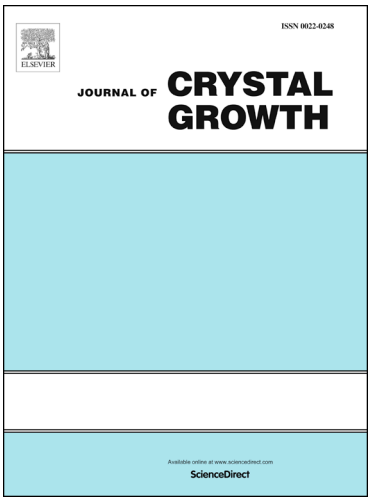

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Crystal Structure and Thermal Expansion of $CsCaI_3$:Eu and $CsSrBr_3$:Eu Scintillators

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Abstract

The distorted-perovskite scintillator materials $CsCaI_3$:Eu and $CsSrBr_3$:Eu prepared as single crystals have shown promising potential for use in radiation detection applications requiring a high light yield and excellent energy resolution. We present a study using high temperature powder X-ray diffraction experiments to examine a deleterious high temperature phase transition. High temperature phases were identified through sequential diffraction pattern Rietveld refinement in GSAS II. We report the linear coefficients of thermal expansion for both high and low temperature phases of each compound. Thermal expansion for both compositions is greatest in the [001] direction. As a result, Bridgman growth utilizing a seed oriented with the [001] along the growth direction should be used to mitigate thermal stress.

Keywords: A1. X-ray Diffraction; B2. Bridgman Technique; B1 Halides; B2 Scintillator Materials

Introduction

In recent years, much research has been focused on the development of novel scintillator materials suitable for gamma ray spectroscopy for national security applications. A large part of this effort has been focused on metal halide compositions that can be grown from the melt in relatively large sizes. Compositions such as $LaBr_3$:Ce and SrI_2:Eu are currently the top performers, with high light yields and excellent energy resolutions [1, 2]. Many of these compositions are grown via the vertical Bridgman method, yielding single crystals up to 2 inches in diameter [3, 4]. However, there are challenges in the development of metal halide crystals; for example, the majority of the halide scintillators are hygroscopic. As a result, sealed quartz ampoules are used during growth to prevent exposure to the atmosphere. One unintended side effect is the constriction on the crystal during heating and cooling, which can lead to stresses and cracking due to thermal expansion and contraction. Rapid changes in temperature, which detectors deployed in the field will undergo, can also induce cracking in grown crystals due to thermal stress. In order to better understand these properties, the thermal expansion coefficients have been calculated for crystals such as SrI_2, $CsCe_2Cl_7$, and Lu_2SiO_5 [5-7] via high temperature powder X-ray diffraction (XRD).

National security applications require large crystals with uniform optical quality. Two potential compositions that have been studied at the University of Tennessee are $CsCaI_3$:Eu and $CsSrBr_3$:Eu [8, 9]. These materials show promise for gamma ray spectroscopy, with light yields of 40,000 ph/MeV and energy resolution of 4 % and 5% at 662 keV, respectively. Both compositions are distorted perovskites with cloudy appearances due to solid-to-solid phase transitions [10-12]. Previous work has shown that eliminating phase transitions yields superior crystals; for instance, substituting some of the iodine in $CsCaI_3$:Eu suppresses the phase transition to below room temperature, resulting in extremely transparent crystals. Both compounds crystalize into a previously unknown phase, and transform into room temperature orthorhombic *Pnma* phases at ~250°C [13, 14]. The goal of this work is to utilize powder diffraction at high temperatures to resolve these phases, as well as to quantify the thermal expansion in both $CsCaI_3$:Eu and $CsSrBr_3$:Eu

Experimental

Due to the hygroscopic nature of these compositions, special procedures were taken during preparation, handling, and measurement. All raw materials were purchased from APL or Sigma Aldrich in the form of anhydrous beads with purity levels of 99.99% or greater. The crystals for powder diffraction were prepared inside of a nitrogen maintained glovebox with less than 1 ppm oxygen and moisture. Starting materials of CsI, CaI_2, CsBr, $SrBr_2$, and