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Effect of OH content in the quartz crucible on the growth and quality of CsI single crystals and remedies

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ABSTRACT

We have investigated the effect of hydroxyl (OH) content in fused silica crucible on the scintillation and optical properties of the CsI single crystal, but not limited to, grown by Bridgman technique. For the purpose, 0.1 mol% Tl doped CsI single crystals were grown in crucibles made from fused silica of different grades with OH content varying from 20 ppm to 200 ppm. Silica glass of crucibles was characterized by FTIR and UV–VIS-NIR spectroscopy for the estimation of OH content. Grown crystals were tested for their scintillation performance and a correlation between OH content in silica glass and crystal quality is established. The possibility of 'OH' out-diffusion from silica crucible into the melt at higher temperature was further established by temperature dependent study of outgassing from silica crucible by residual gas analyzer (RGA). Further, an optimized process for silica crucible annealing to remove OH (< 20 ppm) is proposed to achieve excellent crystal quality of a 5.6% energy resolution at 662 keV without any co-doping in Tl doped CsI.

1. Introduction

Single crystals of alkali and rare earth halides(NaI, CsI, KBr, SrI_2, $LaBr_3$, $CeBr_3$ etc) are functional material finding various applications in gamma ray and particle detectors and as optical windows and beam splitters [1–6]. The conventional methods for growing these crystals use directional crystallization of the corresponding melt in a crucible employing Bridgman technique [7–10]. It is relatively simple and commercially viable technique to grow small to medium size crystals (10 mm – 80 mm diameter) with melting temperature in 400–800 °C range [11,12]. Crucible shape and size plays a central role in Bridgman technique as it contains melt and facilitate directional solidification and grain selection during single crystal growth. In general, when it comes to halide and rare earth halides, fused silica or quartz is material of choice for crucible fabrication owing to its excellent thermo-mechanical and chemical properties featuring very low thermal expansion coefficient, high temperature stability, inertness and low cost [13–17]. Different grade of fused silica with varying impurity contents and concentration are commercially available for crucible fabrication. Depending on the source material and manufacturing process, impurity and OH content of fused silica may vary from as high as 1000 ppm to as low as few ppb [18,19]. Here, though the crucibles are thoroughly cleaned by due process before use in crystal growth, impurities and OH content remain present in the bulk of crucible wall. At room temperature these impurities are fixed in the glass matrix but there is a high possibility that at elevated temperature it may diffuse in the melt from the bulk of crucible wall and affect the quality of grown crystals. 'OH' content in silica glass crucible may play a detrimental role as many alkali and rare earth halides are highly hygroscopic [17,20,21]. To our best knowledge, we could not find any literature addressing this phenomenon and its effect on crystal growth and its quality.

In this paper we have investigated the effect of OH content in fused silica crucible on the quality of the single crystal of CsI grown using Bridgman technique. The crystals were grown in crucible made from fused silica of different grades with varying OH content. Grown crystals were characterized to assess their quality and a correlation between OH content and crystal quality is established. Further, quantification of maximum permissible OH content is done and possible heat treatment to reduce the OH content to permissible level in the fused silica tube is also elaborated. Here, though CsI is chosen to the study the phenomena, the findings can be extended to all materials grown in quartz crucible.

2. Experimental methodology and procedures

In this study, 0.1 mol% Tl doped CsI single crystals are grown by Bridgman Technique. To study the effect of OH content in silica glass crucible on the crystal quality a variety of fused quartz crucibles containing OH ranging from 20 to 200 ppm were selected for fabrication of

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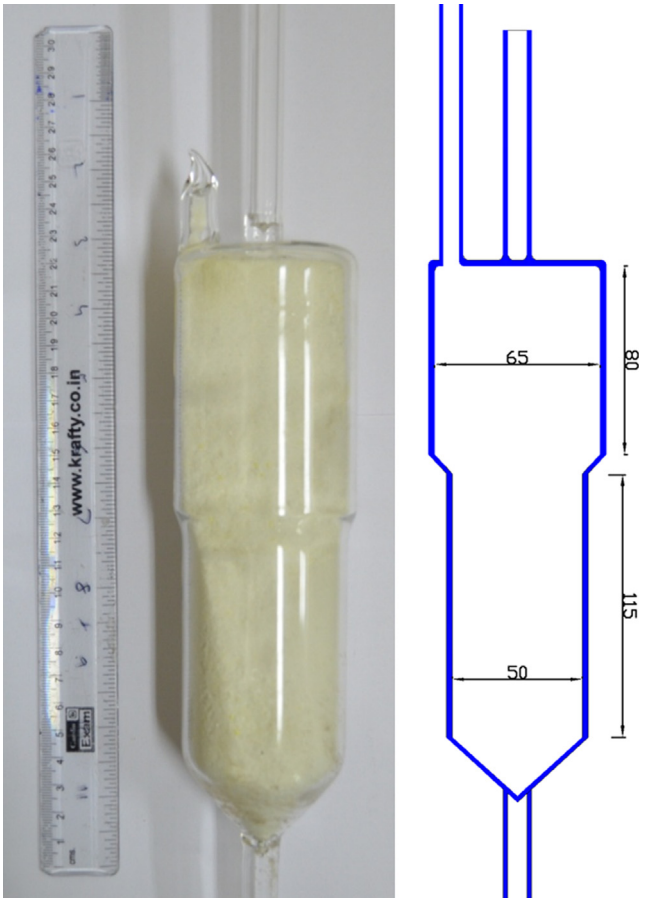

Fig. 1. Photograph of quartz crucible loaded with dehydrated material and sealed under vacuum ($1x10^{-5}$ mbar) along with the schematic drawing.

crucibles and subsequent crystal growth. A typical photograph of crucible is shown in Fig. 1. Before loading the material, the crucible's inner walls were cleaned by acetone followed by immersion in a 10% HF solution for 2 min and ultrasonication in DM water to remove grease and other surface contamination. After cleaning, crucibles were baked at 700 °C for 2 h under running vacuum at $2x10^{-3}$ mbar pressure to degas the crucibles. Some of the crucibles were systematically baked at 900 °C and at $2.5x10^{-6}$ mbar pressure for removal of OH from silica glass. High purity (99.999%) polycrystalline powders of CsI and TlI (0.1 mol%) were used in each crystal growth experiments. To remove any residual moisture, the material was dehydrated by heating under vacuum ($2x10^{-5}$ mbar) at 350 °C for 10 h.

An in-house designed Bridgman crystal growth system with slight modification for crystal retrieval was used for the growth. It consists two independently control heating zone separated by a baffle. To achieve the desired temperature gradient each zone was made of two independently controlled resistive heating elements. After loading the crucible inside the furnace, the temperatures of the top and bottom zone of the furnace were raised to 650 °C and 550 °C respectively. This setting provides a temperature gradient of 20 °C/cm in the adiabatic zone. Melt was allowed to thermalize for 6 h, afterwards it was lowered at a variable rate of 0.5–2 mm/h to the bottom zone of the furnace through the temperature gradient for complete solidification of the melt into single crystal. Finally, the furnace was cooled down to room temperature at a uniform rate of 30 °C/h. After growth, crystals were removed by cutting the quartz crucible. Details of crystal growth system and process can be found in the reference [22]. The crystals were cut into different shape and sizes and polished for characterizations.

The grown crystals and silica glass crucibles were characterized employing various techniques to estimate and quantify the effect of OH content in silica crucible on crystal properties. UV–Vis-NIR spectroscopy is used to estimate the OH content in silica glass crucible. The transmissions of the quartz tubes, used for crucible fabrication, were recorded for 2000–3000 nm wavelength range employing Shimadzu make UV-3600 spectrophotometer. To monitor the evolution of gases from the silica crucible with temperature, crucible were annealed under high vacuum and emission of gaseous species was monitored by residual gas analysis employing a Pfeiffer vacuum make PrismaPlus® QMG 220 M1 RGA in the atomic mass unit range from 1 to 100. Analysis was done in the temperature range from 150 to 900 °C. Before subjecting to annealing, crucibles were cleaned following procedure described in previous section and fired at 150 °C for 2 h for removal of physiosorbed moisture.

FTIR measurements were performed on CsI raw material and grown crystals using a VERTEX 80v FTIR spectrometers (make: Bruker Optiks, Germany) in the range of 400–7000 cm^{-1} to estimate various functional groups present at trace level. To see the effect of OH on scintillation properties, two samples of 20x20x20 mm^3 were cut from single crystals grown in crucible containing varying amount of OH and processed into detector element. About 5 layers of 0.1 mm thick Teflon tape were used as reflectors and optical grease was used for the optical coupling with photomultiplier tube (Hamamatsu: R6095, 25 mm diameter). A ^{137}Cs gamma-ray source was used to check the pulse height characteristic of the detector. A pulse shaping of 10 μs was used in read out.

3. Results and discussion

After growth, CsI single crystal ingots (47 mm diameter and 75 mm length) were recovered after cutting open the quartz crucible. All the grown crystals were crack free, however, few of the grown crystals were containing 3D defects in the form of black particles distributed in the bulk (Fig. 2a). It was observed that inclusions content varies from crystal to crystal as recovered from different quartz crucibles, though all the growth parameters were same in each growth run. Based on the level of inclusion, the grown crystals could broadly be put in three categories; (i) Type-I: crystals that contains large number of black particle distributed in top half of the bulk, (ii) Type-II: crystals that contain inclusion only in top 15 mm of the grown crystal and (iii) Type-III: crystals free of any visible inclusions. It was also observed that for most of the crucibles there was a layer of black particles/coating inside the crucibles wall. The thickness of black layer coating inside the crucibles was found to be roughly correlated to the amount of black particles inclusion in the grown crystals.

Due to the observed rough correlation between black particles coating on inside wall of crucibles and occurrence of inclusion in grown crystals, it was decided to analyse the crucible material for possible contaminant. Fused silica crucibles used to grow of all three types of crystals were subjected to UV–VIS-NIR transmission spectroscopy in the 2000–3000 nm wavelength range. The transmission spectra, in Fig. 2b, show absorption band at 2720 nm related to hydroxyl group [23] in silica that varies in all three type crucibles and is maximum in Type-I and minimum in Type-III. This indicates that the hydroxyl content in silica crucible may be responsible for the inclusions and defects in the grown crystals. Further we also suspected the OH in raw material as probable culprit for the inclusion in grown crystals. To analyse it, pellets of CsI raw material before and after dehydration were prepared and subjected to transmission spectroscopy by FTIR. Transmission spectra of CsI pellets are given in Fig. 3a. It shows that in raw material there is some amount of moisture (3490 cm^{-1} peak corresponding to OH stretching); however, this moisture was completely removed by dehydration of the raw material at 350 °C for 10 h under $2x10^{-5}$ mbar pressure.

Transmission spectra of 3 mm thick single crystal samples from Type-I and Type-III crystals are shown in Fig. 3b. When compared with the transmission spectra of dehydrated raw material, it is observed that

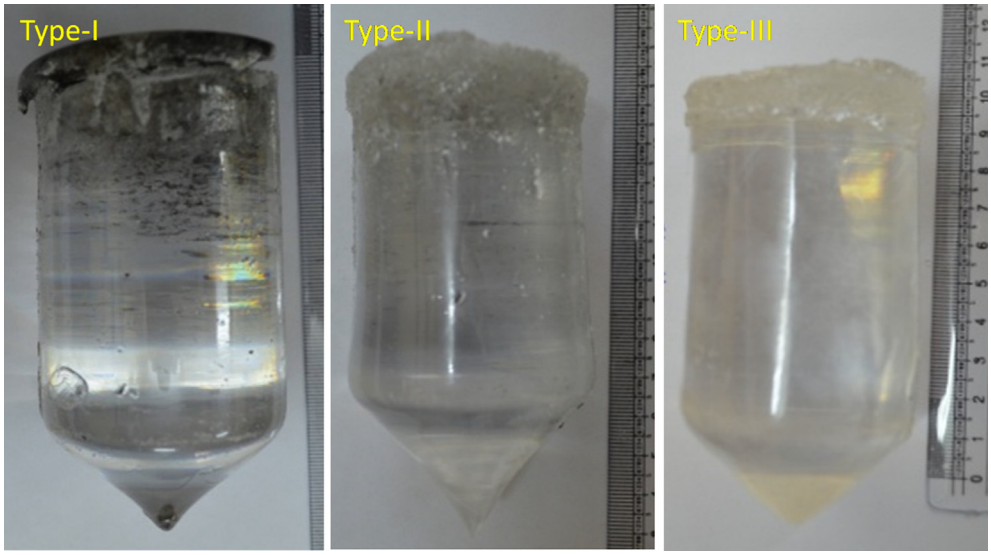

Fig. 2a. Photograph of CsI single crystals grown in quartz crucible containing OH in decreasing order form Type-I to Type-III.

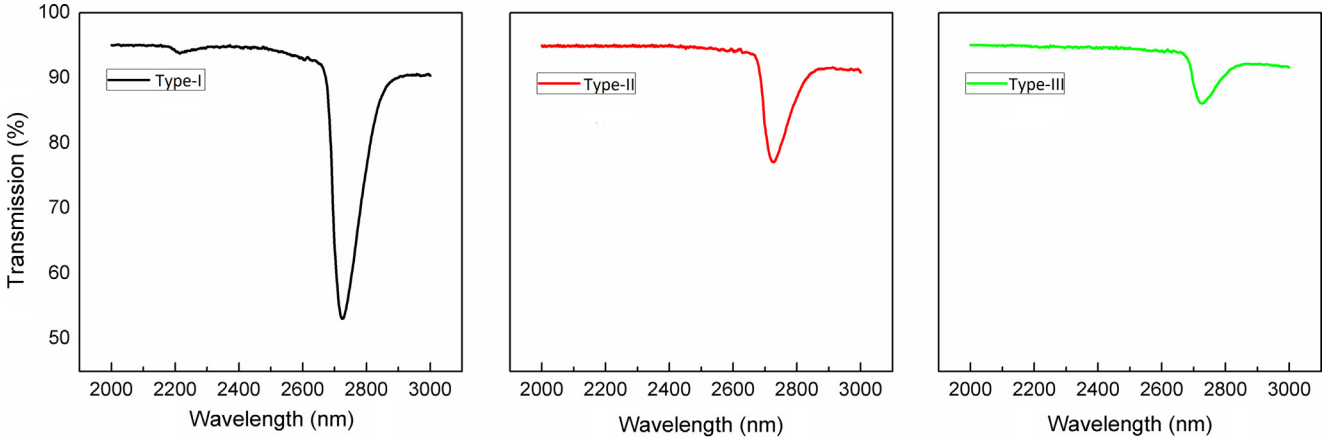

Fig. 2b. NIR Transmission spectra of silica glass crucibles used for the growth of Type-I, Type-II and Type-III crystals (Absorption peak at ~ 2730 nm corresponds to OH and its intensity is proportional to amount of OH in quartz).

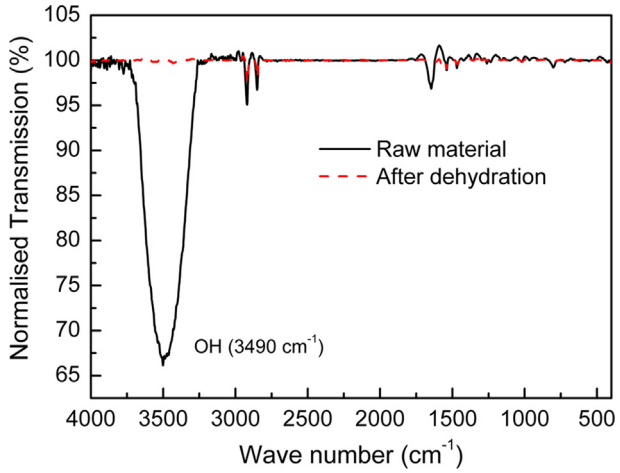

Fig. 3a. IR transmission spectra (450–4000 cm^{-1}) of raw material, before (solid black line) and after dehydration (dashed red line). 3 mm thick pellets prepared by cold compaction were used for the measurements.

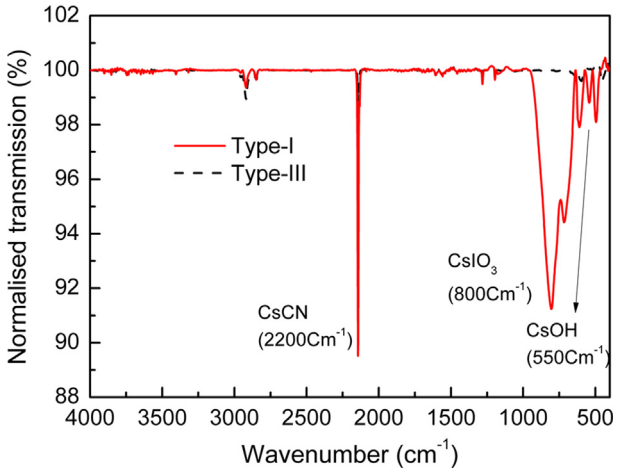

Fig. 3b. IR transmission spectra (450–4000 cm^{-1}) of 3 mm thick discs of Type-I (solid red line) and Type-III (dashed black line) crystals.

while Type-III samples have spectrum identical to dehydrated raw material, Type-I sample have prominent additional peaks at 2200 cm^{-1}, 700–800 cm^{-1} and around 450–650 cm^{-1}. With the help of available literatures, these bands are identified as related to CsCN (2200 cm^{-1}), $CsIO_3$ (800 cm^{-1}) and CsOH (550 cm^{-1}) [24,25]. The possible explanation of these additional peaks is contamination of melt with the gasses diffusing into the melt from crucible walls.

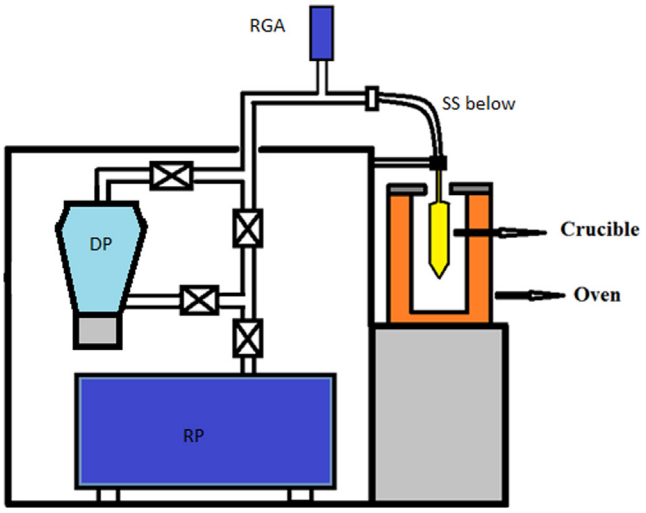

Fig. 4a. Schematic of the arrangement of RGA for measurements of residual gas composition during baking of silica glass crucible.

In literature it is reported that H_2, OH and other trace gaseous impurities in silica start diffusing through the matrix at high temperature [23]. To establish the fact that the same process may be responsible for the diffusion of OH into the melt at high temperature during single crystal growth, a silica glass crucible containing OH at approximately 200 ppm level was subjected to annealing up to 900 °C under vacuum. The composition of residual gas was observed using a RGA as a function of temperature (schematic of experimental setup is shown in Fig. 4a). The data from the RGA was analyzed using standard mass spectrum of gases like O_2, H_2O, H_2, N_2, and CO_2 and net evolution of H_2, and OH and O was calculated and is plotted in Fig. 4b.

It is observed that the evolution of OH starts at low temperature (200 °C) preceding O and H_2. This may be because of physio-sorbed water molecule at the surface of crucible as well as on the vacuum line. As the temperature increases H_2 starts evolving along with the OH at around 300 °C. In silica, hydrogen may have two origins, one is from absorbed hydrogen during the manufacturing process of the silica glass and other source is dissociation of H_2O or OH group present in silica. At

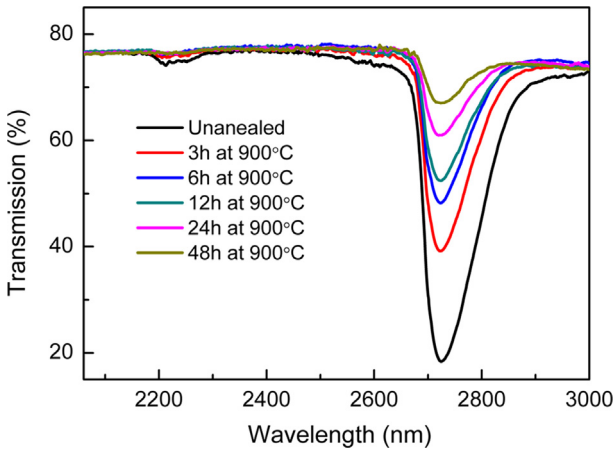

Fig. 4c. Absorption spectra of Silica glass for different annealing time at 900 °C showing the change in OH with annealing.

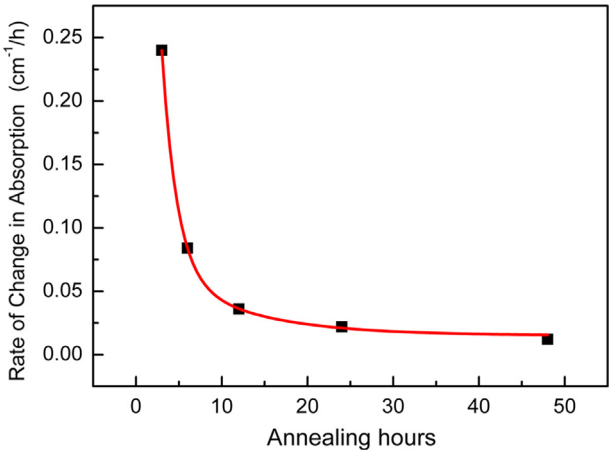

Fig. 4d. Rate of change in OH related absorption as a function of annealing time.

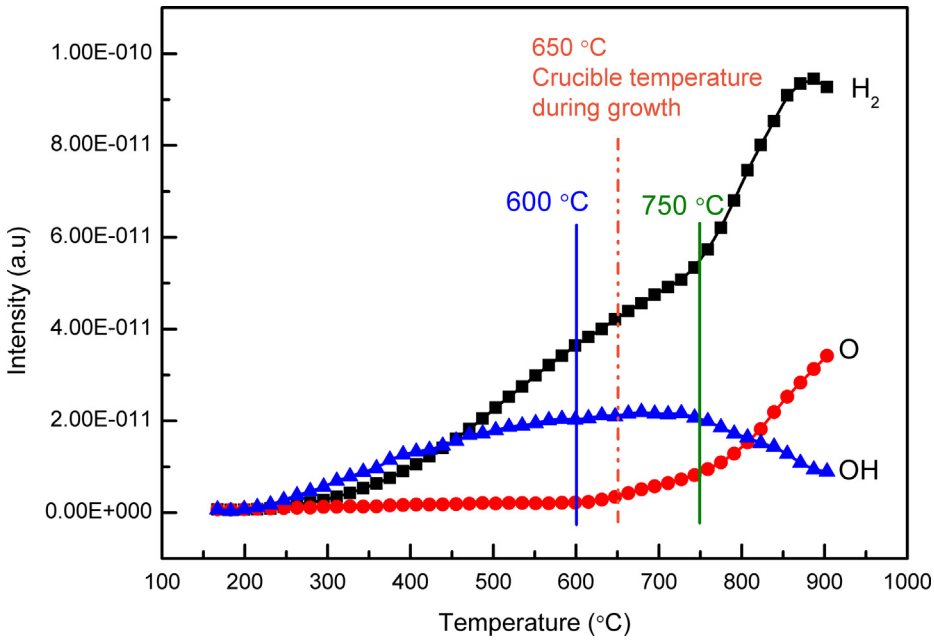

Fig. 4b. RGA analysis of residual gases and evolution of H_2 (-■-), O (-●-) and OH (-▲-) as a function of temperature during annealing of silica crucible.

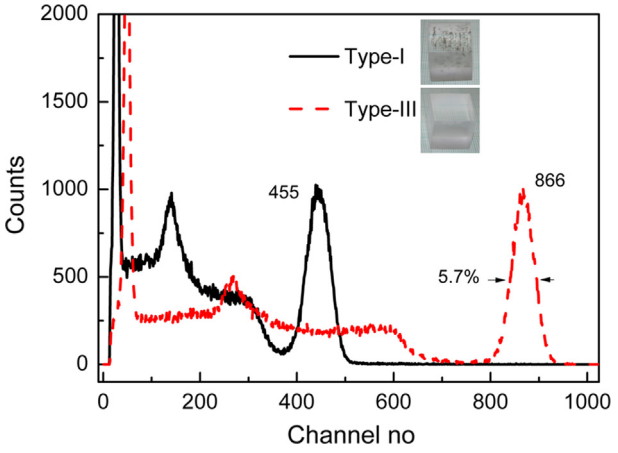

Fig. 5a. Pulse height spectra of ^{137}Cs recorded using Type-I and III crystals as detector (sample size: 20x20x20 mm^3, shaping time: 10 μs).

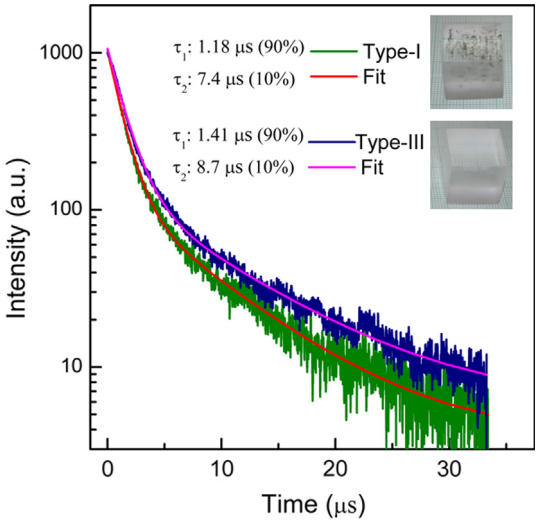

Fig. 5b. Decay profile of Type-I and III crystals (sample size: 20x20x20 mm^3, gamma source: ^{137}Cs).

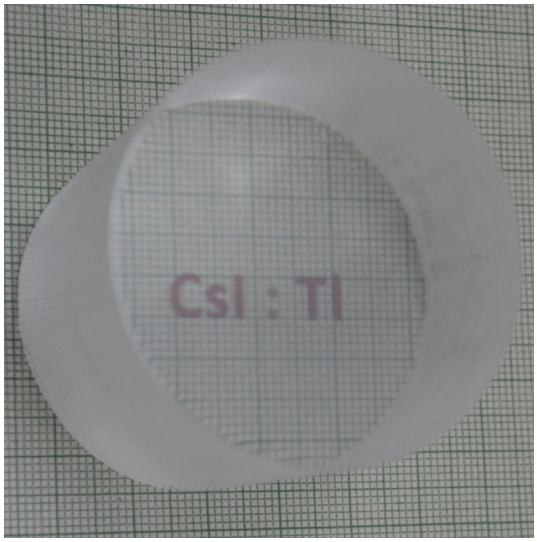

Fig. 6a. Scintillator detector (dia: 45 mm, L: 48 mm) fabricated using crystal grown under optimum condition (OH content in crucible < 10 ppm).

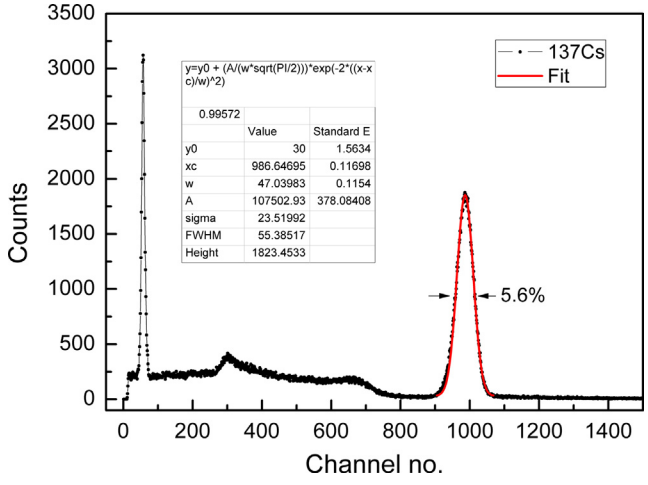

Fig. 6b. A gamma spectrum of ^{137}Cs showing 5.6% resolution at 662 keV recorded by fabricated detector (dia: 45 mm, L: 48 mm).

lower temperature it is absorbed hydrogen that diffuses first. At around 400 °C, one can observe a decrease in slope of OH partial pressure that indicate that beyond this temperature the contribution of OH absorbed at surface is decreasing and diffusion of OH from bulk (silica glass) is dominating consequently reducing the rate, as diffusion is a relatively slow phenomenon. As the temperature increases further, oxygen start evolving at 600 °C at slow rate indicating the dissociation of OH in O and H and subsequent out diffusion. At further high temperature (at 750 °C), a clear increase in slope of 'O' and H_2 can be seen that is accompanied by decrease in OH. This indicates that at temperature beyond 750 °C, dominating process is dissociation of OH or H_2O and out diffusion of O and H_2. These observations indicate that there is sufficient out diffusion of OH (and possibly other trace gaseous impurity) at 650–700 °C that may contaminate the melt contained inside the crucible.

To confirm the out diffusion of OH from the silica crucible at higher temperature, we annealed the crucible (containing hydroxyl group at 150–250 ppm level) and monitored the change in absorption intensity at 2720 nm corresponding to hydroxyl group in silica. The results are shown in Fig. 4c. The absorption intensity corresponding to OH group reduces with annealing time at 900 °C. Fig. 4d shows the dependence of rate of change in absorption with annealing time. The rate almost dropped by one order in 48 h of annealing at 900 °C and total OH content in silica was reduced to below 20 ppm. This indicate that if silica crucible is annealed at 900 °C for 48 h or more, the contamination of melt with OH will reduce by more than a factor of 10. To validate the hypothesis, we grew single crystals of CsI in a 50 h annealed crucible while keeping all the other growth parameters same as Type I, II, and III crystals. We find that the optical quality of crystal improved remarkably.

To assess the effect of 'OH' contamination and consequent 3D inclusions on crystal's scintillation properties, two samples of 20x20x20 mm^3 one each from middle parts of Type-I and III crystals were processed to fabricate gamma detector as given in experimental section. Pulse height spectra of ^{137}Cs were recorded for both the samples and are presented in Fig. 5a. Type-III crystal shows nearly two times more light output than Type-I crystals. The decay profile of both the samples for ^{137}Cs excitation, in Fig. 5b, shows that Type-I crystal is about 20% faster than the Type-III. The smaller pulse height and faster decay time of Type-I crystals indicate a very high density of defects resulting in scintillation quenching and poor detector performance. Further, the crystal grown under optimum condition (crucible containing < 10 ppm OH) was processed in a scintillator element for gamma ray detection as shown in Fig. 6a. The fabricated detector showed an energy resolution of 5.6% at 662 keV (Fig. 6b) that is one of the best

performances that can be achieved by CsI and PMT combination.

4. Conclusion

Single crystals of Tl doped CsI are grown by vertical Bridgman technique and the effect of OH content in fused silica crucible on the quality of the grown crystal are investigated. It is established that OH in silica diffused in the melt at high temperature that adversely affect the crystal quality and is main cause behind the inclusion in the grown crystals. The temperature dependence of OH diffusion is analysed by RGA. Silica crucible annealing temperature and time is optimized to remove OH level below acceptable level (< 10 ppm). Finally, a Tl doped CsI single crystal is grown under ideal condition and tested as gamma ray spectrometer. The crystal showed a 5.6% resolution at 662 keV that is one of the best reported values with PMT and CsI:Tl. Here, it can be concluded that quality of quartz crucible plays a very important role in crystal quality and the quality of crucible can be monitored by quantifying OH level by IR absorption spectroscopy. Further, the quality of crucible can be improved by annealing at 900 °C for more than 50 h.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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