ACCELERATED DISCOVERY OF ELPASOLITE SCINTILLATORS

SL12-ElpasoDisc-PD2Jh

PI: F. P. Doty, Sandia National Labs
Contributors: Pin Yang and Xiaowang Zhou

1. INTRODUCTION

Elpasolite scintillators are a large family of halides which includes compounds reported to meet the NA22 program goals of <3% energy resolution at 662 keV[1]. This work investigated the potential to produce quality elpasolite compounds and alloys of useful sizes at reasonable cost, through systematic experimental and computational investigation of crystal structure and properties across the composition space. Discovery was accelerated by computational methods and models developed previously to efficiently identify cubic members of the elpasolite halides, and to evaluate stability of anion and cation exchange alloys.

2. SELECTION OF COMPOSITIONS

The rare earth elpasolite halide system conforms to $A_2BB'X_6$, where A and B represent monovalent cations, B' represents trivalent cations such as lanthanides, and X represents halogen ions . This system comprises over 1,400 compounds and infinite possible alloy compositions, many of which have unstable or highly distorted structures causing difficulties for low cost manufacturing. Therefore, compositions were selected for study using the embedded ion method (EIM) to predict crystal structures in this system.

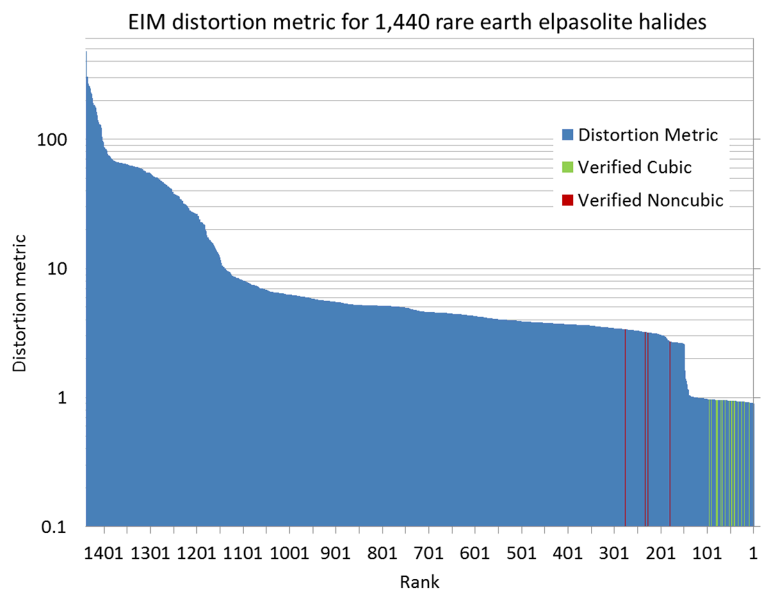

Figure 1 Embedded Ion Method for structure prediction validated by XRD on samples prepared in-house. Distortion metric $\leq$ 1 for all known cubic elpasolites.

[1] J. Glodo, et al., IEEE Transactions on Nuclear Science, 58:333-338, 2011.

EIM identifies all of the cubic elpasolite halides, and enables prediction of properties and stabilities of mixed elpasolite crystals. Figure 1 illustrates the efficacy of this approach by plotting 1,440 compositions in our data base ranked in order of a calculated distortion metric. This enabled unstable and highly distorted structures to be eliminated from consideration, and robust cubic composition to be identified prior to experimental studies.

3. RESULTS, DISCUSSION AND CONCLUSIONS

A number of positive findings were reported during this project, including discovery of a new scintillating elpasolite compound, synthesis and characterization of a large number of new alloys, and sensitization of light yield by partial exchange of La^{3+} with Gd^{3+}. But the most important results of this work are the identification of decomposition reactions for elpasolite compounds, including those previously reported to be stable; and demonstration of an alloy stabilization approach to suppress decomposition, and improve performance and manufacturability.

We reported that inhomogeneity and poor optical quality are often observed in different regions of single crystal elpasolites grown from the melt. Commonly, the first-to-freeze region is cloudy, transitioning to a relatively clear middle region, while the last-to-freeze region may be cloudy to opaque. We have discovered the cause of this degradation: Many $A_2BB'X_6$ compounds decompose partially during growth to form undesired phases or light-scattering particles which degrade scintillation properties. For example, the important gamma scintillator $Cs_2LiLaBr_6$ decomposes according to the reaction:

$$2\ Cs_2LiLaBr_6 \Rightarrow Cs_3La_2Br_9 + 2\ LiBr + CsBr$$

The $Cs_3La_2Br_9$ phase was detected by differential scanning calorimetry (DSC) in a cloudy section of a crystal grown in our lab, and positive identification of the structure was made using powder x-ray diffraction (XRD). Many such phases were identified in elpasolite compounds and their cerium-activated alloys. A partial list of elpasolites and light-scattering decomposition products we identified is tabulated below:

Table I

Elpasolite	**Second phases detected by XRD**
$Cs_2NaCeBr_6$	Cs_3CeBr_6
Cs_2LiYCl_6	Cs_3YCl_6
$Cs_2LiGdCl_6$	Cs_2GdCl_6
Cs_2NaScI_6	$Cs_3Sc_2I_9$, $Cs_3Sc_2I_6$
$Cs_2NaGdBr_6$	$Cs_3Gd_2Br_9$
$Cs_2LiGdCl_6$:Ce3+	Cs_3GdCl_6
$Cs_2NaGdBr_6$:Ce3+	$Cs_3Gd_2Br_9$
$Cs_2LiLaBr_6$:Ce3+	$Cs_3La_2X_9$

A major finding of this work is that these reactions can be suppressed by alloy stabilization. Figure 2 is a set of photos showing dramatic improvement for an elpasolite scintillator; the unstabilized specimen contains light-scattering decomposition products, whereas the stabilized specimen is water clear, and shows practically no scattering. Alloying also produced changes in the photoluminescence quantum efficiency, and a substantial improvement in the energy resolution for the 662 keV gamma spectrum. We anticipate that, when optimized, this breakthrough will enable higher yield, lower cost, and improved performance of many scintillators for gamma ray spectroscopy.

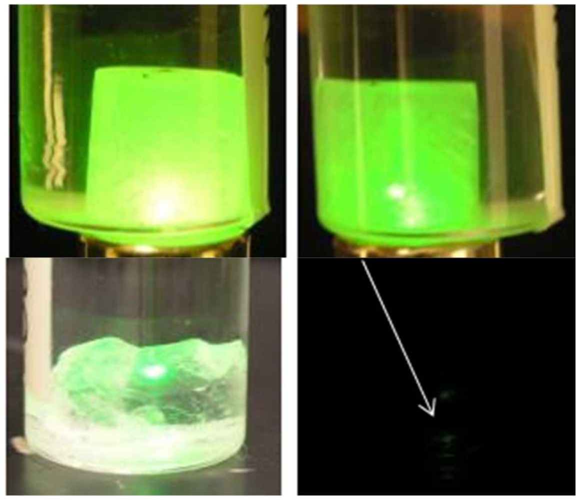

Figure 2 Light scattering is eliminated in Cs2NaCeBr6 by suppressing decomposition. Top: Cs2NaCeBr6 crystal illuminated from below with green laser and room lights on (left), off (right). Bottom: stabilized Cs2NaCeBr6 alloy; white arrow indicates position of the laser beam.

Publications

Crystal Growth and Scintillation Properties of Cs2NaGdBr6:Ce3+, Pin Yang, Xiaowang Zhou, Haoran Deng, Mark A. Rodriguez, Patrick L. Feng, Edgar V. D. van Loef, Kanai S. Shah, and F. Patrick Doty, IEEE TRANSACTIONS ON NUCLEAR SCIENCE, VOL. 60, NO. 2, APRIL 2013.

Optical Spectroscopy and Scintillation Properties of a Cerium Activated Cs2NaYBr6, 2014 SORMA Symposium on Radiation Measurements and Applications held June 8-12, 2014 in Ann Arbor, MI.

Isovalent Substitution in Elpasolite Halide Scintillators, Pin Yang, Marlene Bencomo, F. Patrick Doty, Xiaowang Zhoul, Mark Andrew Rodriguez, 2014 SORMA Symposium on Radiation Measurements and Applications held June 8-12, 2014 in Ann Arbor, MI

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