

Characteristic Features of Automated Growth of Large Scintillation Alkali Halide Single Crystals Free of Oxygen-Containing Impurities

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Abstract. Influence of some oxygen-containing impurities on the spectrometric characteristics and radiation resistance of CsI(Tl) crystals has been studied. Borate-ions are shown to be no less dangerous impurity comparing to carbonate-, sulphate- and hydroxide-ions. The content of borate ions in the trace amount caused the crystal colouring under gamma-rays and light output becomes less. A method has been suggested so that the melt should be purified from impurities right when crystal are pulled therefrom automatically. Grown from the purified melt the crystals do not contain any absorption band in the IR-spectrum, which is characteristic of borate-, carbonate-, and sulphate-ions, and possess a higher radiation resistance.

Keywords: Automated pulling; Oxygen-containing Impurities; Melt purification; Radiation resistance

Introduction

Development in high-energy physics stimulated modern automatically controlled processes of growing scintillation alkali-halide single crystals. Institute for Single Crystals of National Academy of Science of Ukraine has elaborated and mastered to use in industrial production highly-efficient methods of pulling the melt onto a seed and feeding it with melted [1] and powdery [2] initial row materials. The methods are so productive that they will soon replace the Stockbarger-Bridgman crystal growing method that appears to be out-of-date for its low productivity. Controlling the crystallization rate with feeding rate transducer [1] and melt level transducer [2] makes it possible to maintain the cross-section of a growing crystal with accuracy up to 1% even if very big ingots (over 500mm in diameter) are being grown.

However, crystal quality does not depend only on crystallization rate stability but also on purity of row material. Since the above methods suggest that the crystals weighing several hundred kilograms should be pulled from the melt while the melt is being fed in the crucible, impurities will be distributed in the crystals according to Pfann equation [3] for zone melting. This means that the methods indeed solve the task of homogeneously distributing the activator along the ingot. However, to obtain the crystals having minimum quantity of harmful impurities (including oxygen) along their length, one should use a very pure raw material. For a number of applications and high energy physics, in particular, scintillator should allow a very homogeneous light output along their length and resist to radiation rather well. For example, inhomogeneity of the light going out of the truncated CsI(Tl) pyramids, over 300 mm long, which is required for the calorimeter of the Stanford accelerator, should not exceed 6%. The requirement for radiation hardness is determined as no more than 20% worsening of light output when a scintillator is exposed to gamma-irradiation dose 10^4 rad. Sulphates carbonates, hydroxides, nitrates and other oxygen-containing impurities are always present in the initial raw material and sometimes their quantity exceeds the limits specified in standards. Cleaning the raw material from impurities additionally is not always effective but always makes the material to cost much more.

Analysis shows that the sodium- and cesium iodides produced by various companies and graded as "specially pure products" contain, however, approximately the same amount of oxygen impurities. This points to the fact that the raw material purification methods applied during raw material synthesis have reached their limit. Manufacturers do not always control how much oxygen-containing impurities alkali-halide salts have. Meanwhile, our research has shown that if CsI crystals contain carbonate- and sulphate ions as much as $3 \cdot 10^{-5}$ mass %, the blue luminescence component gets much more intensive making use of these crystals impossible as fast scintillators. As shown in [4, 5], stability of the spectrometric features of CsI(Tl) crystals to be irradiated depends on both activator concentration and the concentration of oxygen-containing impurities. For example, the content of BO_2 -ions in the trace amount causes the intensive colouring of crystals under irradiation and releases much less light. So, development of scintillation crystals growing processes to obtain crystals having oxygen-containing impurities as less as possible is a rather topical task to accomplish.

Experiment and discussion of results

CsI(Tl) crystals, 200 to 450mm in diameter and 350 to 450mm high, were grown by means of automated pulling from the melt available in a conic crucible while the melt was being fed [1]. The ingots grown were then cut into blanks along the growth axis which truncated pyramids over 300mm long were made from. To make scintillators, selection of crystals was performed to satisfy the following requirements. Inhomogeneity of thallium distribution along the ingot centre line must not exceed 10%. Total content of carbonate- and sulphate ions must not exceed $2 \cdot 10^{-4}$ mass %. Concentration of the activator was measured every 10mm. The optical method was used to determine transparency at the fall-off in A-absorption band of the activator. The calibration curve was plotted according to the samples in which known thallium concentration has been found by the polarographic method. Oxygen-containing impurities in different parts of the ingot were determined with the help of IR-spectroscopy. The light output was measured for both medium-size surveillance specimens $\varnothing 25 \times 25$ mm and ready-made scintillators shaped as truncated pyramids 306 to 327mm high. The radiation resistance of the crystals was determined by an original technique based on measuring the optical density $\ln(I_0/I)$ by the Tailor method [6]. Samples $\varnothing 30 \times 60$ mm that had been cut out of different parts of a boule were used. Their relative optical density $\ln(I_0/I)$ in the wavelength of $\lambda = 550$ nm was determined before and after irradiation by $5 \cdot 10^5$ rad. CsI standard with absorption coefficient $\kappa_{550} = 0.005 \text{ cm}^{-1}$ was used to compare. By numerical value of radiation resistance (RR) we mean the value of deviation $\Delta \ln(I_0/I)$ that is determined to be ≥ 0 . It has been experimentally found that if $\Delta \ln(I_0/I) < 1.1$, the change in ready-made product light output $\Delta L/L < 20\%$ after being exposed to dose 10^4 rad.

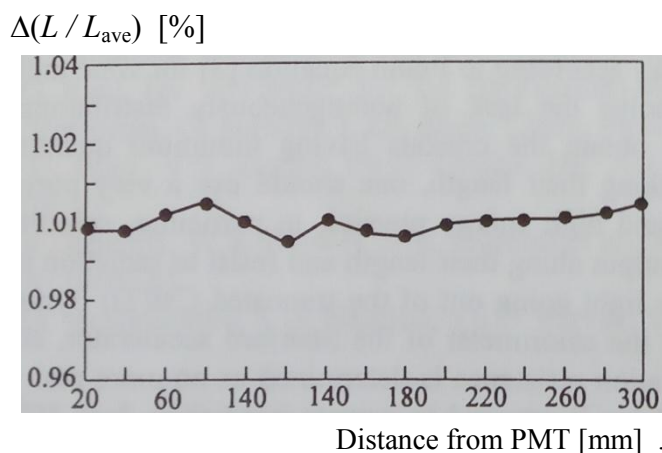


Fig.1. Relative change of light output along the pyramid axis

To provide for uniformity in the light output it is necessary first of all to assure activator distribution all over the crystal as homogeneous as possible. The necessary distribution can be ensured if the growth rate and diameter of a growing crystal are kept constant [7]. Table 1 shows examples of thallium distribution along the growth centerline for three crystals. Deviation in the activator concentration from the average value most often does not exceed $\pm 5\%$ in the boule cylindrical part 30 mm long.

Such a high homogeneity in distributing the activator and a good transparency of the crystal (0.01 cm^{-1} on wavelength 550 nm) make it possible to attain a high uniformity of the light output ($\sim 1\%$) along the scintillator axis comparatively easy. Fig.1 shows an example how the light output is distributed along the axis of a pyramid.

The radiation damage of crystals is caused by deterioration in their transparency that takes place as a result of color center formation after the crystals have been irradiated [8]. The color centers are linked to impurity-induced defects and structural defects in the crystal lattice. Some authors [9] believe that after irradiation conversion efficiency η degrades too. Comparison of changes in the light output after irradiation for crystals of different length shows that the change in η may be disregarded if exposure doses are about 10^4 rad. It is the impurity composition of crystals that affects their radiation resistance exclusively much. Such doped ions as CO_3^{2-} , OH^- and SO_4^{2-} are known to considerably reduce the radiation resistance of CsI(Tl) crystals [4]. The mechanism of forming stable radiation-induced defects with CO_3^{2-} and OH^- ions is described in detail in [10]. As shown in [5] and confirmed herein, BO_2^- ions are harmful that much too. Fig.2 shows how CsI(Tl) crystal radiation resistance depends on the content of borate ions.

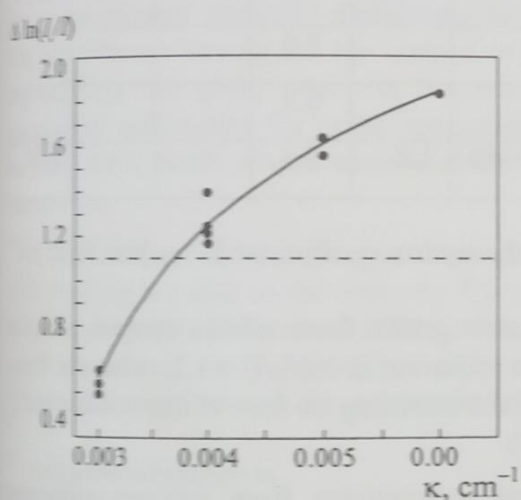


Fig.2. Dependence of optical density change $\Delta \ln(I_0/I)$ from the content BO_2^- -ions in CsI(Tl) crystals at isodose radiation 0,5 Mrad.

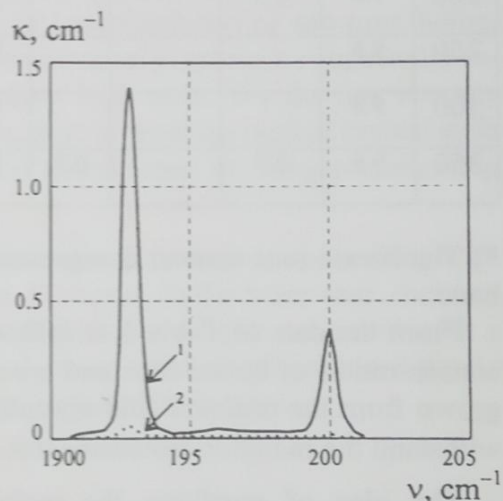


Fig.3. Absorption coefficient (κ_{1930}) in ν_3 -variation BO_2^- -ions in CsI(Tl) crystals, grown with the treatment of melt (2) and without it (1).

Since presently we have no independent and reliable method to determine the amount of BO_2^- in alkali-halide crystals at the level of $1 \cdot 10^{-5} - 1 \cdot 10^{-4}$ mass %, the borate-ions content was controlled according to the absorption in 1930 cm^{-1} band which is characteristic of valent ν_3 -variation. The IR-absorption spectrum in ν_3 -variation of BO_2^- -ion in crystal is given in Fig.3. Need for purification the melt from borates has emerged in connection with processing of crystal machining wastes (small pieces, chip cuttings). This mainly concerns those rejected scintillators whose surfaces have undergone grinding and polishing with boron-containing abrasive materials. Since CsI(Tl) crystals are very easy to be colored at the presence of borate ion traces and boron is available enough in the environment, the undesirable quantity of this impurity may get in the growth installation feeder when it is charged with raw material.

Table 1 gives quantities of activator concentration C_{Tl} and impurities by CO_3^{2-} ; SO_4^{2-} and BO_2^- as well as radiation hardness value for the crystals that have been grown from both ordinary salt and salt mixed with industrial wastes.

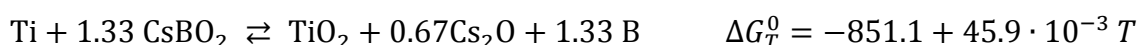
Table 1. Impurities distributed in height of the crystals and the crystal radiation hardness

H, mm	Impurities content in crystals grown from different											
	Salt				100% wastes				Wastes treated by Ti			
	Tl 10 ⁻² mass %	SO ₄ ²⁻ 10 ⁻⁵ mass %	BO ₂ ⁻ κ cm ⁻¹	RH	Tl 10 ⁻² mass %	SO ₄ ²⁻ 10 ⁻⁵ mass %	BO ₂ ⁻ κ cm ⁻¹ (*)	RH	Tl 10 ⁻² mass %	SO ₄ ²⁻ 10 ⁻⁵ mass %	BO ₂ ⁻ κ cm ⁻¹ (*)	RH
10	9.5	1.5	-	0.7	7.7	1.5	0.005	1.6	7.0	-	-	
50	9.6	1.5	-		8.7	1.9	0.005		7.2	-	-	0.72
100	9.4		-		9.8				8.2	-	-	
150	9.7		-	0.75	9.9				8.3	-	-	
200	9.6	2.5	-		9.7	2.3	0.005	1.65	8.2	-	-	0.79
250	9.8		-		9.8				8.5	-	-	
300	9.8		-		9.9				8.2	-	-	
350	9.9	2.7	-	0.8	9.9	2.3	0.006	1.8	8.4	-	-	0.83

(*) The borate-ions content is expressed in terms of absorption coefficient (κ_{1930}) in maximum of absorption band at 1930 cm⁻¹

From the data of Table 1, it follows that the crystals grown from wastes contain a higher concentration of borate-ions and are not resistant to radiation $\Delta \ln(I_0/I) > 1.1$, whereas those grown from the ordinary fine crystalline raw material containing no borate impurities, easily withstand the radiation resistance test $\Delta \ln(I_0/I) < 1.1$.

The idea of purifying the melted alkali metal halogenides from oxygen-containing impurities immediately when pulled [11] is that these impurities should be converted into insoluble compounds. The calculation of isobar-isotherm potentials (ΔG_T^0) in the relevant chemical reactions shows that titanium is the most adequate metal for these purposes. As an example we would like to specify the values of ΔG_T^0 and temperature coefficient for some reactions with insoluble TiO₂ being formed.



It should be noted that aluminium can be used for purification of melting salts too, however low temperature of aluminium melting could cause certain problems when the metal is used to purify alkali-halide salts in platinum ware. Contacting directly, the aluminium will dissolve the platinum. However, it may certainly be used for melt purification in ceramic or quartz-ware.

Our experience shows that metal titanium should be preferable used to purify the melted, automatically pulled out, alkali-halide salts. A high melting temperature of this metal (1725°C) and its chemical activity as well as structural features of the make-up and feeder system [1] make it possible to treat the melt immediately in the process of crystal growth

without any complication. The X-ray phase analysis has shown that the powder that is formed and deposited on the feeder bottom is a mixture of TiO_2 (modification of rutile and anatase) and Ti_2O_3 . The data of table 1 and curve 2 (Fig. 3) show that small quantity of titanium added to the melt enable to get rid of sulphate and borate impurities. This method of purification has been comprehensively evaluated in growing large-size, alkali metal iodide-based single crystals, 400 mm in diameter, such as CsI(Tl), CsI(Na) and NaI(Tl). In the grown crystals there was no titanium detected by chemical analysis methods.

Conclusion

The suggested method of purifying melted alkali metal halogenides by means of treating them with the metals forming low-soluble oxides is not only simple and highly effective but also universal. At present, one can be sure to state that the method makes it possible to decrease the quantity of CO_3^{2-} , SO_4^{2-} , OH^- , NO_3^- and BO_2^- ions in alkali-metal iodide-based crystals to the concentrations that are beyond the threshold of sensitivity inherent in chemical and optical methods of determination. This method of purification may turn out to be preferable for obtaining fast scintillators – nonactivated CsI crystals for which presence of any above-mentioned impurity amounting to $3 \cdot 10^{-5}$ mass % is inadmissible. For the time being, CsI scintillators having the low-intensive blue component are usually grown by repeatedly recrystallizing the melt, which is the main reason for their high cost. We do not see any substantial difficulties for using this method to purify the melt in growing optical crystal such as KBr, KCl, NaCl whose transmittance in the IR-region is deteriorated by oxygen-containing impurities.

It should be noted that the purification could be applied not only to automated pulling with melt feeding but also to the ordinary Kyropolous technique. However, in the latter case, the melt is to be prepared beforehand. The process of preparation must cover melt treatment with a metal to subsequently let oxides settle down. The final phase of melt preparation should include filtering the melt from deposited oxides and other insoluble impurities.

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