Introduction

The radiation detectors based on single crystal scintillators have several applications, including high-energy physics, medical imaging, geological exploration, nuclear industry and national security [1, 2]. Due to increasing applications, there is continuous demand and interest in the research for new scintillating materials with improved performances. In recent years, Ce doped materials have attracted the attention of many researchers due to their excellent combination of light output and decay time that involves allowed 5d-4f transition of these ions [3, 4]. Oxide crystals with a garnet structure have proven to be promising host materials due to their high density, broad transmission range and easy doping with rare earth elements like Ce [5, 6].

After Ce doped Y\(_{3}\)Al\(_5\)O\(_{12}\) (YAG) crystals were reported as scintillator detectors in electron microscopy by R. Autrata in 1978, significant material engineering by substituting different cations has been reported for garnet compounds [7]. Recently, Kamada et al. have done extensive combinatorial band gap engineering for multi component garnet compounds [8]. The substitution of Gd or Ga sites with ions of different ionic radii in chemical formula of A\(_{3}\)(B,Al)\(_5\)O\(_{12}\) (where A: Gd, Y, or Lu and B: Ga, La, or Sc), alters the crystal field splitting of the Ce 5d states, and as a result the position of the lowest excited 5d states relative to the minima of the conduction band edge can be optimized for a better scintillation efficiency [8]. Therefore, optimization of different cation concentrations in the lattice could be made to alter the scintillation properties in a desirable manner. It was found that Ce doped Gd\(_3\)Ga\(_3\)Al\(_2\)O\(_{12}\) (GGAG) crystals have promising scintillation properties [9]. These crystals have a high density of 6.7 g/cm\(^3\), high scintillation light output (LO) of over 45000 photons/MeV and a fast decay time of 55 ns [10].

In this communication, we describe a journey starting from the raw oxide materials to the development of a...
USB based portable gamma-ray spectrometer based on single crystal scintillator of GGAG:Ce.

**Experimental**

Single crystals of Ce doped GGAG were grown using the Czochralski technique in an automatic diameter controlled crystal puller system (Model: Oxypuller, Cyberstar). The starting charge was prepared using solid state sintering of constituent oxides Gd$_2$O$_3$, Al$_2$O$_3$, Ga$_2$O$_3$ in their stoichiometric molar ratio with 0.2 at% Ce doping. The sintering was carried in a box furnace at 1400°C. The formation of the single phase compound required for the melt growth was confirmed by X-ray powder diffraction measurements. As-prepared material in the form of pellets was loaded in a suitable crucible and heated to 50°C above its melting point to homogenize the melt. A single crystal seed (not oriented in a specific direction) was employed to initiate the crystal growth. A continuous flow of Ar through the closed growth chamber was maintained during the growth. The optimized parameters used for the growth of GGAG crystals are listed in Table 1.

**Table 1: Crystal growth parameters**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting temperature</td>
<td>1850°C</td>
</tr>
<tr>
<td>Pull rate</td>
<td>1 mm/h</td>
</tr>
<tr>
<td>Rotation rate</td>
<td>10-20 rpm</td>
</tr>
<tr>
<td>Initial chamber pressure</td>
<td>1x10$^{-5}$ mbar</td>
</tr>
<tr>
<td>Ar gas pressure</td>
<td>1100 mbar</td>
</tr>
<tr>
<td>Temperature gradient</td>
<td>30-50°C/cm</td>
</tr>
<tr>
<td>Cooling rate</td>
<td>20-30°C/h</td>
</tr>
</tbody>
</table>

X-ray powder diffraction (XRD) measurements, to verify the phase of the starting material and the grown crystals, were carried out with Cu Kα radiation ($\lambda=1.54056$ Å), employing Rigaku RINT 2000 diffractometer and scanning with a step size of 0.02° in the 2θ range from 10° to 90°.

Transmission/absorption/reflection spectra were measured with a Shimadzu 3600 UV-VIS-NIR spectrophotometer in the range from 185 nm to 800 nm. Photoluminescence (PL) properties were measured with an Edinburgh FLP-920 Spectro-fluorometer. The spectra were corrected for the spectral response of the source, monochromator and the PMT.

Light output and energy resolution measurements were made using a pulse processing chain consisting of a PMT, a pre-amplifier, a spectroscopic amplifier and an 8k MCA. The PMT was directly coupled to each sample using optical grease and a hemispherical Spectalon reflector to maximize the collection of light. The output of MCA was plotted in a graph where the abscissa represents the channel number corresponding to the light output from the crystal while ordinate shows the counts in a given channel. The scintillation decay was measured using a Tektronix digital oscilloscope.

**Results and Discussions**

**Optimization of composition and crystal growth**

X-ray diffraction pattern for Cerium doped gadolinium garnets Gd$_3$Al$_x$Ga$_{5-x}$O$_{12}$ (where 0≤x≤5) having different Ga/Al ratio are shown in Fig.1. The lattice
spacing variations as a result of partial or total Ga substitution at the Al site may be seen from a shift in the diffraction peak. The photoluminescence emission of Ce also shifts as a consequence of Ga substitution and therefore suggests a local re-adjustment of crystal field around the activator site.

The emission was found to shift towards higher energy (lower wavelength) by replacing Al cations with Ga as shown in Fig.2. This blue shift of Ce emission may be attributed to the replacement of smaller Al ions 0.54Å by bigger Ga ions 0.62Å. It may be understood with the help of the crystal structure of these compounds as shown in Fig.3. These materials crystallize in a cubic structure. The Gd/Ce is dodecahedrally coordinated with oxygen while Ga and Al are coordinated with oxygen in octahedral and tetrahedral configurations. A bigger ion at Al sites causes the compression of adjacent dodecahedral around Gd/Ce ion and consequently changes the crystal field. A change in the crystal field splitting of Ce 5d levels changes the position of the lowest excited 5d level with respect to the conduction band leading to the blue shift in the emission. The position of the lowest Ce 5d level relative to the conduction band can therefore be optimized in such a way that helps to minimize the thermal ionization at room temperature by providing a sufficient gap but should not contribute to the negative effect of shallow traps due to the increased gap. Consequently, an enhancement in the scintillation light output could be obtained by altering the material composition. The optimized ratio of Ga/Al was found to be 3/2 for the best combination of light output and decay time. Therefore we have grown single crystals of ce doped Gd$_3$Ga$_3$Al$_2$O$_{12}$ (GGAG) composition to fabricate radiation detectors.

Fig.4 shows photographs of an as-grown GGAG:Ce crystal having dimension of about 25 mm diameter and 60 mm length. The crystal gives a green fluorescence under the UV illumination due to an efficient emission from Ce$^{3+}$ ions suggesting a
possibility of using photodiode as photo sensors with these crystals in order to fabricate compact detectors.

Fig. 5 shows the transmission and emission spectra of GGAG:Ce crystal. The emission band due to the transition from the lowest excited 5d state to the ground 4f state of Ce\(^{3+}\) consists of two bands at 520 and 565 nm due to splitting of \(^{4}F_{5/2}\) and \(^{4}F_{7/2}\) ground state. The emission band lies in the transmission region of the crystal and therefore indicates less self absorption problem in these crystals. Therefore large size detectors can be fabricated using this material without self-absorption. The green emission from these crystals also matches well with the efficiency of photodiodes. This matching with photodiode enabled us to fabricate compact radiation detectors that operate at significantly lower voltages compared to a PMT.

Fig.6(a) shows the effect of annealing on the pulse height spectra of a \(^{137}\)Cs gamma source. The scintillation light output (LO) of the annealed crystals was found to increase after annealing the crystals in air at about 1000°C for 10 h. The results show that the oxygen vacancies could be effectively eliminated by the post growth annealing. The scintillation decay time was also found to improve after the annealing. The major component of the scintillation decay time was measured as 55 ns (Fig.6b). The improvement in scintillation properties after annealing the crystals in air confirms the role of defect centers related to the oxygen sub-lattice.

**Scintillation characterization**

The scintillation light yield measured from as-grown crystals was found to be much lower compared to the reported values. Since the crystals were grown in the Ar ambient, they are prone to have some oxygen vacancies and therefore post growth annealing treatments in air were performed to reduce the defect concentration.

![Fig 5: Transmission and emission spectra of GGAG:Ce crystal.](image)

![Fig 6: Effect of annealing on (a) relative light yield and (b) scintillation decay time of GGAG:Ce crystals.](image)
A USB powered detector Setup

A crystal sample with dimensions as 18x18x10 mm³ was cut from the annealed crystal. The sample did not have any visible inclusion or scattering centers. One surface was optically polished and coupled to a PMT having an active area of 1 inch diameter. The PMT output was given to a pulse processing assembly consisting of a pre-Amp, a shaping amp and an 8k MCA.

The power to all the components including HV to PMT was provided from a single USB port by employing necessary DC-DC converters. It made the whole set-up portable and convenient to use with a laptop as shown in Fig.7.

![Fig. 7: A USB based gamma-ray spectrometer developed using a GGAG crystal.](image)

The data processing was carried out by the Amptek DppMCA software. The setup was calibrated using Cs¹³⁷ and Co⁶⁰ sources and the performance was checked using sources of various other radio-active isotopes.

The parameters like shaping time of spectroscopic amplifier, PMT voltage and gain were optimized to get the well resolved pulse height spectrum. An energy resolution of about 4% has been achieved at 1332 keV gamma-ray from a Co⁶⁰ source, as shown in Fig.8.

![Fig. 8: Pulse height spectrum of a Co60 source recorded using the GGAG crystal based gamma spectrometer.](image)

Conclusions

Single crystals of Ce doped Gd₃Ga₃Al₂O₁₂ crystals were successfully grown for gamma detection. The various characteristics of these crystals were investigated in details. Gd₃Ga₃Al₂O₁₂:Ce crystals grown in argon ambient have defects related to oxygen vacancies which could be eliminated by a post growth annealing treatment of the grown crystals. The light output and energy resolution were improved after annealing the crystal in air. After optimizing the scintillation parameter of the crystal, a portable detector has been fabricated which could be coupled to a USB based electronic set-up that does not need bulky high voltage power supplies or other NIM modules.

References


