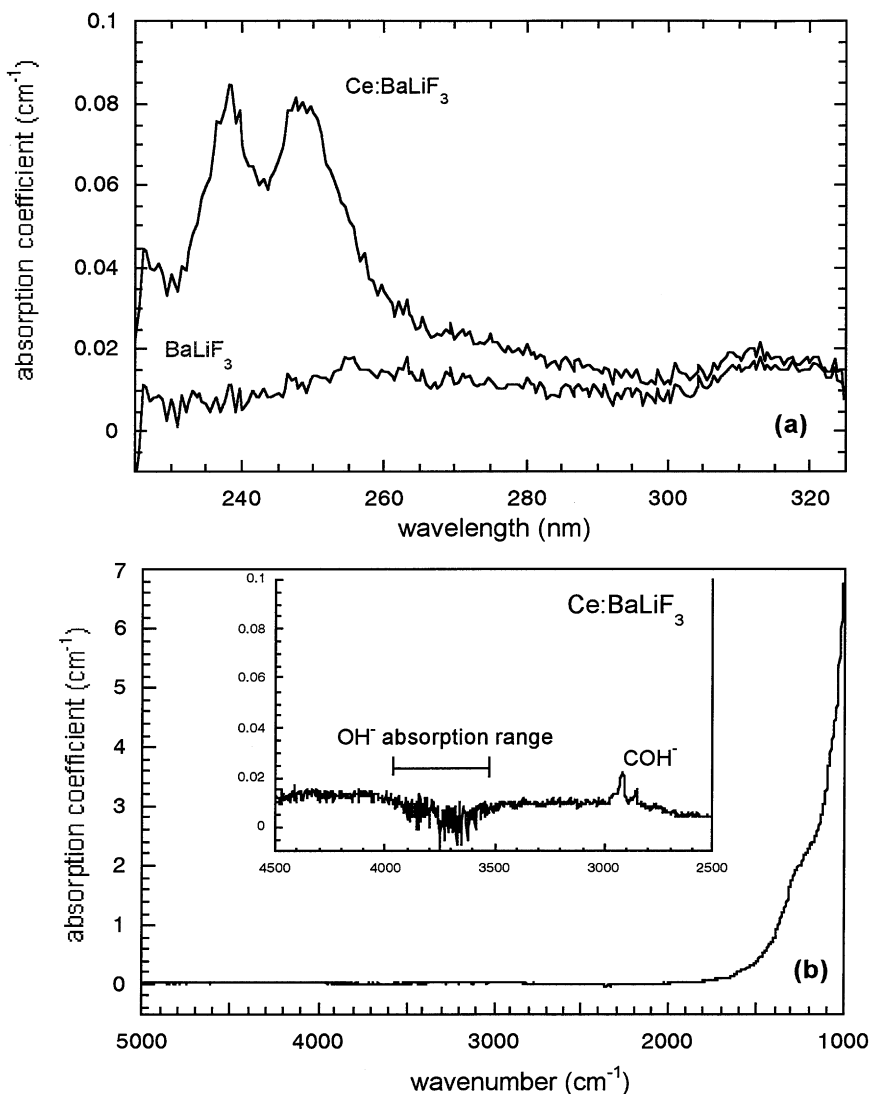
Fig. 5. Absorption spectra at room temperature: (a) UV spectrum of undoped and Ce-doped $BaLiF_3$ (sample size 1 mm); (b) IR absorption spectrum of Ce-doped $BaLiF_3$ crystal (sample size 10 mm).

Fig. 5b we can confirm that the CF_4 treatment eliminates all traces of OH^- impurities. Also seen in this figure are very small absorption bands in the range of 3000–2800 cm^{-1}. These bands were also observed in rare earth doped YLF crystals and were attributed to HCO^- [9], being associated with carbon contamination from the commercial fluorides.

In Fig. 6 we show the emission spectrum of the $BaLiF_3$: Ce crystal excited by the fourth harmonic of a Nd : YAG laser. A broad and structureless band from 300–400 nm was observed. The radiative lifetime was found to be 27 ns. The large emission linewidth makes the Ce : $BaLiF_3$ single crystals a potential source of coherent, tunable, near-ultraviolet radiation.
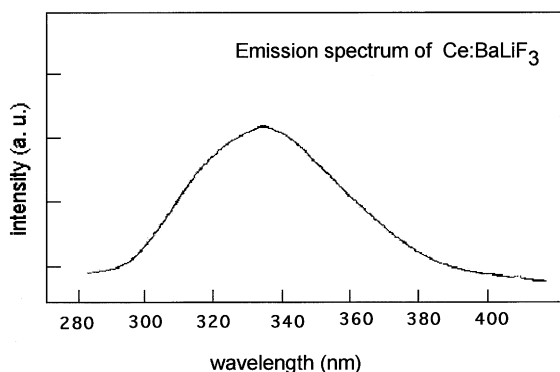
Fig. 6. Emission spectrum of Ce : BaLiF$_3$ single crystal.

4. Summary

We have studied the growth of Ce-doped and Ce : Na-codoped BaLiF$_3$ single crystals. Large and optically clear single crystals were grown by the Czochralski technique under a CF$_4$ atmosphere. The optical characterization of the grown samples showed high transparency, indicating no oxygen complex contamination. We observed a small Ce^{3+}-ion incorporation in the BaLiF$_3$ host attributed to the noncharge compensation. To improve the Ce^{3+} incorporation, we used Na as a charge-compensating impurity. However, Na$^+$ competes with Ce^{3+} for Ba^{2+} site occupation in the host, reducing even more the Ce incorporation. The Na addition also degrades the mechanical integrity of the BaLiF$_3$ host, resulting in very easy cracking of the crystals.

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