Journal of Crystal Growth 198/199 (1999) 865–868

JOURNAL OF CRYSTAL GROWTH

Study of the growth atmosphere effect on optical and scintillation characteristics of large CsI(TI) crystals

A.N. Panova, V.I. Goriletsky, T.B. Grinyova, K.V. Shakhova*, E.L. Vinograd

STC "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Lenin Ave., 310001 Kharkiv, Ukraine

Abstract

In contrast to the traditional growth method of large scintillation alkali halide crystals – in an inert atmosphere, CsI(TI) crystals have been grown in CO_2 atmosphere favoring changes of their impurity composition. Absorption and scintillation characteristics of crystals obtained have been studied in comparison to those grown in the inert gas medium. Effect of different radiation doses on variations in optical and scintillation characteristics has been studied for CsI(TI) crystals grown by various techniques. CsI(TI) crystals grown in CO_2 atmosphere are found to exhibit a higher radiation resistance and a faster restoration of their basic characteristics. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The problem of producing photo- and radiation-resistant CsI(TI) crystals is associated with their wide use, including applications as detectors modules in large supercollider assemblies. Growth of crystals meeting these requirements was a task very difficult to attain heretofore, since the presence of impurities arising due to the melt hydrolysis (e.g. OH^- and CO_3^{2-} ions) in the crystal volume, even in trace amounts, results in CsI(TI) crystal coloration not only under an ionizing radiation action, but also in daylight. As a result, scintillation parameters of the article deteriorate substantially. Absorption spectra of colored crystals have a complex structure where a series of bands is revealed with maxima at 375, 435, 460, 530, 840 nm related to the appearance of hole and electron-type color centers. There are series of works dedicated to the study of the nature of these centers (e.g. Refs. [1–5]), however, the mechanism of photo- and radiation-induced coloration of CsI(TI) crystals is not elucidated conclusively.

During the past few years, a method has been developed at the Institute for Single Crystals (Kharkiv, Ukraine) to grow radiation-resistant large CsI(TI) single crystals in an inert gas medium (in "ROST" and "KRISTALL" units) in the presence of CO_3^{2-} ions in their volume. Today, this method is under patenting in Ukraine (Applications No. 96051870, priority from 14 May 1996) as well as in Russia and USA. The radiation resistance of such crystals in the form of detector modules

* Corresponding author. Tel.: + 38 572 30 74 19; fax: + 38 572 32 02 07; e-mail: shakhova@isc.kharkov.com.

0022-0248/99/$ – see front matter © 1999 Elsevier Science B.V. All rights reserved.
PII: S0022-0248(98)01180-4

($L = 30$ cm) for large-size assemblies has been studied rather comprehensively in comparison with similar products made in China and in USA [6,7].

This communication is the first from a series of works aimed at studying the possibilities for further improving the radiation resistance of large CsI(TI) crystals and elucidating the OH^- impurity role in the radiation damage process by means of investigating the properties of CsI(TI) crystals grown in CO_2 atmosphere. The idea consists in that the growth of these crystals in the reactive (CO_2) gas medium must favor their purification from OH^- ions as a result of the known reaction.

$$OH^- + CO_2 \rightarrow HCO_3^-.$$

Thus, it is just the presence of HCO_3 ions in the grown crystal that evidence the fact of the above reaction in the melt.

2. Experimental procedure

Large CsI(TI) crystals were grown by the automated method described in Ref. [8] by pulling on a seed under the forced mixing of melt. Therewith, the above-mentioned method which allows the production of radiation-resistant CsI(TI) crystals in the presence of CO_3^{2-} ions in the crystal volume was used, irrespective of the gas medium in the growth furnace (inert gas or CO_2). Experiments were conducted using representative samples cut out of various parts of a large-size crystal; the sample size was $\varnothing 30 \times 63$ mm. The activator concentration determined by polarography amounted from 7×10^{-2} to 1×10^{-1}% TI by mass. Optical and scintillation properties of CsI(TI) crystals grown in CO_2 medium (I) were compared to those of crystals grown in an inert atmosphere (II). Absorption spectra in the visible and IR spectral ranges as well as the light yields L_γ (^{137}Cs, 662 KeV) were measured using standard instruments. A ^{60}Co radiation source (dose rate 3×10^4 rad/h) was used to irradiate the samples up to a dose of 10^5 rad.

3. Results and discussion

The content of activator and impurities (molecular anions) in CsI(TI) crystals I and II being typical for samples under study is presented in Table 1.

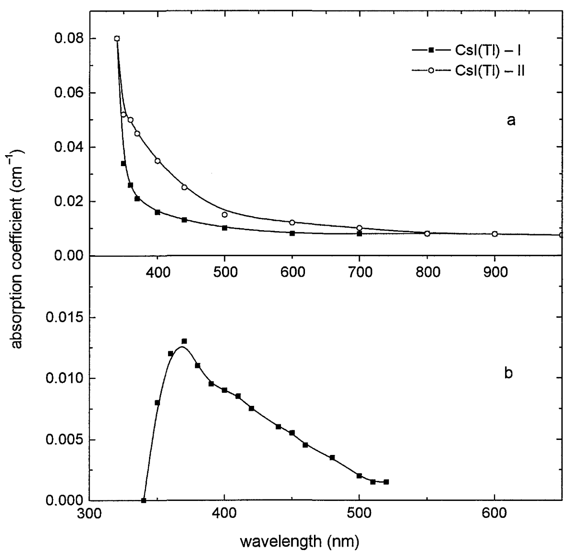

Fig. 1. Dispersion dependencies of the absorption coefficients for type I and II CsI(TI) crystals (a) and of the difference between those dependencies (b).

Table 1
Tallium concentration and relative content of CO_3^{2-} and HCO_3^- ions in CsI(TI) crystals grown in CO_2(I) and inert (II) atmosphere

Crystals	TI, mass%	CO_3^{2-}		HCO_3^{2-} $v = 1680$ cm^{-1}
		$v = 880$ cm^{-1}	$v = 1440$ cm^{-1}	
CsI(TI) I	0.084	0.014	0.088	0.024
CsI(TI) II	0.079	0.017	0.110	Absence

The crystals studied are noticed to be quite similar in the activator and CO_3^{2-} ions but differ substantially in the HCO_3^- ion concentration; this fact proves that the reaction of hydroxyl ion interaction with CO_2 gas medium takes place in the melt.

Fig. 1 shows the dispersion dependence of the absorption coefficient (reflection losses are accounted for) for CsI(TI) crystals grown by various methods. It follows from the Fig. 1a that crystals of type I show enhanced transmittance in the activator emission region (380–700 nm). The absolute value of the absorption coefficient for type I crystals in the emission maximum (560 nm) is $9\times10^{-3}\ cm^{-1}$ as opposed to $1.4\times10^{-2}\ cm^{-1}$ for type II crystals. As to the short-wavelength spectral region, an enhanced transmittance of CsI(TI) crystals grown in CO_2 medium is attained (see Fig. 1b) due to the absence of a series of absorption bands with faint maxima in the 360–500 nm range. Impurities formed due to the melt hydrolysis seem to be responsible for those bands. No improvement in scintillation parameters is however observed for type I crystals as compared to those of type II ones: $\varnothing 20\times63$ nm detectors made from crystals of type I and II are comparable in the light yield.

Further investigation was aimed at studying the effect of different γ-radiation doses on scintillation and optical properties of CsI(TI) crystals grown under various conditions. Fig. 2a and Fig. 2b presents absorption spectra (reflection loss is not accounted for) of I(a) and II(b) type crystals taken before and after irradiation by 10^5 rad dose. The

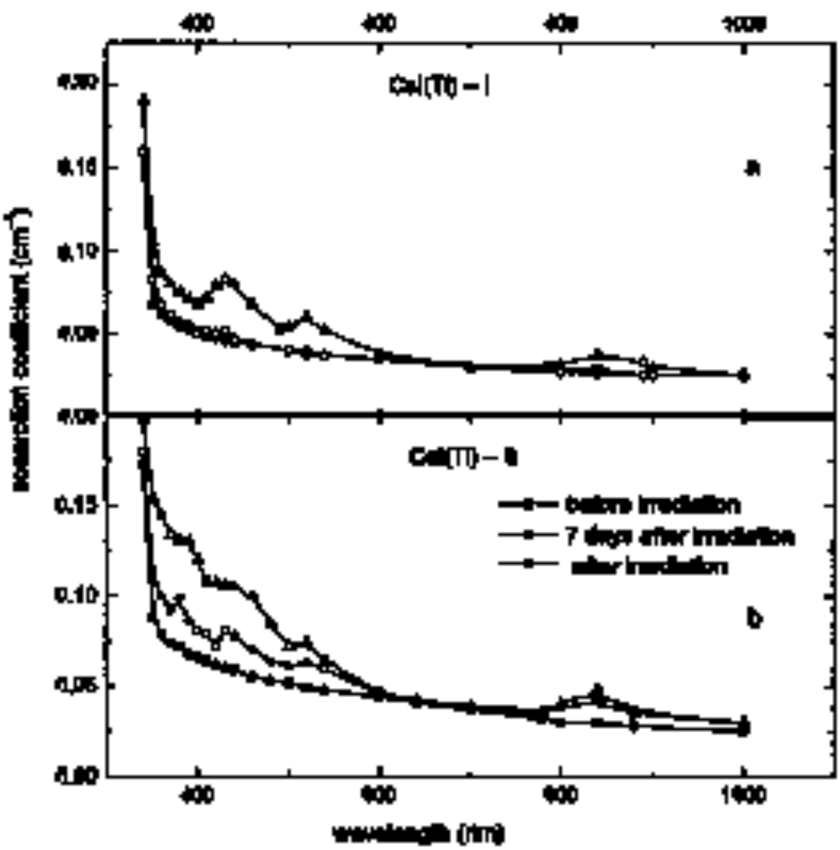

Fig. 2. Absorption spectra of type I(a) and II(b) CsI(TI) crystals before and immediately after irradiation by 10^5 rad dose and 7 days later.

Table 2
Relative change of the light yield (L/L_0 p.c.) of ∅ 30 × 63 mm detectors made from type I and II CsI(TI) crystals irradiated by different doses (^{60}Co)

Crystals	L/L_0, % after irradiation by different doses			
	10^4 rad		50×10^4 rad	
	After 24 h	After 48 h	After 24 h	After 48 h
CsI(TI) I	94	100	87	98
CsI(TI) II	88	91	80	85

radiation-induced coloration of crystals grown in the reactive gas medium is seen to be substantially less intense than of those grown in the inert atmosphere. This is confirmed by the data of Table 2 characterizing the relative change of the light yield due to different radiation doses for ∅ 30 × 63 nm detectors made from CsI(TI) crystals of various origins. It follows also from Table 2 that the initial light yield value is restored during 48 h for irradiated crystals of type I, while for crystals of type II, the light yield recovery during the same period amounts to only 30%. It is seen from Fig. 2 (curves 3) that even 7 days after the irradiation of type II crystals by 10^5 rad dose, the integrated intensity of radiation-induced absorption bands in the activator emission range (400–700 nm) is reduced by 65 or 70%, while the transmittance of type I crystals recovered completely. Experimental data on properties of CsI(TI) crystals grown various techniques points out that scintillation CsI(TI) crystals grown in CO_2 atmosphere have a higher radiation resistance and recover more quickly the initial values of main parameters as compared to crystals grown in inert gas medium.

In the near future, we intend to study mechanisms of the radiation-induced coloration and bleaching of CsI(TI) crystals grown in the reactive gas medium to improve further their radiation resistance.

Acknowledgements

Authors are thankful to A.I. Mitichkin for measurements of IR absorption spectra and to S.K. Bondraenko for assistance in the growing of crystals.

References

[1] L.V. Kovaleva, Y.A. Zakharin, LL. Nagornaya, L.P. Smolskaya, L.N. Shpilinskaya, Crystal Growth and Properties, 6th ed. 1980, p. 24 (in Russian).
[2] R.Y. Zhu, D.A. Ma, H. Wu, VI Int. Conf. of Calorimetry in Energy Physics, Frascati, Italy, 1996.
[3] L.P. Smolskaya, V.V. Dorohova, Zh. Prikl. Spektrosk. 52 (1990) 44.
[4] M. Kobayashi, S. Sakuragi, Nucl. Instr. and Meth. A 254 (1987) 275.
[5] L.P. Smolskaya, T.A. Kolesnikova, Zh. Prikl. Spektrosk. 38 (1983) 150.
[6] P. Schotanus, R. Kamermans, P. Dorenbos, IEEE Trans. Nucl. Sci. 37 (1990) 177.
[7] BELLE Collaboration, Technical Design Report, KEK Report 95-1, 1995.
[8] V.I. Goriletsky, V.A. Nemenov, V.G. Protsenko, A.V. Radkevich, L.G. Eidelman, J. Crystal Growth 52 (1981) 509.