Automated pulling of CsI(Tl, Br) crystals from melt and their scintillated and mechanical properties

A. M. Kudin
National Academy of Sciences of Ukraine

Larisa N. Trefilova
National Academy of Sciences of Ukraine

ELSEVIER

Journal of Crystal Growth 222 (2001) 751–754

JOURNAL OF CRYSTAL GROWTH

www.elsevier.nl/locate/jcrysgro

Scintillation and mechanical properties of CsI(Tl,Br) crystals pulled from melt

B.G. Zaslavsky*, S.I. Vasetsky, A.M. Kudin, V.Yu. Gres', L.N. Shpilinskaya, T.A. Charkina, L.V. Kovaleva, A.I. Mitichkin, A.N. Boyarintsev, S.Yu. Sumarokov

National Academy of Sciences of Ukraine, Institute for Single Crystals, Lenin Avenue 60, 61001 Kharkiv, Ukraine

Received 26 July 2000; accepted 7 November 2000
Communicated by T. F. Kuech

Abstract

Scintillation and mechanical characteristics of combined CsI(Tl)–CsBr crystals have been studied over the concentration range of cesium bromide 0.1–2.7 mass%. In this concentration range, cesium bromide addition has been shown to have no effect on the spectrometric and temporal characteristics of crystals or on their radiation resistance but leads to their significant strengthening. These improved mechanical properties prevent the deformation of large ingots during their pulling from melt onto the seed. The quality of mechanical treatment of the surface of these alloy crystals has a weaker dependence on the crystallographic orientation of the surfaces, thus simplifying the manufacture of scintillators of intricate geometric forms. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: CsI(Tl,Br) crystals; Scintillation properties; Melt; Pulling

High plasticity of CsI-based scintillation crystals gives them an advantage when used as detectors of ionizing radiation under rigid operation conditions, such as heavy mechanical and thermal loading. Along with this plasticity is a serious disadvantage at mechanical treatment of these crystals, particularly in the cases when scintillators are to have an intricate geometric form and high-purity surfaces of different crystallographic orientation. Plasticity of CsI-based crystals is the main reason for their deformation during pulling from melt: this impedes growth of large single-crystalline ingots. Proceeding from the above, one can conclude that additional alloyage of CsI-based crystals by the reinforcing admixtures – not worsening their scintillation parameters is rather topical.

It is known that alloying with bromide increases the microhardness [1] and yield limit [2] of CsI crystals. Thus, according to Ref. [2], a bromine content of 1.2 mass% in CsI–CsBr crystals increases the yield limit 10 times higher than pure CsI. Little is known about the scintillation properties of CsI(Tl) when alloyed with CsBr. Ref. [3] claims that alloys of CsI(Tl) crystals with cesium bromide increase their radiation resistance, RR, as well as the energy and temporal resolution. The

*Corresponding author. Tel.: +38-572-307982; fax: +38-572-321082.

E-mail address: zaslav@isc.kharkov.com (B.G. Zaslavsky).

PII: S0022-0248(00)00966-0

absence of any other confirming publications, concerning scintillation characteristics of these crystals does not allow to consider these data reliable. The purpose of this paper is to study the effect of bromide on the mechanical and scintillation characteristics of combined CsI(Br,Tl) crystals and to determine CsBr level which improves the crystal essential mechanical strength without degrading the scintillation and temporal properties. Determination of this CsBr level would permit the manufacture of scintillators that are reliable and reproducible, with a higher possible commodity yield both at the stage of mechanical treatment and growth of crystals.

Experimental part of the work consisted of growing crystals of a specified composition, cutting and preparing samples from different parts of the ingot, analyzing the composition of crystals by chemical and optical methods, and measuring mechanical (yield limit, microhardness) and scintillation characteristics. Scintillation characteristics were studied more thoroughly. The energy resolution, relative light output, radioluminescence spectra and decay time of the scintillation pulse were measured.

CsI(Br,Tl) crystals 250–260 mm in diameter and 300–450 mm in height were grown by the method of automated pulling from melt with melt replenishment by melted raw material [4]. Ten single-crystalline boules have been grown. The concentration of bromide varied from 0.1 to 2.7 mass% while the nonuniformity of its distribution over the height did not exceed 10% within each ingot.

In all the grown crystals, the content of the dopant (Tl) was in the limits of 8.5×10^{-2}–9.1×10^{-2} mass%. Nonuniformity of the dopant distribution in each crystal did not exceed 10%.

Content of bromide in the samples was determined by the X-ray fluorescence method [5]. Accuracy of this determination was 10%.

The content of the oxygen-containing impurities was evaluated from the IR absorption spectra [6] of the samples cut out of the upper middle and lower parts of the boule.

The yield limit was measured by compressing the samples on the deformation set-up load cell. The samples were oriented along the (1 1 0) crystallographic plane within an accuracy of 2°. The yield limit for five samples was measured and averaged for each concentration of bromide. Microhardness was measured by a version of the Vickers method [7].

Spectrometric characteristics (energy resolution and relative light output) were measured by the γ-line of the isotope ^{137}Cs (622 keV) on the cylindrical samples 25 mm in diameter and 25 mm in height, cut from the upper, middle and lower parts of the boules. The standard method for measurements has been used [8].

Radioluminescence spectra were measured at γ-excitation by the isotope ^{241}Am (60 keV) [9].

The form and kinetics of the scintillation pulse decay were measured by a method of correlated photons counting [9].

Large, transparent and uniform over the volume CsI(Br,Tl) crystals 250–260 mm in diameter and up to 450 mm in height were reproducibly pulled at a content of cesium bromide in the melt not exceeding 3 mass%. The pulling rate in all the experiments was about 5 mm/h. At a higher bromide content, the growth was unstable with a change in the crystallization front form: from convex to flat and then to concave with further degradation of the crystal. The ingots with a cesium bromide content above 2.7 mass% were nonuniform in composition, and possessed large opaque regions.

The data on the mechanical and scintillation characteristics are presented in Table 1. Carbonates and sulphates are the most frequently encountered oxygen-containing impurities in CsI-based crystals. These impurities degrade the scintillation parameters of crystals and their radiation resistance even at a content as low as 1×10^{-4} mass%. Treatment of melts by a metallic titanium [10] decreased the concentrations of CO_3^{2-} and SO_4^{2-} in all crystals down to the level of 2×10^{-5}–4×10^{-5} mass% and minimized the effect of these impurities upon scintillation and mechanical properties of bromide-containing crystals.

The data from Table 1 show that in the studied concentration range neither the light output, L, nor the resolution, R, depends on the concentration of bromide. The same can be referred to the

Table 1
Scintillation and mechanical properties of CsI(Tl,Br) crystals

Type of crystal, content CsBr	Impurity content			Scintillation properties			Mechanical properties	
	$Tl \times 10^{-2}$ mass%	$CO_3^{2-} \times 10^{-5}$ mass%	$SO_4^{2-} \times 10^{-5}$ mass%	L% of NaI(Tl)	R 662 keV	τ (μs)	H kg/mm^2	σ g/mm^2
CsI	—	2	3			0.97	6.0	11
CsI(Tl)	8.5	3	3	45	6.3	1.01	6.9	40
CsI(Tl,Br) 0.10% CsBr	8.7	2	2	42	6.6	1.10	7.0	62
CsI(Tl,Br) 0.18% CsBr	9.0	2.5	2	46	6.5	1.05	9.5	110
CsI(Tl,Br) 0.24% CsBr	8.5	3	4	45	6.3	1.03	11.0	106
CsI(Tl,Br) 0.54% CsBr	8.5	3	4	45	6.3	1.03	11.9	101
CsI(Tl,Br) 1.04% CsBr	8.7	4	2	46	6.7	0.98	13.2	112
CsI(Tl,Br) 1.49% CsBr	8.0	2	2	45	6.3	1.05	12.4	95
CsI(Tl,Br) 2.10% CsBr	9.1	2	2	47	6.4	0.97	10.5	117
CsI(Tl,Br) 2.71% CsBr	8.5	3	2	35–45	6.5–8.1	1.10	14.5	60–104

decay time, τ, which by estimations of different authors approaches 1 μs for CsI(Tl). One could expect that introduction of a significant amount of bromide may lead to the change in the spectral composition of the luminescence. However, measurements of the radioluminescence spectra showed that the luminescence spectrum composition of bromine-containing crystals has no peculiar features and fully coincides with that of CsI(Tl) luminescence. The results of the study of the bromide effect upon radiation resistance, RR, of the alloy crystals are not given in Table 1, however, the method used by the authors for the evaluation of RR (based on the changes in transparency in the maximum of the luminescence spectrum of the crystal – 560 nm) revealed no effect at irradiation of samples by high doses up to 0.5 Mrad. Thus, the obtained results did not agree with the previous data [3] reporting an increase of the RR, scintillation and temporal characteristics when alloying CsI(Tl) crystals with bromide.

The results of measurements of mechanical characteristics demonstrate that alloying CsI(Tl) crystals with bromide, as in the case of CsI crystals [1], results in approximately two times increase of their microhardness, H. The yield limit, σ, of CsI(Tl,Br), determined in the same way as Ref. [2], is higher. However, in the absolute value our data with respect to σ for CsI pure is two times lower than data in Ref. [2]. We believe that previous [2] crystals were contaminated with the hardening impurities, perhaps oxygen-containing anions, since no data were reported concerning their concentration. The spread in the values of σ over the range of 60–104 g/mm^2 for a crystal having 2.7 mass% of CsBr is explained by a possible decomposition of the solid solution and nonuniformity of the composition.

While no improvement in the scintillation properties of CsI(Tl,Br) crystals, as compared to CsI(Tl), was detected, bromide alloying improved other properties. A higher microhardness of CsI(Tl,Br) crystals allows to achieve a higher-quality polishing of the surfaces which is very important in the manufacture of scintillators having an intricate geometrical form. Increase of the yield limit by an order of magnitude made it possible to solve a significant problem connected with the deformation of crystals during their pulling from melt onto the seed. A noticeable deformation of crystals alloyed with bromide in the process of their growth was not observed in any of these experiments.

References

[1] I.P. Antoniv, I.V. Garapyn, N.A. Tsal', Izv. Acad. Sci. USSR, Inorg Mater. 24 (10) (1988) 1749.
[2] M.G. Buravleva, A.I. Chubenko, T.A. Charkina, L.G. Eidelman, Author's Certificate of the USSR No. 1412383, Patent USSR.

[3] V.B. Gutan, L.M. Shamovsky, Author's Certificate of the USSR No 1362088, Bulleten' Isobreteniy 24 (1994) 217, Patent USSR.
[4] B.G. Zaslavsky, J. Crystal Growth 200 (1999) 476.
[5] A.B. Blank, L.P. Eksperiandova, X-ray Spectrometry 27 (1998) 147.
[6] K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1966, pp. 132–151.
[7] B.W. Mott, Micro-Indentation Hardness Testing, Butterworths, London, 1956, pp. 12–16.
[8] I.B. Birks, The Theory and Practice of Scintillation Counting, Pergamon Press, New York, 1964, pp. 305–321.
[9] N.Z. Galunov, V.P. Seminozhenko, The Theory and Practice of Radioluminescence of Organic Condensed Media, Naukova Dumka, Kiev, 1997, pp. 75–93.
[10] B.G. Zaslavsky, J. Crystal Growth 218 (2000) 277.