Development of Ce doped Li$_6$Y(BO$_3$)$_3$ Crystal Based Portable Solid State Detectors for Thermal Neutrons

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Abstract

Single crystals of Ce doped Li$_6$Y(BO$_3$)$_3$ have potential applications to be used as a scintillator to detect thermal neutrons. These single crystals having an optimum Ce concentration been successfully grown using the Czochralski technique. The crystals have been characterized for optical and scintillation properties. A portable detectors set-up that works from a USB port of a laptop has been developed to detect thermal neutrons. The detection efficiencies in excess of 80% have been achieved even for thin slices of the crystal (1 mm thick) mounted on a photo-multiplier tube (PMT).

Keywords: Crystal growth, Scintillator, Neutron Detector.

Introduction

Neutron detectors find several applications in research, defense, security and nuclear industries. The conventional neutron detectors are based on $^3$He and BF$_3$ gas filled chambers. While BF$_3$ is corrosive and toxic, the shortage of $^3$He has made it prohibitively expensive. Due to the dwindling supply of $^3$He, there is an urgent need to explore alternative detector materials. Solid state detectors based on inorganic scintillator single crystals are promising candidates and have the advantage of being portable and durable. These detectors would inherently have a better efficiency due to the higher atomic density compared to other conventional detectors based on gas chambers.

Single crystals of Li$_6$Y(BO$_3$)$_3$ (LYBO) doped with cerium have been proven as a promising neutron scintillator. This material contains $^6$Li (natural abundance 7.4%, $\sigma_{\text{abs}} = 940$ barns) and $^{10}$B (natural abundance 20%, $\sigma_{\text{abs}} = 3835$ barns) that have large cross section for thermal neutrons and produce charged particles ($^{4}$He and $^3$H) after interactions [1]. The alpha particles generated in $^{10}$B ($n, \alpha$) $^7$Li and $^6$Li ($n, \alpha$) $^3$H reactions excite the Ce$^{3+}$ ions resulting in a fast and efficient emission at 420 nm. This emission matches well with the efficiency response of bi-alkali photomultiplier tubes (PMT) and therefore can be easily read out using standard electronics. A reasonable light output of about 1200 ph/MeV enables efficient collection and a clean pulse height spectrum. A lower effective Z of the LYBO compared to other neutron scintillators also helps impart insensitivity to gamma-rays that prevails in mixed field radiations [2].

Experimental

The Ce doped single crystals of LYBO were grown using the Czochralski technique in an automatic diameter controlled crystal puller system (Model: Oxypuller, Cyberstar). The single phase starting charge was synthesized by solid state sintering of constituent oxides (Li$_2$CO$_3$, Y$_2$O$_3$, H$_3$BO$_3$, CeO$_2$, 99.99% purity) taken in a stoichiometric ratio. The cerium concentration was taken 0.2 at% in the starting charge which could be lower in the grown crystal due to the segregation. A two step sintering at 700°C for 24 hours each was used with intermediate mixing. The formation of a single phase compound was confirmed by recording a powder XRD pattern employing a Rigaku RINT 2000 diffractometer [Cu K$_\alpha$ radiation ($\lambda = 1.545056$ A)] with a step size of 0.02° in 2è range of 10-80°. The synthesized charge in the form of pellets was loaded in a platinum crucible. An RF power supply was used to melt the material by induction heating. The power was adjusted to keep the temperature at about 50°C higher than the melting temperature to homogenize the melt which is recommended for the growth of this family of borates [3].

A seed crystal of LYBO was used to initiate the growth in argon ambient. The optimized growth parameters for the growth of LYBO crystal are listed in Table 1.
Transmission/absorption spectra were recorded with a Shimadzu 3600 UV-VIS NIR spectrometer in the range from 185 nm to 800 nm. Photoluminescence (PL) studies were performed over a wavelength range from 250 nm to 500 nm at room temperature employing a fluorescence spectrometer (Edinburg Model-FLP920). The emission was recorded in reflection geometry by positioning the sample at 45° with respect to the excitation beam. A steady state xenon lamp was used as an excitation source and a spectral bandwidth of 1 nm was selected for both excitation and emission arms. The recorded luminescence spectra were corrected for the spectral sensitivity function of the instrument. The scintillation decay was measured by recording the anode pulse from a PMT (Hamamatsu make, Model No. R2154) using a fast digital oscilloscope. The decay times resulted due to both neutrons and gamma exposures were measured. The Pulse height spectra (PHS) were recorded for thermal neutrons in a beamline of the Dhruva reactor. Various shields like lead brick and borated rubber was used to discriminate the spectra from neutron and gamma contributions. The spectra were also recorded at various fluxes of thermal neutrons from Am-Be and 252Cf sources having known neutron fluxes. While 252Cf sources generate fast neutrons via spontaneous fission, fast neutrons in Am-Be sources are generated by α particles (emitted from 241Am) via the following reaction:

$^9\text{Be} + \alpha = n + ^{12}\text{C}^* + Q (5.704 \text{ MeV})$

The fast neutrons are thermalized using graphite moderators.

**Results and Discussions**

**Crystal growth**

Fig.1 shows differential thermal analysis (DTA) plots of the synthesized charge. The melting and freezing behavior of the material indicates a large supercooling of more than 250°C which is common among the families of borates. Hence, the growth station was modified to achieve a higher temperature gradient of about 100°C/cm just above the melt.

![DTA plot of Ce doped LYBO](image)

The as-grown single crystal of LYBO is shown in Fig.2. The grown crystal was about 20 mm in diameter and 25 mm long. The crystal was free from any visible inclusion or impurity. Due to a high viscosity of the melt, the formation of bubbles is a common problem in these crystals which has been avoided by applying a higher temperature gradient and slow pull rates. Thus the crystals could be grown bubble-free as shown in the figure. A slow cooling rate was employed and the as-grown crystals were annealed at 500°C for 24 hours to reduce thermal stresses. This eventually helped to reduce cracking of crystals.

![As-grown single crystal of Ce doped LYBO](image)

The powder XRD pattern of an as-grown crystal is shown in Fig.3. The phase of the material has been verified by the JCPDS data [4]. The lattice parameters have been calculated and found to match with the

<table>
<thead>
<tr>
<th>Table 1: Crystal growth parameters</th>
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<tbody>
<tr>
<td><strong>Melting temperature</strong></td>
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<tr>
<td><strong>Pull rate</strong></td>
</tr>
<tr>
<td><strong>Rotation rate</strong></td>
</tr>
<tr>
<td><strong>Ar gas pressure</strong></td>
</tr>
<tr>
<td><strong>Temperature gradient</strong></td>
</tr>
<tr>
<td><strong>Cooling rate</strong></td>
</tr>
</tbody>
</table>
reported data. The structure parameters for the LYBO crystal are listed in the Table 2.

Table 2: Crystal structure data of LYBO

<table>
<thead>
<tr>
<th>Structure</th>
<th>Monoclinic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameters</td>
<td>a=7.15 Å, b=16.378 Å, c= 6.62 Å</td>
</tr>
<tr>
<td>Space group</td>
<td>P21/c</td>
</tr>
</tbody>
</table>

Optical characterization

The transmission spectrum for a polished sample (~2 mm thickness) prepared from the as-grown crystal showed more than 80% transmission in the wavelength range from 185 nm to 1100 nm, as shown in Fig.4. The emission originating due to Ce3+ centers at 420 nm is in the transmission region of this crystal as shown in the same figure. This indicates that the self absorption in these crystals will not be a serious problem. The á particles generated from (n, á) reaction cause ionization of Ce3+ ions. A radiative de-excitation of electrons from 5d to 4f energy levels of Ce3+ centers cause the emission band peaking at 420 nm. It mainly consists of two bands peaking at 390 nm and 410 nm due to splitting of 4F_{5/2} and 4F_{7/2} ground state [5].

This blue emission matches well with the response of a standard bi-alkali PMT and therefore a standard scintillation setup may be employed to record the pulse height spectra. The scintillation decay profiles of the crystal measured due to the excitation from gamma rays and neutrons are shown in Fig.5. A single exponential decay with a decay time of 27 ns for neutrons and 48 ns for gamma rays has been observed. Though the difference in the decay times by these two excitations is not significant, still it can be useful to discriminate the gamma rays from neutrons by a suitable pulse shape discrimination technique.

Setup for a USB powered neutron detector

Scintillator discs of 10 mm diameter and about 1 mm thick were processed from the as-grown crystal. One face of the crystal was polished and optically coupled to a 1 inch diameter PMT (Hamamatsu make). The scintillator was wrapped with reflecting Teflon tapes and finally with aluminum foil. The reflecting tapes ensure efficient collection of light towards the PMT while Al foil minimizes the dark current of the PMT that may arise due to background light. The output from the PMT was given to a pulse processing chain consisting of a Pre-Amp, a shaping Amp and an 8k multi-channel analyzer (MCA). The power to all components including HV to the PMT was fed through a USB port of a laptop by employing suitable DC-DC converters. The data processing was done by the Amptek DppMCA software. The amplifier parameters...
like shaping time, gain, LLD etc., were optimized to obtain a clean pulse height spectrum. A typical set-up used for recording the PHS is shown in Fig.6. The portability of the detector set-up makes it useful and an easy choice in various applications.

**Performance characteristics of neutron detector**

The interaction of neutrons with LYBO crystals takes place via following reactions:

**With $^{10}$B**

\[ ^{10}B + \gamma n \rightarrow ^{7}Li \text{ (ground state)} + ^{4}\frac{2}{3}He \quad (Q \text{ value} = 2.792 \text{ MeV}) \]

\[ ^{10}B + \gamma n \rightarrow ^{7}Li^* + \rightarrow \text{(excited)} + ^{4}\frac{2}{3}He + \gamma (0.48 \text{ MeV}) \quad (Q \text{ value} = 2.310 \text{ MeV}). \]

**With $^6$Li**

\[ ^{6}Li + \gamma n \rightarrow ^{4}\frac{2}{3}He (2.05 \text{ MeV}) + ^{3}H (2.75 \text{ MeV}) \]

The smaller size (~ 1mm thickness) of the crystal was chosen to minimize the contribution from gamma background. However due to higher atomic density of lithium and boron atoms in these materials, the thickness is still sufficient to achieve good efficiency. The other important parameters of LYBO:Ce crystals are listed in Table 3. Pulse height spectra (PHS) recorded by this set-up for thermal neutrons from a Am-Be source is shown in Fig.7 [6].

The pulse height spectra comprised of two peaks near channel No. 190 and 950 corresponding to $(n,\alpha)$ reaction with $^{10}$B and $^4$Li, respectively. The integrated count for the two peaks have been calculated and found to be in agreement with the ratio of two fluxes within the standard deviation. With a neutron shield, the absence of these two peaks in the PHS, confirmed the origin as interactions of neutrons with the crystal.

It could be noted that although the alpha energies produced in the $^{10}$B and $^6$Li reaction are 1.47 MeV and 2.2 MeV respectively, the pulse height corresponding to $^6$Li is about five times larger than that due to $^{10}$B. This is because the generation of relatively light charged particles ($^3H$ & $^4\frac{2}{3}He$) in the case of $^6$Li as compared to $^{10}$B ($^7Li$ & $^4\frac{2}{3}He$) due to which a larger equivalent electron energy is deposited in the crystal for the nuclear reaction with $^6$Li [1]. However the lower relative intensity of the peak due to lithium is due to a lower cross section as well as a lower abundance of $^6$Li (about 7%) as compared to $^{10}$B (about 20%) in the natural constituents used for the growth of the crystals. The PHS due to thermal neutrons in a beamline of the Dhruva reactor has also been recorded as shown in Fig.8.

The relatively poor resolution of the peak due to $^{10}$B reaction can be attributed to heavy gamma background present in the reactor. Keeping a gamma shield makes the spectrum better. The peak due to $^4$Li interaction can be enhanced several folds by using a

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**Table 3: Properties of LYBO:Ce crystal**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Properties</th>
<th>Numerical value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Neutron capture peak</td>
<td>2.22 ($^6$Li capture)</td>
</tr>
<tr>
<td></td>
<td>electron energy</td>
<td>0.46 ($^{10}$B capture)</td>
</tr>
<tr>
<td></td>
<td>equivalent (MeV)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Scintillation decay time</td>
<td>27 ns (0.1 at.% Ce)</td>
</tr>
<tr>
<td>3</td>
<td>Density (gm/cm$^3$)</td>
<td>2.8</td>
</tr>
<tr>
<td>4</td>
<td>Atomic density</td>
<td>3.28 ($^6$Li capture)</td>
</tr>
<tr>
<td></td>
<td>($10^{22}$ atoms/cm$^3$)</td>
<td>1.64 ($^{10}$B capture)</td>
</tr>
<tr>
<td>5</td>
<td>Macroscopic capture cross section (cm$^2$)(at thermal)</td>
<td>30.9 ($^6$Li capture)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>63.3 ($^{10}$B capture)</td>
</tr>
<tr>
<td>6</td>
<td>Calculated neutron Detection efficiency (eV)</td>
<td>99.8% Due to high atomic density of ~ 3 x $10^{22}$ atoms/cm$^3$[1]</td>
</tr>
</tbody>
</table>

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Fig. 6: A photograph of a USB based neutron detector employing LYBO:Ce scintillator crystal

Fig. 7: Measurement of pulse height spectra at from a thermal neutron source having known flux [6]
material enriched in $^6$Li that would consequently lead to better pulse height discrimination from low energy gamma background.

**Conclusions**

Defect-free single crystals of Ce doped LYBO were successfully grown. The grown crystals have been characterized for their phase and optical properties. Scintillation characteristics show their potential to detect thermal neutrons. After optimizing the scintillation parameter of the crystal, portable neutron detectors have been developed, which could be powered from a USB port of a laptop.

**References**

4. JCPDS card No. 80-0843