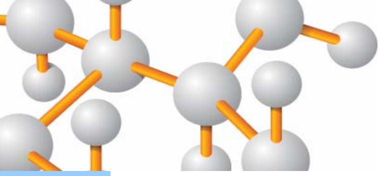

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Scintillation and optical properties of LuAP and LuYAP crystals

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***Abstract*—In this paper properties of LuAP ($LuAlO_3$:Ce), and LuYAP ($Lu_{0.7}Y_{0.3}AlO_3$:Ce) crystals are studied. The previously reported self-absorption has been confirmed, and a possible mechanism is discussed. The thermal stability of the material was evaluated, and both LuAP and LuYAP have been found to readily decompose when heated to a sufficiently high temperature. XRD studies were done to determine that a solid-solid phase transformation occurs under those conditions. In addition, thermoluminescence studies reveal the presence of additional traps in the LuYAP crystal, apparently the result of the yttrium addition to the crystal lattice.**

Introduction

Cerium activated lutetium orthoaluminate $LuAlO_3$:Ce (LuAP) and yttrium containing LuYAP are materials of interest in the scintillator community. These materials are attractive because of their high density (up to 8.34 g/cm^3 for LuAP), short scintillation decay time (primary component as short as ~18 ns), and potential high light output (close to 11 000 ph/MeV for LuAP). However, due to self-absorption the scintillation efficiency is lowered significantly and therefore the light output of these materials is strictly dependent on the thickness of the crystal. Under some conditions the pure $LuAlO_3$ phase can become contaminated by other phases, including a garnet phase, $Lu_3Al_5O_{12}$, and a monoclinic phase, $Lu_4Al_2O_9$. One theory is that such contamination is the source of the self-absorption. Further development of these materials requires a deeper understanding of the scintillation mechanisms and optimization of the crystal growth process.

Experimental Procedures

The Czochralski technique was used to grow cerium-doped (0.4% Ce) single crystal boules of LuAP and LuYAP. The boules were grown in inductively heated iridium crucibles in an atmosphere consisting of a small % of O_2 in bulk N_2. Lu_2O_3, Al_2O_3, Y_2O_3 and CeO_2, were at least 99.99 % pure.

Annealing in N_2 experiments were done in a Lindberg tube furnace, model STF54434C. The samples were annealed at 1500 °C, with 11°C/minute ramp rates and a 3 hour soak time.

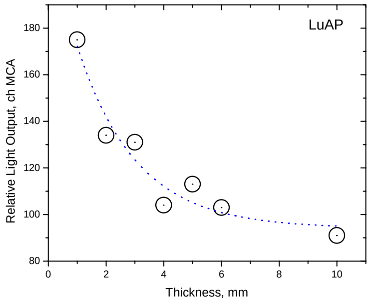
Results

Scintillation properties of “as grown” and annealed in Air samples

Sample	*Atmosphere*	*Light Output [channel MCA]*	*Decay Time[ns]*
LuAP 0.4%Ce	“As grown”	180	18.5, 56, 455
LuAP 0.4%Ce	Air	215	18.5, 46, 413
LuAP 0.4%Ce	Nitrogen	223	18.6, 50.5, 445
LuYAP 0.4%Ce	“As grown”	62	23.5, 125, 692
LuYAP 0.4%Ce	Air	67	23.6, 120, 724
LuYAP 0.4%Ce	Nitrogen	73	24, 123, 763

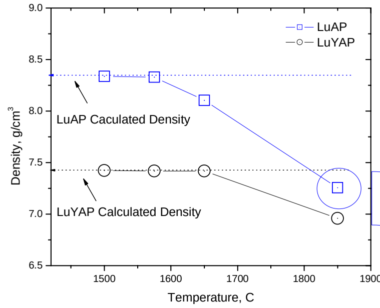
A BGO sample measured under the same conditions had a light output centroid at 100 channels of the MCA. The above data were not corrected for the quantum efficiency of the PMT

Light Output vs. sample thickness

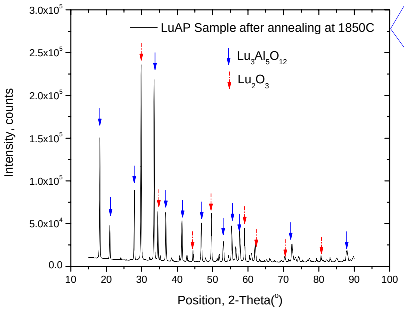


Results

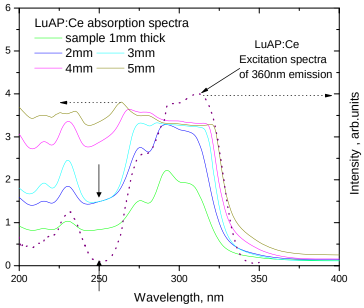
Density Measurements



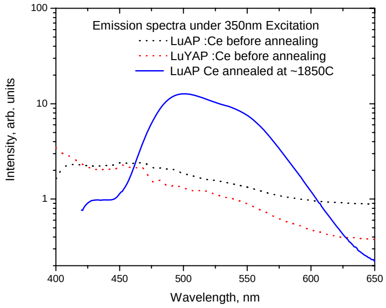
XRD data obtained from a LuAP sample after a heat cycle at ~1850 C



Absorption spectra of LuAP “as grown” samples measured for different crystal thickness are shown as solid lines. The excitation spectrum of cerium emission 360 nm in LuAP is shown as a broken line.



Emission spectra under 350 nm excitation measured for LuAP, and LuYAP crystals ”as grown” and for LuAP sample after heat cycle up to ~1850 ºC .



Discussion

The growth process of LuAP crystals is potentially hindered by the formation of other crystal phases, including a garnet phase, $Lu_3Al_5O_{12}$, a monoclinic phase, $Lu_4Al_2O_9$, and an oxide phase, Lu_2O_3. The isostructural LuYAP crystal is more thermally stable than LuAP, which is widely believed to be due to the presence of yttrium in this compound.

The studies of thermal stability of LuAP and LuYAP crystals were based on experiments with heat cycles at different temperatures. At a sufficiently high temperature, a solid-solid phase transition and material decomposition were observed.

The percentage of solid-solid phase transition in these materials is dependent on temperature and time and may be detected by **changes in the density and the XRD patterns** of the material measured before and after annealing. The experiment showed noticeable changes in density after annealing at temperature equal to or higher than 1575 °C for LuAP, and equal to or higher than 1650 °C for LuYAP. These results confirm that LuYAP composition is less subject to thermal decomposition than pure LuAP.

Detailed studies of the decomposition products of LuAP heated to ~1850 °C were carried out using x-ray powder diffraction (XRD). Data show that the LuAP crystal partially decomposed to a combination of the garnet, $Lu_3Al_5O_{12}$, and oxide, Lu_2O_3, phases.

Based on the thermal stability studies discussed above, a temperature of 1500°C was chosen for annealing experiments to improve scintillation properties. In the case of both LuAP and LuYAP the annealing process slightly improved the scintillation performance of the materials independently of the atmosphere used, suggesting that the affected defects are not related to oxygen vacancies, which commonly occur in oxide compounds. **Light output** increased by ~20 % and ~15 % respectively for LuAP and LuYAP. This result suggests that the defect correction process during heat treatment may be related only to internal diffusion of the ions comprising the structure of the crystal. Moreover, the annealing process does not affect the scintillation decay time in either material.

It is commonly known that a self-absorption effect is responsible for a significant decrease in light output of LuAP crystals. The results of light output measurements are dependent on a sample thickness. The difference in light output between samples 1 mm and 10 mm thick is more than 50 %. The absorption spectra measured for LuAP show at least two absorption bands in addition to cerium excitation bands. One of them has a maximum at 250 nm, while the other one overlaps with the cerium excitation band with a maximum at 310 nm, causing broadening of that band. The overlapping of the absorption bands with the cerium emission may result in the observed self-absorption effect.

Emission spectra measured under excitation at 350 nm for LuAP and LuYAP “as grown“ crystals show a low intensity emission in the ~400-630 nm range. The presence of this emission indicates the existence of unknown radiative centers generated in the material during the crystal growth process. The LuAP sample heat-treated at ~1850 °C clearly shows the presence of the garnet phase, with its characteristic emission at 500 and 540 nm. This result is consistent with the idea that contamination of the pure LuAP phase with other phases affects the scintillation performance of the material. Because the perovskite phase is unstable at high temperature it seems possible that a small percentage of contamination of the pure LuAP phase with other phases may take place during or after growth. If these phases are sufficiently effective quenching centers then it may be possible that they result in self-absorption at low enough levels to be difficult to detect via XRD or density changes.

The introduction of yttrium into the crystal structure improves the thermal stability of the perovskite phase during the crystal growth process.