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Journal of Crystal Growth 225 (2001) 445–448

JOURNAL OF
**CRYSTAL
GROWTH**

www.elsevier.nl/locate/jcrysgr

Material and laser characterizations of intermediate compositions of $\text{Ce:LiSr}_x\text{Ca}_{1-x}\text{AlF}_6$

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Abstract

The development of solid state tunable lasers in the ultraviolet region would have a wide range of applications, including atmospheric remote sensing, atmospheric spectroscopy and pollution monitoring. The first work with Ce:LiCAF was published in 1993, with subsequent reports on favorable results with Ce:LiSAF . While the optical quality of Ce:LiSAF is superior, it suffers from solarization. In contrast, Ce:LiCAF shows minimal solarization and higher efficiencies, even with the typically high-scatter materials available. This presentation will summarize the crystal growth and material characterization of a series of colquiriite crystals with various Sr:Ca ratios. Based on these results, in addition to laser measurements, an optimum composition of $\text{Ce:LiSr}_x\text{Ca}_{1-x}\text{AlF}_6$ will be determined. © 2001 Elsevier Science B.V. All rights reserved.

PACS: 39.30; 78.40; 61.66.F; 81.10

Keywords: A1. Crystal structure; A1. Phase diagrams; A2. Czochralski method; B1. Inorganic compounds; B1. Lithium compounds; B3. Solid state lasers

1. Introduction

Potential private-sector commercial markets for the cerium-doped colquiriites can be broken down into two main categories. The first would be as a new add-on component for research scientists who already have fourth harmonic (266 nm) laser systems in their laboratories. The addition of this component would allow generation of tunable laser radiation in the ultraviolet region of the spectrum. The second would be as a tool for the environmental monitoring industry. Many chemi-

cal species, such as ozone, SO_2 , O_3 , toluene, benzene, NO_2 , ClO , and xylene, could be accessed, if a highly efficient, broadly tunable, all-solid-state ultraviolet system were available. Additionally, there are several government-based markets for tunable Ce-doped colquiriite solid state lasers. Some of the non-classified applications include anti-ship missile defense devices, shipboard threat warning systems, short-range urban communication systems in the solar blind region of the ultraviolet, and covert communications systems to be utilized during in-flight fueling by Navy and Air Force pilots. There is also a need for a moderate energy source (10–100 mJ, 10 Hz, 280–320 nm) for standoff detection of biological warfare monitoring and detection. Tryptophan, which is

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a chemical complex typically used to carry biological agents in the battlefield, has a broad absorption from 280–310 nm. Finally, 290 nm sources would be useful for ground-based line-of-sight monitoring of chemical pollutants from refineries, power plants, and smokestacks.

Cr:LiSr_{0.8}Ca_{0.2}AlF₆ was first reported as a potential tunable laser in the visible region in November 1992 [1]. In this report, it was noted that LiSAF exhibits a weaker crystal field strength, resulting in a larger cross section than Cr:LiCAF. The LiCAF host, however, has more favorable mechanical properties. The mixed crystal reportedly had spectroscopic and lasing properties similar to LiSAF and mechanical properties more typical of LiCAF. In the case of cerium doping of the colquiriites, Ce:LiSAF grows readily with fewer material defects. Conversely, Ce:LiCAF crystals are usually grown with scatter sites, resulting in a “foggy” appearance, even to the naked eye. Surprisingly, even though the LiCAF crystals are sub-optimal in appearance, their laser performance is superior. The purpose of this work is to determine which Sr:Ca ratio in Ce, Na:LiSr_xCa_{1-x}AlF₆ will produce a solarization-free, high efficiency laser material.

2. Crystal growth

2.1. Crystal growth of samples

A series of seven crystals was grown for comparison of the growth and material characteristics of this system. 0.5 mol% CeF₃ and 0.5 mol% NaF codoping was used for the seven growth runs, which included Sr:Ca ratios of 100:0, 80:20, 65:35, 50:50, 35:65, 20:80, and 0:100. The use of Na⁺ as a potential charge compensator has previously resulted in crystals with the least amount of cracking, more uniformity in Ce³⁺ doping, and a lower tendency for solarization. While many of these crystals cracked heavily, some small, clear sections were obtained for spectroscopic measurements. The reasons for cracking were mainly due to seed misorientation and poor seeding. The 0.5%Ce, 0.5%Na:LiSr_{0.2}Ca_{0.8}AlF₆ and LiSr_{0.8}Ca_{0.2}AlF₆ boules were grown success-

fully and produced uncracked sections approximately 14 mm in diameter and 30 mm in length.

2.2. Investigation of phase diagram

In previous work, it was found that slower growth rates were preferable for lower stress growth of the Ce-doped colquiriites. This knowledge allowed the uncracked growth of other intermediary crystals, with the only limitation being the success in finding the dipping temperature. The phase diagram of the LiSAF–LiCAF systems has been published previously [1]. In this referenced work, it was stated that LiSr_{0.8}Ca_{0.2}AlF₆, the composition at which there is a minimum temperature point on the phase diagram, was the only intermediary composition that was congruent in nature and produced crystals that were uniform and uncracked. The growth of Cr³⁺-doped crystals, however, is different from Ce³⁺-doped crystals, with the main difference being the size of the cerium ion. Ce³⁺ is significantly larger than Al³⁺ and is closer to the size of the Sr²⁺ ion. However, substitution into the Sr²⁺ site results in a charge imbalance.

Due to the near-identical growth conditions of the series of Ce:colquiriites grown for this work, it is possible to compare dipping temperatures to plot the rough shape of the LiCAF/LiSAF phase diagram. In order to verify the shape of the phase diagram for the LiSAF/LiCAF system, crystalline samples from the seven different grown boules were collected and sent to II–VI, incorporated (Saxonburg, PA) for differential thermal analysis (DTA). The values obtained for melting temperatures from the differential thermal analysis, when plotted, generally followed the published phase diagram. The plotted solidification temperatures, however, followed the dipping temperatures. The minimum dipping temperature occurred at an extrapolated Sr:Ca ratio of approximately 70:30, rather than at 80:20 as indicated in the published phase diagram.

2.3. Analysis of chemical composition

Three-gram samples of crystals of the seven compositions were sent to Shiva Technologies, Inc.

(Syracuse, NY), where they were analyzed using a VG9000 GDMS mass-spectrometer. According to the results, the strontium concentration increases linearly from LiCAF to LiSAF, as expected. The lithium concentration varies, with highest concentrations occurring for LiCAF and in the Sr:Ca=50:50 to 80:20 range. Aluminum tends to increase in concentration from LiSAF to LiCAF. There does not seem to be a clear, simple structural explanation for these variations. Additionally, the cerium concentration remains nearly constant for all of the samples, except for a large peak at the Sr:Ca=80:20 composition. These data seem to indicate that a similar amount of Ce^{n+} is incorporated into the crystal regardless of starting Sr/Ca ratios. Another interesting feature in the data was the dramatic increase in sodium concentration toward the Sr:Ca=0:100 composition. This could play a role in the charge compensation for Al^{3+} , if it is substituting in some manner for Ca^{2+} in LiCAF.

3. Absorption spectroscopy

Absorption measurements for this research were conducted on samples from seven of the boules of Ce-doped colquiriites using a Cary 5 spectrophotometer. Two Glan Taylor prism polarizers were inserted in the reference and sample beams and were held fixed, polarizing the beams vertically for the duration of the experiment. The prisms and sample holder were adjusted with an alignment beam and a baseline scan was performed to eliminate characteristic variations in absorption due to the system. Before performing the absorption measurements, the orientation of the *c*-axis in the samples was determined by viewing the extinction of the light between crossed polarizers. Scans were taken with the *c*-axis in vertical and horizontal orientations. The original samples from the Sr:Ca=80:20 boule were significantly off-axis. New samples are being fabricated for measurement. Additionally, the Sr:Ca=100:0 samples were polycrystalline and valid polarized spectra could not be obtained. This crystal is in the process of being regrown, and revised data should be available in the future.

Several observations were made from the data obtained from the top and bottom samples of the five remaining boules. First, in the LiCAF host the distribution coefficient of Ce in the crystal is greater than unity. That is, the concentration at the top of the boule is greater than at the bottom of the boule. As the Sr:Ca ratio changes from 0:100 to 50:50, the distribution becomes much less than unity. Second, the magnitude of the absorption coefficient for an identical amount of dopant in the melt changes with the variation of the Sr:Ca ratios. There is also evidence indicating that the 50:50 composition may result in the highest absorption coefficient for a given dopant level in the melt. Finally, there is some structure in the absorption spectra occurring in the 250 nm range. It is either due to band edge absorption in the fluoride lattice, or impurity ions measurable only in the UV.

It is interesting that, while the absorption curves show a definite increased absorption for the Sr:Ca ratio at 50:50, the concentration of cerium in the crystal, per the GDMS data, does not change markedly from LiSAF to LiCAF. The only exception is a large peak at the Sr:Ca=80:20 composition. A comparison of these data indicates that a similar amount of Ce^{n+} is incorporated into the crystal regardless of starting Sr:Ca ratios. However, the Sr:Ca=50:50 composition may result in the maximum quantity of optically active Ce^{3+} ions incorporated in the crystal, which give rise to the absorption peak at 266 nm.

4. Laser testing

Slope efficiencies have been measured for Ce:LiSAF, Ce:LiSr_{0.8}Ca_{0.2}AF and Ce:LiCAF. While, at a given pump energy, the output energy for LiSr_{0.8}Ca_{0.2}AF [2] is lower than for LiCAF [3], it is higher than that for LiSAF [3]. The tuning range for Ce:LiSAF [3] is from 283 to 310 nm and from 282 to 313 nm for LiCAF [3]. The maximum output energy for LiCAF, however, was approximately 2.5 times higher than for LiSAF (1.65 mJ vs. 0.65 mJ). In comparison, the tuning range for Ce:LiSr_{0.8}Ca_{0.2}AF [2] spanned from 286 to 300 nm with a peak output energy of 1.1 mJ.

New samples with various Sr:Ca ratios are currently being fabricated for laser testing.

5. Summary and conclusion

During the course of this work, the growth of the cerium and sodium codoped colquiriites was investigated. Historically, Ce:LiSAF can be grown with a very high optical quality and is very sensitive to thermal gradients and growth rates. Ce:LiCAF, conversely, is less sensitive to gradients and is extremely difficult to grow with a high optical quality. Initial analysis of the LiSAF/LiCAF system indicates that the compositional aspects of the system are not trivial. Additionally, it is feasible to produce high quality crystals of mixed compositions with favorable laser characteristics. As far as performance is concerned, LiCAF currently stands out as having the highest efficiency and broadest tuning range. Through continued research and experimentation, an optimized composition of the cerium-doped colquiriites can be determined, which

could readily be incorporated into an all-solid-state-laser system for a variety of applications.

Acknowledgements

The authors wish to recognize that the work reported herein was funded through the Naval Air Systems Command in the form of a Phase II SBIR contract #N00019-96-C-2058. In conjunction with this Phase II SBIR research program, Vida Castillo is pursuing her dissertation research for her Ph.D. program in Applied Physics at the University of South Florida.

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