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Divalent europium doped and un-doped calcium iodide scintillators: Scintillator characterization and single crystal growth ☆

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ABSTRACT

The alkaline-earth scintillator, $CaI_2:Eu^{2+}$, was initially discovered around 1964 by Hofstadter, Odell, and Schmidt. Serious practical problems quickly arose, however, that were associated with the growth of large monolithic single crystals of this material due to its lamellar, mica-like structure. As a result of its theoretically higher light yield, $CaI_2:Eu^{2+}$ has the potential to exceed the excellent scintillation performance of $SrI_2:Eu^{2+}$. In fact, theoretical predictions for the light yield of $CaI_2:Eu^{2+}$ scintillators suggested that an energy resolution approaching 2% at 662 keV could be achievable. As in the case of the early $SrI_2:Eu^{2+}$ scintillator, the performance of $CaI_2:Eu^{2+}$ scintillators has traditionally suffered due, at least in part, to outdated materials synthesis, component stoichiometry/purity, and single-crystal-growth techniques. Based on our recent work on $SrI_2:Eu^{2+}$ scintillators in single-crystal form, we have developed new techniques that are applied here to $CaI_2:Eu^{2+}$ and pure CaI_2 with the goal of growing large un-cracked crystals and, potentially, realizing the theoretically predicted performance of the $CaI_2:Eu^{2+}$ form of this material. Calcium iodide does not adhere to modern glassy carbon Bridgman crucibles—so there should be no differential thermal-contraction-induced crystal/crucible stresses on cooling that would result in crystal cracking of the lamellar structure of CaI_2. Here we apply glassy carbon crucible Bridgman growth, high-purity growth-charge compounds, our molten salt processing/filtration technique, and extended vacuum-melt-pumping methods to the growth of both $CaI_2:Eu^{2+}$ and un-doped CaI_2. Large scintillating single crystals were obtained, and detailed characterization studies of the scintillation properties of $CaI_2:Eu^{2+}$ and pure CaI_2 single crystals are presented that include studies of the effects of plastic deformation of the crystals on the scintillator performance.

1. Introduction

The divalent-europium-doped alkaline-earth halide scintillator, $CaI_2:Eu^{2+}$, was initially reported by Hofstadter, Odell, and Schmidt [1,2]. This scintillator was subsequently patented by Hofstadter [3]. At that time, the material was reported to be a promising scintillator based on the light yield alone. Another alkaline-earth-iodide scintillator, namely $SrI_2:Eu^{2+}$, was also discovered by Hofstadter and patented [4], but the performance of the $SrI_2:Eu^{2+}$ scintillator at that time was not impressive in terms of its light yield and energy resolution, and no significant further development of this detector took place for decades. The $SrI_2:Eu^{2+}$ scintillator was essentially re-discovered in 2008 [5,6], and as reported in Refs. [5,6], outstanding energy resolution and light yields of the material were achieved through the application of significantly improved modern purification and synthesis methods, the use of increased Eu-activator doping levels, and modern crystal-growth techniques [7,8]. These more recent findings have resulted in a plethora of new research efforts leading to the continuing development, refinement, and current commercialization of the (now) high-resolution $SrI_2:Eu^{2+}$ scintillator.

In principle, $CaI_2:Eu^{2+}$ has the potential to exceed the excellent scintillation performance of $SrI_2:Eu^{2+}$ due to its reported theoretically

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predicted higher light yield (114,000 photons/MeV [theoretical]) [5]. Unlike the case of recent work on SrI_2:Eu^{2+}, however, further developmental studies of CaI_2:Eu^{2+} have not been extensively pursued, and therefore, its performance has not been improved – apparently due primarily to observations in both the early and recent literature regarding the lamellar micaceous-like crystal structure of this material and the associated formation of "layered" single crystals that exhibit mechanical instability (e.g. cracking and cleavage) problems – both during crystal growth and subsequent detector fabrication. Accordingly, the primary goal of present work was to apply high-purity compounds, modern crystal-growth methods, and non-reactive crucible materials to address the issue of the scintillator performance that could, in fact, be achieved with CaI_2:Eu^{2+} Bridgman-grown scintillator crystals. Additionally, since un-doped CaI_2 is also a scintillator, pure CaI_2 scintillator single crystals were also grown using the same methods applied to the growth of Eu-doped CaI_2, and their scintillator performance properties were investigated. A major premise on which these studies were based was that mechanical deformation of the scintillator crystals due to adherence to the growth crucible (or other mechanical interactions) would severely degrade the scintillator light yield and energy resolution—or potentially even suppress the scintillation mechanism completely. The results reported here show that, in fact, this premise did not prove to be well founded.

As noted, one goal of this work was to move toward a realization of the predicted theoretical high-resolution scintillator performance of CaI_2:Eu^{2+}. Accordingly, in addition to the use of high-purity crystal-growth-charge materials and the ORNL-developed molten salt filtration process [7,8] for the removal of insoluble oxy-halides and other insoluble compounds from the melt prior to Bridgman growth, this work proceeded along two additional major promising research and development paths. These were: first, the use of vitreous carbon Bridgman crucibles for the growth of CaI_2 and, second, the application of an extended vacuum/melt pumping procedure [8] prior to the encapsulation of the glassy carbon Bridgman crucible in a sealed quartz ampoule under 0.5 atm of Argon.

The availability of the large single crystals of both CaI_2:Eu^{2+} and un-doped CaI_2 that were produced during the course of this work also provided an opportunity for investigations of the effects of deliberate/intentional mechanical deformation (specifically plastic deformation) on the scintillator performance of CaI_2:$Eu^{2+}$and un-doped CaI_2. These plastic deformation experiments yielded performance results that were both unanticipated and intriguing in the sense that they ran counter to traditional/intuitive expectations of the effects of mechanical deformation on the single-crystal scintillator light yield and energy resolution.

2. Experimental

2.1. The use of high-purity materials for the growth of CaI_2:Eu^{2+} and un-doped CaI_2

Starting crystal-growth-charge materials (specifically the CaI_2 host material) are currently commercially available whose purity exceeds that of the CaI_2 compounds generally available during the 1960s-era period of Hofstadter's initial discovery of the CaI_2:Eu^2 scintillator [1,2]. Accordingly, in the crystal growth experiments described here, anhydrous −10 mesh CaI_2 beads of 99.999% purity (with respect to metals) were used that were obtained from SAFC Hitech (Sigma Aldrich Co., LLC). It is important to note that the traditional chemical analysis supplied by the compound vendor does not, however, address issues of the stoichiometry of the material. The EuI_2 activator dopant was also obtained from SAFC Hitech with a stated purity of 99.99%. This level of purity/stoichiometry was found to be generally unsatisfactory for the growth of high-quality CaI_2Eu^{2+} single-crystals, and therefore, further purification of the EuI_2 material was carried out via zone refining by the research group of Arnold Burger at Fisk University, Nashville, TN. In our experience, this additional step of the purification of EuI_2 is critical. The mixed CaI_2/EuI_2 (or pure CaI_2 in the case of un-doped crystal growth) materials were dried in the growth ampoule system described in detail below by heating under vacuum in a system that utilized a liquid nitrogen cold trap to remove condensable vapors.

2.2. Bridgman growth of CaI_2:Eu^{2+} and un-doped CaI_2 in vitreous carbon crucibles

The crystallographic structural basis for the mechanical fragility and tendency for cleaving or cracking of CaI_2 is illustrated in Fig. 1 along with the basic structural data for this material (Rhombohedral, hP3; Space group P-3m1, No 164, octahedral coordination). This figure clearly shows the planar micaceous-like structure created by continuous two-dimensional sheets of polyhedra that form the CaI_2 *a–b* plane. These structural sheets are separated along the *c*-axis direction by a distance of 3.487 angstroms. This structure results in an easy *a–b* basal-plane cleavage and is in contrast to the crystal structure of orthorhombic SrI_2 – as illustrated in Fig. 1 of Ref. [7] – i.e., a continuous SrI_2 crystal structure is formed by 3-dimensionally linked polyhedral chains, and there are no clearly defined cleavage planes in this case.

As noted above, we have investigated the application of the advanced, modern crystal growth crucible material, namely vitreous (or glassy) carbon, to the Bridgman growth of Eu-activated and pure CaI_2. Solid calcium iodide does not adhere to glassy carbon. The original premise behind this approach was that by eliminating crystal/crucible interactions one could eliminate adherence of the crystal to the crucible and the associated stress-induced cracking on cooling (due to differential thermal contraction). Accordingly, in the absence of other perturbations, it should be possible, to grow large un-fractured single crystals of pure or Eu-doped calcium iodide. High-quality glassy carbon (Sigradur GCG125) Bridgman growth crucibles with a volume of 125 ml were obtained from Hochtemperatur-Werkstoffe GmbH in Thierhaupten, Germany and used in the experiments described here.

The application of vitreous carbon Bridgman crucibles to the growth of pure and doped CaI_2 was used in conjunction with the ORNL-pioneered method of physically filtering the molten salt of the material to be grown using quartz frit filters to remove

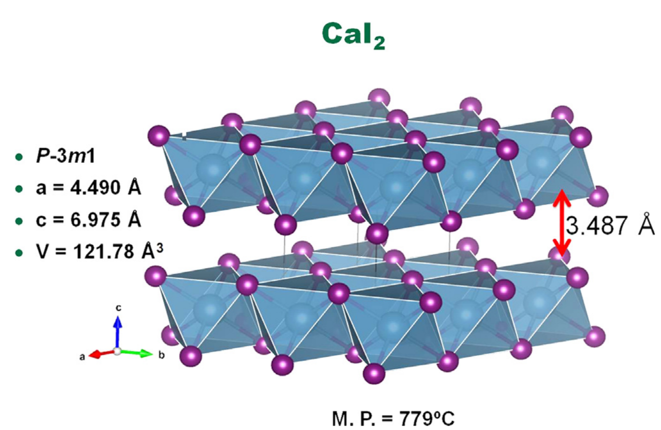

Fig. 1. Calcium iodide has a lamellar structure with the basal-plane layered "sheet-like" arrangement shown in the figure. This structural arrangement accounts for the ease with which single crystals of the material can be mechanically separated along the *a–b* plane into either thin sheets or slabs. The material is very soft, extremely hygroscopic, highly reactive, not readily amenable to either mechanical or solution polishing, and it can be easily plastically deformed via bending of the *a–b* plane.