INVESTIGATION OF THE LiCaAlF₆:Eu SCINTILLATOR FAMILY FOR NEXT-GENERATION NEUTRON DETECTION

OR12-LiCaAlF-PD3Yj

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Date: October 1, 2013
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1. INTRODUCTION

LiCaAlF$_6$:Eu (LiCAF:Eu) is a promising scintillator that possesses several fundamental advantages over CsLiYCl$_6$:Ce (CLYC). This scintillator, however, is just one member of a much broader family of materials known as colquiriites, designated as LiMe$^{II}$Me$^{III}$F$_6$, where Me$^{II}$ and Me$^{III}$ can be any number of divalent and trivalent cations, respectively. The LiCAF system has incredible potential for a wide variety of substitutions in the Me$^{II}$ and Me$^{III}$ sites, and its members are recognized as excellent hosts for luminescing activator dopants (e.g., Ce$^{3+}$, Eu$^{2+}$, Cr$^{3+}$, Pb$^{2+}$ and Yb$^{2+}$) in order to tune the nuclear and luminescence performance in several ways. We intend to fully exploit this versatility by investigating the effects of substituting other alkali, alkali-earth, rare-earth, Group III, and Group XIII elements. The objective of this work is to explore the colquiriite system of scintillating materials, most notably LiCaAlF$_6$:Eu, to identify and characterize new scintillators with improved scintillation performance, simplified crystal growth, and tunable neutron and gamma sensitivities.

2. OVERVIEW OF PROJECT PROGRESS

FY 2013 began with the Czochralski crystal growth system inoperable due to facilities issues, but progress in modeling the LiCAF family of scintillators forged ahead very well. A number of candidate compositions were identified through modeling as being promising. In Q2, the Czochralski system was brought online, and significant progress was quickly made in growing and characterizing well-known LiCAF compositions. In that short time frame, a number of large single-crystalline samples were grown, characterized, and shown to align with previous results produced by others. Unfortunately, by the end of Q2 we faced a shortage of raw materials from all available vendors. We then tried to reuse materials as much as possible, but fluorine vapors corroded the weighing head in the Czochralski system, rendering it again inoperable at the beginning of Q3. Fortunately, we had begun experimenting with Bridgman growth as an alternative path to progress near the end of FY 2012. Roughly a year after beginning the Bridgman work, we were able to successfully grow samples of LiCAF via the Bridgman route. Hence, while the Czochralski system has been problematic to say the least, we have developed an alternative crystal growth method through the Bridgman method. Despite being fairly immature in comparison to Czochralski, the Bridgman method now developed for LiCAF does provide an interesting, likely less expensive alternative for the production of LiCAF.

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Fig. 1. Large single-crystal samples of LiCaAlF$_6$:Eu grown via Czochralski.
3. RESULTS, DISCUSSION, AND CONCLUSIONS

Progress was retarded by a number of factors as described above; however, some critical steps forward were achieved. A bulleted list of key points of progress is provided below.

- Most notably, we have now developed a method for encapsulating the melt during Bridgman crystal growth so as to contain the vapors above the melt to both inhibit corrosion of system components and to maintain melt stoichiometry. This key advancement has enabled the growth of LiCAF compounds via a new growth technique not previously performed.
- A number of novel activation schemes were modeled for LiCAF, and two low-risk and three moderate-risk promising alternatives were identified.
- The Mg and Sr analogues of LiCAF were modeled, and their thermal stability was established relative to the Ca analogue. The Mg analogue appears to be quite promising and is as yet unexplored.
- The synthesis process for LiCAF was refined and confirmed to produce very good, phase-pure starting material.
- The process for growing large single crystals of LiCAF via Czochralski was developed and confirmed to produce good results.
- The process for growing acceptably large single crystals of LiCAF via Bridgman was developed and confirmed to produce acceptable results, albeit at a lower quality than those from Czochralski at the moment.
- A number of crystals produced via Czochralski were characterized and confirmed to behave similarly to results previously published on similar compositions. This point of progress established that our synthesis and growth processes produce material on par with those previously published.
- Two samples of LiCAF produced via the Bridgman method were characterized and found to behave somewhat differently than expected. While it is not yet understood why the dynamics of the light emission differed, our results offer us a great opportunity for further investigation through modeling and further characterization.
- A number of refinements were made to the characterization systems to improve accuracy and speed.

4. PATH FORWARD

At this point, we have repaired the Czochralski system, modified components to inhibit corrosion, and are beginning to bring the system back online. Bridgman growth continues, although samples are not yet of the quality produced by the Czochralski system. As such, we have planned to use the Bridgman method as a production method for first-tier candidate characterization and selection. Candidate compositions yielding promising results from the Bridgman method will then be grown via Czochralski to obtain higher quality samples for more extensive candidate characterization.
Although we have now solved many of the rather substantial hurdles encountered with the growth of LiCAF compounds, we are unfortunately behind schedule. We have therefore reduced the breadth of the investigation by focusing on the candidate compositions that appear most promising, as we simply cannot realistically maintain the breadth of the investigation within the time remaining. Based on modeling efforts, LiMgAlF$_6$ appears to be quite promising and our work will be focused there.

5. PRESENTATIONS AND PUBLICATIONS