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# Study on Growth and Optical, Scintillation Properties of Thallium Doped Cesium Iodide-Scintillator Crystal

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**ABSTRACT**

Single crystal of Thallium doped Cesium Iodide –Scintillator crystal was grown using vertical Bridgeman technique. The grown crystal was included for cutting and polishing for the characterization purpose and this crystal was studied by optical transmission properties, photo luminescence and thermally luminescence characteristics. Gamma-ray detectors were fabricated using the grown crystal that showed good linearity and nearly 7.6% resolution at 662 keV.

**Key words:** Scientillator crystal, optical properties, TSL, Scientillator Test.



## INTRODUCTION

Room temperature semiconductor radiation detectors such as CdZnTe, CdTe, and HgI2 are widely investigated in nuclear measurements (Carini *et. al.,* 2007). These semiconductors offer very good energy resolution compared with scintillator detectors, but detection efficiency and physical rigidity is very low. Currently, compound semiconductor materials are more expensive than scintillator crystals. So, scintillator detectors are still promising candidates for an NDT and a radiation monitoring system[1]. Thallium doped Cesium Iodide, a scintillator crystal which is a high-potential detector material, due to its wide applications in photocathode, gamma ray detectors and particle detectors in nuclear experiments[2-5]. Tl doped CsI single crystal is old and well known scintillator material. It has good scintillation efficiency and is less hygroscopic and less brittle than NaI. This material could not achieve its full potential in the past due to the unavailability of a matching PMT. However, use of PIN photodiodes, which show good efficiency at longer wavelengths and compact in size, has renewed the interest in the CsI(Tl) crystals. Also, since CsI:Tl shows different decay times for different charge particles, pulse-shape discrimination techniques can be effectively used for the particle identification . Single crystals of CsI:Tl can be grown by Bridgeman as well as Czochralski methods. Though, the crystal growth using the Bridgman method is not a problem, sticking of the crystal with crucible wall and hence recovery of the crystal after the growth and thermal and mechanical stresses generated there in are important issues of considerable interest[6]. In this paper we are reporting

the growth of Thallium doped CsI single crystals in Glassy carbon crucibles by vertical Bridgeman technique. Gamma-ray detectors were fabricated and characterized to study the effect of growth conditions on the quality of crystals.

**CsI:Tl crystal growth process**

Glassy carbon crucible having 35 mm in diameter with conical bottom was taken for the growth experiment. High purity (99.995%) CsI and Tl were taken in the Glassy carbon crucible and sealed it after the vacuum de-hydration process. This vacuum de-hydration process has done under $10^{-4}$ mbar argon ambient at 150°C using vacuum pump for avoiding the formation of impurities during raw material preparation connecting with the salt hydrolysis process under heating and of oxygen containing impurities.

The crucible was then put inside the furnace on a growth station and temperature was raised so that the bottom of the crucible was at 630°C. Melt was kept at this temperature for 12 hours. After The temperature stabilizes, the ampoule is lowered slowly into the lower temperature gradient zone at a rate of 1mm/h to initiate crystal growth from the ampoule's conical bottom. The upper zone has temperatures above the melting point of Cesium iodide. The lower zone has a temperature below melting point and an adiabatic zone as a baffle between the two. One K type thermocouple with the motor has attached for measuring the axial temperature gradient along the furnace.

To prevent cracking resulting from thermal stress in the crystals, as grown ampoule was annealed in the lower zone during growth. After the growth had finished, the furnace was cooled to room temperature at a rate of 20 ~ 50°C/h.

The temperature profile in the melt is also shown in Fig. . A fine single CsI :Tl crystal has been grown as shown in fig. 2[a] and fig. 2[b].

**Result and analysis**

**Transmission Characteristics**

Transmission spectrum was recorded in the wavelength range 200–1100 nm employing a double beam photo-spectrometer Chemeto 2500. The polished samples (20 mm thickness) were used for these transmission characteristics (Figs.3)

From the curve shown in Fig 3., the cut off wavelength of the transmission is around 300 nm. So we can observe that the grown crystal have the ability to absorb a wide range of energy spectrum. It enables the property of scintillation test [7].

**Luminescence Characteristics**

For the photoluminescence measurements, samples (2mm thick) were cut from the crystal ingot and polished to optical finish. This luminescence spectrum was recorded in the range 200-900 nm in a reflecting geometry, employing a florescence spectrometer Edinburgh model FLP-920.

The emission spectra of Tl doped CsI crystals were measured at room temperature. The Fig.4 shows the emission spectrum of Tl-doped CsI crystals. The addition of Tl by 0.02% exhibits peaks at 550nm. The light emission spectrum of CsI(Tl) excited by ionizing radiation has different components. The main contribution is due to the charge recombination near a Tl+ centre, giving a broad band at 550 nm [8,9]. From earlier reports it was found that for 0.02% doping of Tl the peak at 550 nm is mainly due to the Tl dimer centres . The peak at 550 nm can be attributed to the exitons of the CsI (Tl) and this forms the major luminescence part due to doping of Tl. The emission spectrum is having the maximum at 550 nm, which allows photodiodes to be used to detect the emission. The output of the photoelectrons from CsI(Tl) (photodiode) crystal is higher than that for NaI (Tl) photomultiplier detector. The increase in doping concentrations may increases the intensity of exciton emission when compared to dimer. The small peak at 550nm in the emission band is due to excitonic emission. As reported, the 345nm peak is suppressed in crystals activated by Tl. This clearly indicates the vacancy type defects suppression due to doping It is evident that (halogen ion) lattice defects mainly contribute to this lattice emission than structural defects due to plastic deformation.

**Thermally Stimulated Luminescence (TSL)**

Thermally stimulated luminescence (TSL) glow curves of the crystals were recorded in the 25–200 1C range employing a heating rate of 0.5 $^0$C/ min. Luminescence spectra as well as after- glow

spectra were recorded in the range 200–900 nm In a reflecting geometry, employing a florescence spectrometer Edin- burgh model FLP-920. The TSL emission spectrum was recorded by holding the sample at 45°C.

The phenomenon of TSL is explained using a hand picture of solids with respect to its electronic energy levels. It is known that a crystal contains certain number of lattice defects such as vacancies. Interstitials and dislocations present in it as well as some additional defects created by doping them with chemical impurities. These defects introduce localized energy levels (i.e donor and acceptor levels) in the forbidden energy gap. These levels either belong to the impurities / lattice defects present in the crystal or the host lattice under the influence of them.

Free electrons and holes are generated in a crystal, upon exposure to ionizing radiation and most of them recombine immediately resulting in the emission of light or in lattice vibrations. However, some of the electrons and holes are trapped at the donor and acceptor levels respectively resulting in the formation of color centers. Most of them are trapped charges at vacancies (like F-centres, F-aggregates, etc.) or at interstitials (like V centers). According to Pooley, this process of colour centre production by radiolysis is known to proceed through an excitonic mechanism**.** On warming the crystal after irradiation. Electrons (or holes) are released from their traps, become mobilized and wander through the crystal. When they meet their counterparts, recombination between electrons and holes occurs with a part of the recombination energy released in the form of light and this is termed as TSL[10,11].

Usually in TSL studies, the irradiated sample is heated at uniform heating rates. The plot of total light intensity emitted with temperature of the sample is called as glow curve and the spectral distribution of the luminescence at a particular temperature is called as TSL emission spectrum. The energy required to release the electrons (or holes) from the trap is called thermal activation energy 'E' and the area under the glow peak is related to the concentration of filled traps**.** Normally, a number of trapping sites may exist with different activation energies. On heating the material with uniform heating rate, charge carriers are released from these traps at different temperatures. This results in the appearance of a number of glow peaks in a glow curve with their maxima at different temperatures, each glow peak representing the thermal annihilation of particular type of defect *1* color centre in the crystal.

The glow curve for grown crystal (for radiation dose of 200 Gy) is shown in Fig. 5. The peak temperature shifts towards higher temperatures for crystal. As UV light does not have sufficient energy to create new defect centres in the CsI (Tl), the root cause of coloration of the grown crystal may lie somewhere else. One possibility for such coloration could be proposed as the capture of electrons by defect centers already formed during the crystal growth process. It is known that thermally stimulated luminescence peak at near 50°C.

**Scintillation tes**

It is generally accepted that the scintillator contribution to an overall energy resolution, called the intrinsic resolution, is a fundamental limitation of the attainable energy resolution of scintillation detectors[12]. Scintillation studies were carried out on a 15 mm diameter and 20mm long crystal. The crystal was wrapped with 10 layers of Teflon tape leaving one face open to connect with a photo multiplier tube (PMT).Optical grease was applied to couple the crystal with the PMT avoiding any trapped air bubbles. To verify the linearity of the detection systems, five different isotopes were used: 137Cs, 134Cs, 60Co, 22Na and 57Co, having a dominant gamma emission at roughly 662 keV, 605 keV, 1173 keV, 511 keV, and 1332 keV, respectively[13]. The Gamma ray spectra of 137Cs, 134Cs, 60Co, 22Na and 57Co sources were recorded using the detector assembly consisting of CsI:Tl scientilators , a PMT, a preamplifier, a spectroscopic amplifier and an 8k multichannel analyzer. A shaping time constant of 3 microsecond was used.

Linearity of the pulse height response of the gamma detector was checked upto 1332 keV gamma-rays .Calibration curve for the detector and a typical 137Cs gamma spectrum are shown in figure 7 From it is noted that an energy resolution of about 7.6% at 662 keV. Energy resolution studies determine the ability of a detector to distinguish

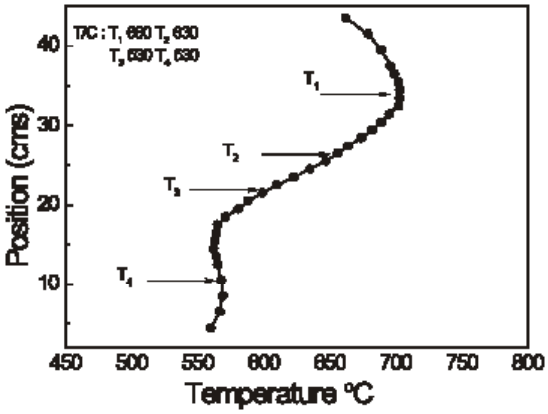


**Fig. 1: Temperature Profile**

Gamma sources with slightly different energies, which is of importance for gamma spectroscopy.

In CsI(Tl), the gamma ray (137Cs) interactions are almost entirely due to the photo-electric effect, and the scintillation response can be attributed to primary photo-electrons and the subsequent electrons that appear as the result of filling the vacancy in the ionized atom[14]. The samples used were of good optical quality, with dimension of 1 cm diameter and 1 cm height cylindrical shape crystals. All crystal surfaces were polished and the crystals coupled to PMT using the


**Fig. 2(a): Grown unpolished CsI:Tl Crystal**

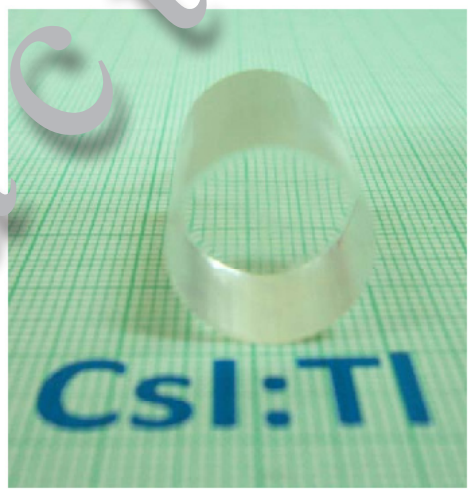


**Fig. 2(b): Polished crystal**

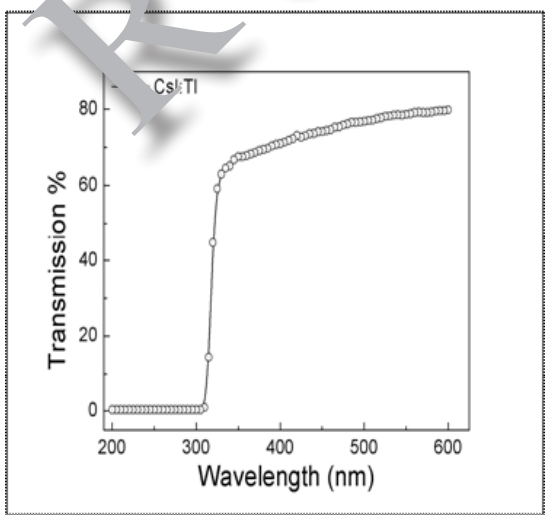


**Fig. 3: Transmission spectra**

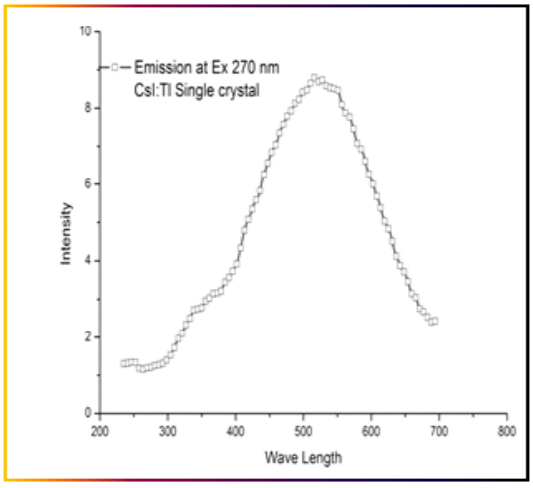


**Fig. 4: Photo luminescence spectra of grown crystal of CsI:Tl**

BICRON optical grease. The crystals were packed before measurements into aluminium foils with wall thickness of 4 mm. To ensure light collection only through the contact area scintillator-PMT and to avoid the photocathode exposure to scattered radiation, the container was covered from all surfaces, including the photocathode side, by black absorbing tapes. For measurements, we used gamma quanta source 137Cs. The reported energy resolution with respect to the 137Cs are 11.270.2% for CsI(Tl). But the present study shows the better energy resolution 7.6% for CsI for the optimized Tl concentration of 0.02 mole% at room temperature. Energy resolution studies determine the ability of a detector to distinguish gamma sources with slightly different energies, which is of great importance for gamma-spectroscopy[15,16].

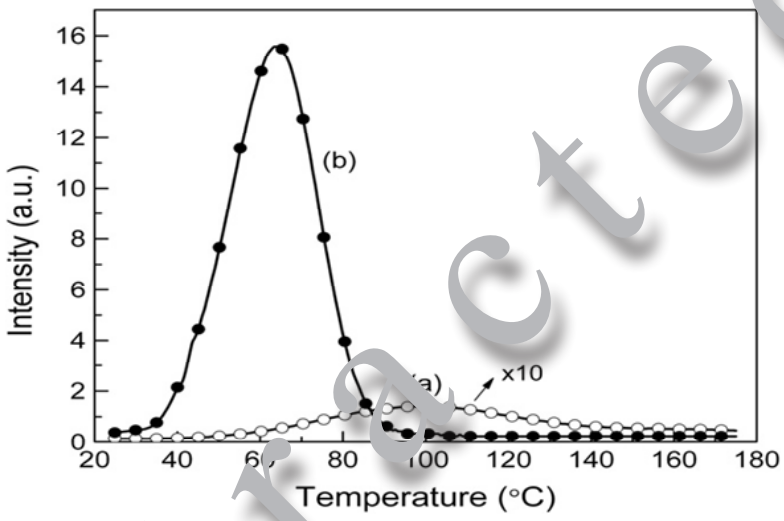


**Fig. 5: The TSL glow curve for grown crystal**

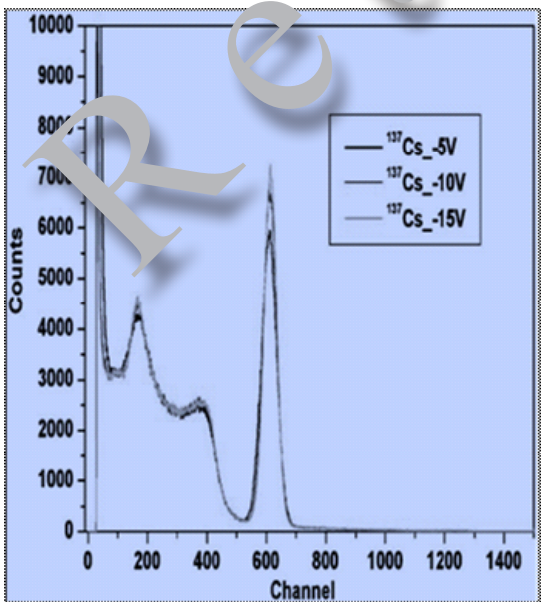


**Fig. 6: Scintillator performance grown CsI(Tl) crystal**

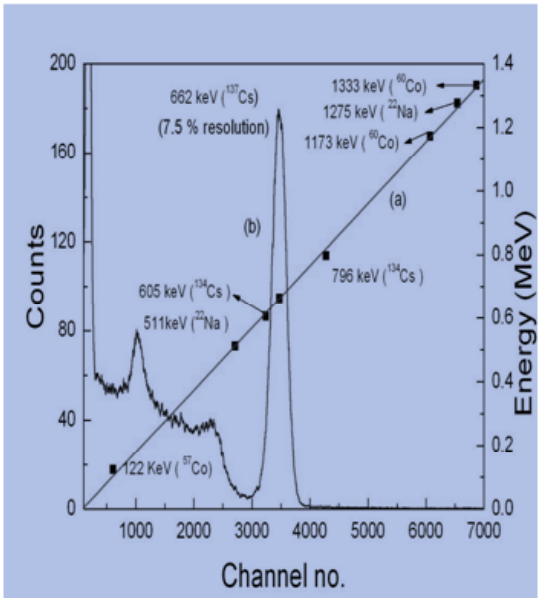


**Fig. 7: With calibration curve drawn from detector to different radio nuclides**

Fig.6-7. Scintillator performance grown CsI(Tl) crystal with calibration curve drawn from detector to different radio nuclides

## CONCLUSION

High quality single scintillator crystal of 0.02 mole % Tl doped Cesium Iodide was grown by vertical Bridgeman technique. Glassy Carbon crucible was used to avoid sticking of crystal with the crucible wall. The grown crystal was extracted from the crucible without involving an inversion process thereby avoiding thermal and mechanical stresses. The transmission and luminescence measurements shows that the purity of the crystal quality and wide transparency. Using these crystals $\gamma$- ray detectors were fabricated which show good linearity and 7.6% resolution at 662 keV.

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## REFERENCES

1. Han Soo Kim, Jang Ho Ha , Se Hwan Park, Seung Yeon Chob, Yong Kyun Kim , *Appl. Radia. Isotopes*, **2009,** *67*, 1463–1465.
2. Sciver, W. Van; R. Hofstadter, *Phys. Rev.* **1951**, *84,* 1062–1063.
3. Suryanarayanana, S.; Karelisa A., Vedantham S., *Nucl. Instrum. Methods. A*, **2004** *533,*560.
4. Fioretto, E.; Innocenti, F.; Vies, G.; Cinausero, M.; Zuin, L.; Fabris, D.; Lunardon, M.; Nebbia, G.; Prete, G., *Nucl. Instrum. Methods. A,* **2000,***442*, 412–416.
5. Gonnelle, J.; Parmentier, M., *Nucl. Instrum. Methods. A,* **2003**, *504, 321*–324.
6. Borilo, V.I., Nemenov, V.A. ; Protsenko, V.I. ; Radkevich, A.V.; Eidelman, L.G., *J. Cry. Growth* **1981**, *52*, 509–513.
7. Sathyanarayana, D.N. , *Vibrational spectroscopy*, 2nd edn, New Age International Limited, New Delhi,(**2004**)
8. Hamada M.M. ,et al., *IEEE Trans. Nucl. Sci.* **2001**, *48* .
9. Timothy H. G**,** *Encyclopedia of Analytical Chemistry,* R.A. Meyers (Edi.) Copyright of Jonn Wiley & Sons Ltd.(**2003**)
10. Bo, Yang Xin-, Jun Xu, Li Hong-Jun, & et. al., *Chin. Phys. B* **2010**, *19*, 047803
11. Gala, M.; Daoa, L.V. ; Krafta, E.; Johnstona, M.B. ; Carmodya, C.; Tanb, H.H.; Jagadish, C., *J. Lumin.,* **2002**,*96*, 287–293
12. Moszyn´ski, M.; James, R. B.; Franks, L. A.; Burger, A.; Eds, *Proc. SPIE-Int. Soc. Opt. Eng.*, **2005,** *5922*, 592205-1
13. Bai1, Jin Hyoung ; Whang, Joo Ho; *Pro. In Nucl. Sci. And Tech.*, **2011**, *1*,.308-311.
14. Chowdhury, M.A.H. ; Imrie, D.C. ; *Nucl. Instrum. Methods. A* ,**1999**, *432* , 138–146.
15. Preston, D.W.; Dietz, E.R.; The Art of Experimental Physics, Wiley, **1991,**376-385,**.**
16. Serway, Raymond A.; Moses, Clement J.; Moyer, Curt A., *Modern Physics,3 edi,* Thomson Learning, Belmont, **2005**., 431-432 & 389-392
17. Liua, Y.; Chenb, C.P.; Lib,c, H.B.; Tangc, C.H., *Nucl. Instrum. Methods. A,* **2002,** 482, 125.
18. Birks, J. B. ; *The theory and practice of scintillation counting*, Pergamon press, Oxford, **1964**.96-103,