



Spectroscopic and neutron detection properties of rare earth and titanium doped LiAlO₂ single crystals



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ABSTRACT

In this study, LiAlO₂ crystals doped with rare-earth elements and Ti were produced by the CZ method and spectroscopic and neutron detection properties were investigated. Photoluminescence revealed no clear luminescent activation of LiAlO₂ by the rare-earth dopants though some interesting luminescence was observed from secondary phases within the crystal. Gamma-ray pulse height spectra collected using a ¹³⁷Cs source exhibited only a Compton edge for the crystals. Neutron modeling using Monte Carlo N-Particle Transport Code revealed most neutrons used in the detection setup are thermalized, and while using natural lithium in the crystal growth, which contains 7.6% ⁶Li, a 10 mm Ø by 10 mm sample of LiAlO₂ has a 70.7% intrinsic thermal neutron capture efficiency. Furthermore, the pulse height spectra collected using a ²⁴¹Am-Be neutron source demonstrated a distinct neutron peak.

1. Introduction

Detection of radioactive isotopes among a background of natural radiation is a difficult challenge for homeland security and atomic/nuclear physics. Additionally, with a shortage of He-3, which is commonly used to detect neutrons in He-3 filled proportional counters, there is a national research drive to find novel neutron detectors [1]. New neutron detectors commonly use Lithium-6 or Boron-10 for neutron capture reactions because of their high thermal neutron capture cross-sections [2]. ⁶Li capture of a neutron causes the release of a 2.05 MeV alpha particle and a 2.75 MeV triton which can be detected using a scintillator [3]. Recently, research on Lithium Aluminate (LiAlO₂ or LAO) as a new neutron scintillator has begun since the high lithium content in the material yields a high probability for neutron capture [4,5].

Lithium Aluminate is an inorganic material which at 1 atm pressure crystallizes into a low temperature hexagonal structure (α -phase) but undergoes an irreversible phase transition around 900 °C to a tetragonal unit cell (γ -phase) with dimensions of $a = 5.169 \text{ \AA}$ and $c = 6.268 \text{ \AA}$ [6–8]. LAO has a wide bandgap of $\sim 6.2 \text{ eV}$, melts congruently at 1700 °C, and is non-hygroscopic, making it ideal as a detector material [4,9]. With LAO's congruent melting point, single crystals have been produced from melt using the Czochralski (CZ) method, though dissociation of LiAlO₂ and subsequent volatilization of Li₂O causes the melt to deviate from stoichiometry [10,11].

With LAO's wide band gap, dopants can and have been used to modify the band structure and produce luminescence in both single crystals and powdered ceramics [9,12,13]. Recently, research groups using methods of powder processing and single crystal growth have researched and published on LAO luminescence using transition metal activators [9,13–17]. Additionally, Pejchal et al. and Fujimoto et al. have recently reported on neutron detection with Ti, Mn, or Cu doped LAO crystals grown by the micro-pull-down method [3,5,18]. Their results demonstrated LAO's ability to detect neutrons with crystals 3 mm in diameter [3,5].

In this article, LAO crystals grown by the CZ method and doped with rare-earth elements are presented, and the spectroscopic and radiation detection properties are explored. X-ray diffraction was used to analyze possible secondary phase formation, while photoluminescence was used to investigate luminescent properties. With photoluminescence, several emission centers were identified as well as unique green and red luminescence in Eu doped crystals. Low temperature thermoluminescence peaks were found in some of the samples and the initial rise method was used to calculate the trap depth. Additionally, Monte Carlo N-Particle Transport Code was used to model the neutron detection setup and investigate the intrinsic neutron detection efficiency of LAO. Finally, scintillation detection of both neutrons and gamma-rays was performed.

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Table 1

Ce: YAG boules: dopant concentrations, growth parameters, and evaporation. Cerium and lithium concentrations are both with respect to yttrium.

Dopant	Dopant Concentration	Pulling Rate	Crucible Rotation	Growth Atmosphere	Weight loss (g/h)
None	–	5 mm/h	20 rpm	1000 ppm O ₂ balanced N ₂	0.93
Ce	0.05 at%	5 mm/h	20 rpm	1000 ppm O ₂ balanced N ₂	1.15
Eu	0.1 at%	5 mm/h	20 rpm	1000 ppm O ₂ balanced N ₂	0.86
Eu	2.0 at%	5 mm/h	20 rpm	5000 ppm O ₂ balanced N ₂	1.12
Pr	0.1 at%	5 mm/h	20 rpm	5000 ppm O ₂ balanced N ₂	1.06
Ti	0.5 at%	5 mm/h	20 rpm	5000 ppm O ₂ balanced N ₂	1.01

2. Experimental procedure

Six LAO boules were grown under similar conditions by the CZ method. The doping concentrations, pulling rate, and growth atmosphere are listed in Table 1. Additionally, as LAO is known to dissociate at high temperatures and lithium oxide to evaporate at temperatures above 1200 °C, the approximate weight loss from the crucible was measured and is listed in Table 1 [10]. The raw materials used were high purity powders of lithium aluminate (LiAlO₂, 99.995%), and lithium carbonate (Li₂CO₃, 99.998%) purchased from Pro Chem, Inc. Due to the evaporation of lithium oxide from the melt, 10 at% excess lithium, in the form of lithium carbonate, was mixed into each charge. The powders were weighed with 10 mg precision (adjusting for inherent moisture content within the powders) to a target weight of 300g, then ball milled using high purity (99.8%) alumina milling balls for 18 h. After mixing, the powder was compressed in an isostatic press to ~20 kpsi to make the final charge. The charge was calcined in the CZ furnace under the growth atmosphere for 7–10 h at ~900 °C to decompose the Li₂CO₃ into Li₂O without any lithium evaporation.

The crystals were grown using an iridium crucible (86 mm Ø × 60 mm tall) with a RF induction coil operated at 20 kHz frequency. An iridium lid with a 40 mm Ø hole was placed 1 cm above the top of the crucible using zirconia as a spacer. The lid allowed the middle of the melt surface to be melted without excessive heating of the side walls which would have resulted in increased melt evaporation. First, the 300 g charge was melted over the course of ~15 h and then cooled. After this, a second, charge of 200 g was added to the crucible to increase the melt volume to 500 g for improved heat flow and to maintain stable flow patterns during growth.

An undoped LAO seed was obtained from an undoped LAO crystal, not reported in this manuscript, pulled with an iridium wire. This crystal was then cut into several 5 mm x 5 mm rods which were subsequently used as seeds. The crystals were pulled from the melt using the LAO seed. The crucible was rotated at 20 rpm while the seed was not rotated. The crystal weight was monitored through the pulling arm and the power was adjusted via a proportional-integral-derivative (PID) controller. Each boule was around 200 g and between 26 and 30 mm Ø and approximately 110 mm in length. The crucible remainder was weighed after the growth and the overall weight loss, weight evaporated from the melt, was found to be ~40g, though the Ce doped crystal only had 30g weight loss.

Right cylinders of 10 mm Ø by 10 mm thick were cut from the bottom of the as-grown boules, though for the 2.0 at% Eu boule, the sample was taken from the top due to poor optical quality at the bottom. Additional 10 mm Ø by 1 mm thick samples were cut from adjacent locations for absorption/transmission and room temperature photoluminescence measurements. The 1 mm thickness assured any dopant lines would not become saturated in optical absorption measurements. All samples were cored from a sectioned part of the boule and were mechanically polished with alumina slurry to a final grit of 0.3 µm.

X-Ray Diffraction (XRD) was performed with a PANalytical X'Pert Pro MPD X-ray diffractometer (PANalytical B.V. Almelo, The Netherlands) outfitted with a rotational sample holder in reflection geometry to investigate possible secondary phases. Scans were per-

formed in the range of 20–140° 2θ with a 0.05° step size and a 90 s dwell time. Multiple scans were performed to ensure the maximum peak height exceeded 15,000 counts. All sections used for XRD were cut from the region surrounding the cored samples to ensure relevance of the tested pieces, and were powdered using a porcelain mortar and pestle or a WC disk mill. Rietveld refinement was performed using PANalytical Highscore Plus software to least-squares fit the lattice parameter of LAO.

Absorption/transmission measurements were carried out with an Ocean Optics PC2000 Spectrometer using a deuterium light source to measure UV and visible absorption in the 1 mm thick samples.

Room temperature photoluminescence (PL) was measured using a Horiba Jobin Yvon Fluorolog-3 Spectrofluorometer with a deuterium arc lamp for excitation down to 180 nm, which allowed for the identification of optically active point defects or impurities within the band gap. For the PL measurements, a 1200 grating density was used, and each spectrum was corrected for instrument inhomogeneities and detector response.

Thermoluminescence (TL) was measured on the 10 mm Ø by 10 mm samples using a Janis CCS-150 Cryodyne Refrigerator with a CTI 8200 Compressor. Samples were cooled to ~10 K, solarized for 1 h using a deuterium lamp (185–650 nm emission), and TL was measured from 30 to 300 K using a 6 K/min heating rate. The TL emission signal was integrated from 325 to 400 nm, which is where the emission peak was found, though all wavelengths from 200 to 800 nm were analyzed for emission peaks.

Scintillation performance, both gamma and neutron, were recorded by wrapping the 10 mm Ø by 10 mm right cylinders in seven to ten layers of Teflon tape. They were then coupled to a XP2018B photomultiplier tube (PMT) with a VD200KB base using Visc 10 M optical grease and biased at +1000 V. An Ortec 113 preamplifier and Ortec 673 amplifier with a shaping time of 6 µs provided the best results for all analyzed samples. Sample data was collected for 1000 s for all measurements. Gamma-ray performance was characterized using a 10 µCi ¹³⁷Cs source. For neutron detection performance, an ²⁴¹Am-Be neutron source (from a CPN Inc. Hydroprobe 503) was used to characterize neutron detection capabilities of the samples. A 9" Ø polyethylene Bonner sphere was used to thermalize the neutrons for capture by the ⁶Li within the sample, and a lead brick was used to absorb some of the high energy gamma rays from the neutron source. The neutron detection setup used is displayed in Fig. 1.

3. Results and discussion

3.1. Crystal Growth

Most crystals grew with no abnormalities or problems during growth, with the exception of the 0.05 at% Ce doped crystal. During the growth of the 0.05 at% Ce doped crystal, the PID allowed for the crystal diameter to exceed the set target diameter. Due to this, it was uncertain as to whether the crystal could be separated from the melt successfully as the large diameter crystal could have caught on the iridium lid and caused the crystal to fall off. To avoid loss of the crystal, the crucible rotation was stopped and the entire crystal and crucible melt was slow cooled.

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