Progress in the crystal growth of Ce : colquiriites

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Abstract

The search for an efficient solidstate laser with tunable emission in the ultraviolet wavelength region has resulted in the growth and development of cerium-doped colquiriite crystals, such as $LiCaAlF_6$ (LiCAF) and $LiSrAlF_6$ (LiSAF). Unfortunately, the doping of LiSAF and LiCAF with Ce^{3+} introduces different variables into the growth of high optical quality crystals, due to the charge imbalance induced when this trivalent ion substitutes for the divalent site. Charge compensation with Na^+ tends to produce a more uniformly doped crystal with improved laser properties. Although preliminary research indicates that Ce : LiSAF may be the preferred material of the colquiriite hosts, Ce : LiCAF has also proved to be quite promising.

Keywords: Ultraviolet; Laser; Colquiriite; Charge compensation; Cerium; Solidstate

1. Introduction

The success or failure of a potential laser crystal doped with any ion depends on the crystal field, the size and charge of the site designated for substitution, as well as many certain details regarding the interaction of the impurity ion with the crystal lattice. Recently, there has been a great deal of interest in the doping of fluoride crystals of the colquiriite type with the cerium ion for the production of a laser emitting in the ultraviolet region [1, 2]. The crystal lattice of the colquiriites belongs to the space group D^3_{3d} with two formula units per unit cell and is derived from the Li_2ZrF_6 structures [3, 4]. Surrounded by fluorine ions, each of the three metal ions are located in octahedral sites,

which differ both in size and in charge. The cerium activator ion carries a 3 + charge, is 1.15 Å in ionic radius and has a $4f^1$ electron configuration. The size of the Ce^{3+} ionic radius has led researchers to postulate that any such ion dopant, such as Ce^{3+}, would preferentially substitute into the Sr^{2+}/Ca^{2+} sites (1.27 Å/1.14 Å), rather than the 0.67 Å Al^{3+} site. Even though the divalent sites are sufficiently large to accommodate the trivalent cerium ion, there is a charge imbalance which demands that compensation be present somewhere else in the lattice.

2. Crystal growth of Ce : LiSAF

The initial Ce : $LiSrAlF_6$ (Ce : LiSAF) boule produced at VLOC (formerly Lightning Optical Corporation) was grown with an oriented, a-axis

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Cr : LiSAF seed, using a Czochralski growth process, operating under weight control. The thermal profile of the furnace was determined based on a series of experiments for the optimization of the growth of Cr : LiSAF. This Ce-doped LiSAF boule, nominally 15 mm in diameter and 90 mm in length, contained heavy scatter and cracked regions, but the top 20 mm of length still did contain optically clear areas large enough to yield two pieces that were approximately $3 \times 3 \times 6$ mm in size. The crystal was grown from a stoichiometric charge, composed of commercially available high purity powders of CaF_2, LiF, SrF_2 and AlF_3. A cerium concentration of 1 at% in the melt was used in this growth run, which resulted in approximately 0.011 at% in the crystal [5]. Passive-loss measurements indicated that the sample had very low scatter losses of less than $0.1\%/cm^{-1}$. Subsequently, the growth rate was modified in an effort to eliminate the opaque growth and the cracking of the boules. These modifications produced Ce : LiSAF boules which were scatter-free, but severely strained.

During the course of our investigations, two series of boules were grown. The first involved a comparison of different doping levels in LiSAF and LiCAF ($LiCaAlF_6$). The second involved constant doping levels in the melt and comparisons between hosts and compensating ions. Results of Ce^{3+} doping levels and distribution coefficients are included in Tables 1 and 2. In order to calculate the doping percentage of Ce^{3+} ions in the LiSAF and LiCAF crystals, a few assumptions must be made. First, we assume that the Ce^{3+} ion substitutes only onto the Sr^{2+} site in LiSAF and onto the Ca^{2+} site in LiCAF, since the Al^{3+} site, with a radius of 0.67 Å, is too small to accommodate the Ce^{3+} ion (1.15 Å). EPR spectra taken by Dr. Larry Halliburton at West Virginia University indicate that, while multiple sites can be seen within the crystal for the Ce^{3+} ions, it is most likely that the Ce^{3+} ions are all at Sr^{2+} sites and that a local charge compensator is responsible for the unique nature of the various sites [6]. Previous wet chemistry research was carried out on various Ce : LiSAF and Ce : LiCAF samples to determine Ce^{3+} ion densities as a function of starting CeF_3 in the melt [5]. This ICP-MS analysis showed that typically less

than 13% of the Ce^{3+} in the melt was incorporated into the crystals. This can be justified by the fact that according to the charges and sizes of the available sites, there is no favorable site for cerium in the crystal lattice. Thus, the cerium ions will tend to be rejected from the crystal and remain in the melt. Since the measurement of Ce^{3+} content by spectroscopic determination of the peak Ce^{3+} absorption coefficient indicates that only a portion of the cerium in the cerium-only crystals is optically active Ce^{3+} when compared to the ICP-MS data, some of this cerium is believed to be of the other oxidation states [5]. To date, the nature of these states has not been determined, although it should be noted that when the crystals are codoped with Na^+ and cerium, the Ce^{3+} by ICP-MS and Ce^{3+} content via absorption measurements are essentially the same.

In well-behaved systems, the distribution coefficient and the segregation coefficient are identical. The distribution coefficient is a relative measure of the dopant density throughout the crystal

Table 1
Ce^{3+} doping and distribution coefficients in LiSAF and LiCAF

Boule number	CeF_3 at% in melt	Approx. at% Ce^{3+} in crystal	Distribution coefficient
95-3-3	1.0% in LiSAF	0.0110	0.4
95-2-2	1.5%	0.0105	–
95-6-9	2.9%	0.0079	0.2
94-6-7	1.4% in LiCAF	0.0089	1.3
95-6-6	2.1%	0.0144	1.1
95-6-8	3.5%	0.0045	1.6

Table 2
Ce^{3+} doping and distribution coefficients in codoping

Boule number	CeF_3 at% in melt	Approx. at% Ce^{3+} in crystal	Distribution coefficient
94-6-24	2% in LiSAF	0.0220	0.48
94-6-23	2%Ce:2%Na	0.0235	1.25
95-7-4	2%Ce:4%Na	0.0200	0.85
94-6-27	2%Ce:6%Na	0.0155	4.25
94-6-1	2%Ce:2%Zn	0.0190	–
94-6-29	2% in LiCAF	0.0141	1.4
95-6-2	2% in LiCAF	0.0247	1.3

according to the formula $c = c_0 k(1 - p)^{(k-1)}$, where c_0 is the dopant concentration, k is the distribution coefficient, p is the fraction of the total grown crystal volume, and c is the dopant concentration in g. For our purposes, since the Ce^{3+} concentration in the crystal is so much less than the starting dopant density, the distribution coefficient will be considered only as a relative Cr^{3+} distribution in the crystal, and c_0 is taken as an arbitrary constant. The absorption coefficients calculated from absorption spectra of samples from the top and bottom of the different boules, were used to determine the distribution coefficients. The resulting calculated values for Ce:LiCAF were fairly consistent, ranging from 1.1 to 1.6. This indicates that the Cr^{3+} concentration is lower at the bottom of the boule than at the top. In essence, the distribution coefficient in Ce:LiSAF is less than unity, since the Cr^{3+} concentration is lower at the top of the boule than at the bottom. For Ce:LiSr$_{0.8}$Cr$_{0.2}$AlF$_6$ (Ce:LiSCAF), the coefficient was approximately 1.3, which is comparable to that of Ce^{3+} in LiCAF. Surprisingly, the sample compensated with 4% NaF also shows a distribution coefficient less than unity, while the sample compensated with 2% NaF has a distribution coefficient greater than unity. This implies that there may be an optimum ratio of CeF$_3$: NaF in order to achieve uniform doping in the crystal. The extremely high distribution coefficient obtained for the 2% MgF$_2$ co-doped sample indicates that very different conditions are present in this crystal, which was further verified by its absorption spectra.

Although LiSAF and LiCAF belong to the same structural family [3, 4], the growth parameters and techniques to grow each crystal differ substantially. The first difficulty encountered in the growth of LiCAF is that, due to a melting point approximately 50°C higher than that of LiSAF, there is a considerable amount of lithium and aluminum loss from the melt due to evaporation. This causes the melt to deviate from its initially stoichiometric condition. In addition, the evaporation causes an instability in the weight-controlled growth system in the laboratory, due to the accumulation of the excess evaporated material on the seed rod. Typically, the interior quality of a boule is directly related to its diameter control. Another problem

with LiCAF is the particulate scatter and planes formed throughout the grown boules. These defects have been observed in Cr:LiCAF and are also present in the Ce-doped crystals. Optical examination of the grown boules revealed a series of parallel planes running across the diameter of the boule. These planes not only have a detrimental effect on the wavefronts, but also are large enough to scatter the probe laser beam, making the majority of the material in the LiCAF boules less than ideal as laser material. The elimination of the particulate defects in LiCAF has been previously studied to some extent [7]. It has been found that by annealing grown boules of Cr:LiCAF, the amount of particulate scatter in the boule can be reduced. While the removal of this particulate scatter by annealing has been tested on a few boule sections of Cr:LiCAF at VLOC, the elimination of the planes in Ce:LiCAF has not yet been investigated. While there seem to be many negative growth issues concerning Ce:LiCAF, one favorable characteristic is lower as-grown stress, resulting in very low tendency to crack.

3. Spectroscopy and laser results

Absorption measurements were conducted on samples from all of the boules of Ce-doped colquiriites using a Cary 3 Spectrophotometer. A pair of UV-grade calcite polarizers were inserted in the reference and sample beams, and were held fixed, polarizing the beam vertically for the duration of the experiment. Absorption measurements were taken on boule slices from the cores at the top of the boule and from the constant diameter section near the bottom of the boule. A previous measurement of a Ce:LiSAF sample with 1% CeF$_3$ in the melt showed a peak with a maximum absorption coefficient of approximately 7 cm^{-1} at 266 nm for the π-polarization [8].

The Ce-doped sample, which had an initial 2% CeF$_3$ in the melt, had a peak absorption coefficient of approximately 14.5 cm^{-1} at 266 nm in the π-polarization, which is double than that measured in the initial 1% in the melt Ce:LiSAF sample. This indicates that there is a linear relationship between the amount of cerium in the starting melt and the

amount of Ce^{3+} in the crystal in Ce : LiSAF boules. It was also noted that the σ-polarized spectrum was shifted toward slightly longer wavelengths relative to the π-polarization and had an additional foot in the 255 nm region. Near the bottom of the boule, as the strontium concentration in the melt decreases, more cerium is incorporated into the crystal lattice.

Charge compensation with Na^+ by substitution into the Sr^{2+} site is perhaps the most logical step in order to achieve a higher cerium concentration in the crystal. An ionic radius of 1.15 Å should allow sodium to easily substitute into the strontium site to compensate for the excess positive charge in the lattice, resulting from the Ce^{3+} incorporation into the Sr^{2+} site. With 2% NaF and 2% CeF_3 in the starting charge, the co-doped sample had an absorption coefficient which was more than 20% higher in the σ-polarization than that observed in the 2% Ce boule. The σ-polarized absorption spectrum was also red-shifted as compared to that of the 2% Ce boule. Finally, the cerium distribution was nearly uniform from the top to the bottom of the boule.

The LiSAF structure consists of alternating layers of Al–Li and Sr ions, separated from each other by a layer of fluorine ions. Since the Al^{3+} and Li^+ ions are closer to the Sr^{2+} ions than other neighboring Sr^{2+} ions, the substitution of a divalent ion for Al^{3+} should be more effective for charge compensation. The selection process for an appropriate compensator is complicated by the fact that the divalent ion must be small enough to fit into the 0.67 Å aluminum site to avoid an undesired substitution directly into the strontium site. Magnesium was investigated as a possible charge-compensating divalent ion for substitution into the Al^{3+} site. Mg^{2+} is electronegative and ionic, however, with an ionic radius of 0.85 Å, it would have to enter the aluminum site with nearly a 30% size mismatch. The absorption data indicates that doping with magnesium may induce the presence of multiple sites for the cerium ion. The amount of Ce^{3+} incorporated into the boule is less than in the singly CeF_3-doped boule, and the Ce^{3+} concentration decreases as the boule grows.

A final growth run with Zn^{2+} as the compensating ion, intended for substitution into the Al^{3+} site, was attempted. Zinc is more covalent than magne-

sium and less electronegative, making it more similar to aluminum. Although the nature of the site may be more suitable for Zn^{2+}, the 0.89 Å ionic radius of zinc may cause more problems with incorporation into the aluminum site. Since only a small crystal could be produced, preliminary absorption measurements were only taken on a sample from the cone of the 2% Ce, 2% Zn co-doped boule. The peak absorption coefficient in the π-polarization in the co-doped sample was nearly 25% lower than that in the top of the 2% Ce boule.

A single laser resonator was used to compare 2% Ce : LiSAF, 2% Ce : LiCAF and 2% Ce, 2% Na:LiSAF crystals when pumped at room temperature at 266 nm, using an output coupler with 30% transmission at the laser output wavelengths. The 2% Ce : LiSAF sample shows a 16.8% slope efficiency at 290 nm with an absorbed pump energy threshold of 0.09 mJ. For 2% Ce : LiCAF, the threshold was 0.1 mJ, which could be attributed in part to the high scatter loss in the sample and the lower absorption efficiency at 266 nm. However, the slope efficiency was 25.8%, nearly 60% higher than the efficiency for the Ce:LiSAF system. The 2% Ce, 2% Na : LiSAF sample exhibited the lowest threshold of the three at 0.05 mJ, and the highest efficiency, at 33.1%.

4. Conclusion

Cerium-doped LiSAF may soon be incorporated into an efficient, solid-state laser system with tunable, broad-band emission in the ultraviolet region. However, before this can happen, the Ce : LiSAF material must be thoroughly investigated and characterized. A growth technology must be developed through which a variety of doping concentrations and laser rod sizes may be achieved.

The initial research conducted at VLOC, Division of II–VI Incorporated indicates that the running atmosphere, melt–solid interface shape, and growth rate are all critical in order to obtain high optical quality Ce : LiSAF boules. Co-doping with singly charged ions, such as Na^+, may assist in the incorporation of more Ce^{3+} into the lattice. Another benefit of Na^+ co-doping is to maintain a uniform Ce^{3+} doping concentration throughout

the bond length. The addition of divalent ions such as Mg^{2+}, into the starting charge may promote the formation of multiple cation sites. Recent advances in Ce:LiSAF and Ce:LiCAF crystal growth and material characterization indicate that high-purity Ce:colquiriite boules with high yields should be commercially available in the near future for incorporation into systems for applications including atmospheric remote sensing, pollution monitoring, and atmospheric spectroscopy.

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