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**SOLID-STATE  
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## Photo- and Radiation-Chemical Transformations of Carbonate Ions in CsI and CsI(Tl) Crystals

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**Abstract**—It is shown that irradiation of CsI and CsI(Tl) crystals containing carbonate and hydroxyl ions induces radiation defects there in the form of color centers,  $\text{HCO}_3^-$  ions, and  $\text{H}_2\text{O}$  molecules.  $\text{HCO}_3^-$  ions are formed in the bulk of crystals, whereas water molecules are formed only in the surface layer. IR spectra offered no evidence of decomposition of  $\text{CO}_3^{2-}$  ions into CO and  $\text{CO}_2^-$  and of formation of  $\text{CO}_3^-$  ions in the course of growth nor in the course of irradiation of CsI( $\text{CO}_3$ ) and CsI(Tl,  $\text{CO}_3$ ) crystals. Electron activator color centers in CsI(Tl,  $\text{CO}_3$ ) crystals are likely to be stabilized by hole near-activator centers and by  $\text{HCO}_3^-$  ions produced in radiation-induced chemical reactions. © 2000 MAIK “Nauka/Interperiodica”.

### INTRODUCTION

Pure and activated cesium iodide crystals are extensively used in science and engineering as high-efficiency scintillation materials. Single crystals grown from a melt often contain a cesium carbonate impurity. In the case of CsI( $\text{CO}_3$ ) scintillators, this impurity is deliberately introduced into crystals [1], but it is extremely undesirable for CsI(Na) [2] and especially for CsI(Tl) [3] and CsI [4]. One can quantitatively determine the content of carbonates by chemical analysis and IR spectroscopy. In the latter case, the content is determined from the intensity of vibrational absorption bands of  $\text{CO}_3^{2-}$  ions taking into account the transition factor. According to [5, 6], the vibration frequencies of  $\text{CO}_3^{2-}$  ions in the CsI lattice are found in regions of 880 ( $\nu_2$ ), 1360–1415 ( $\nu_3$ ), and 680  $\text{cm}^{-1}$  ( $\nu_4$ ). The irradiation of crystals causes a decrease in the intensity of bands typical of  $\text{CO}_3^{2-}$  ions and the appearance of new bands [5, 7]. The  $\text{CO}_3^{2-}$  and  $\text{OH}^-$  ion impurities were found to accompany one another, no matter which of the two dopants  $\text{Cs}_2\text{CO}_3$  or  $\text{CsOH}$  was chosen, and only their relative contents were changed. According to [5], under the action of ionizing radiation,  $\text{CO}_3^{2-}$  ions in CsI( $\text{CO}_3$ ) crystals are partially transformed through hole capture into single-charge  $\text{CO}_3^-$  ions. Moreover, they are disintegrated into CO molecules and  $\text{CO}_2^-$  ions. It is the authors' opinion that the latter process takes place in the course of crystal growth as well.

In our opinion,  $\text{OH}^-$  ions dissociate under the action of ionizing radiation, and this reaction produces  $\text{H}^0$  and  $\text{O}^-$  ions [8]:



As shown in [7], in the presence of  $\text{CO}_3^{2-}$  ions, the diffusion of  $\text{H}_i^0$  atoms in a crystal lattice is accompanied by the reaction

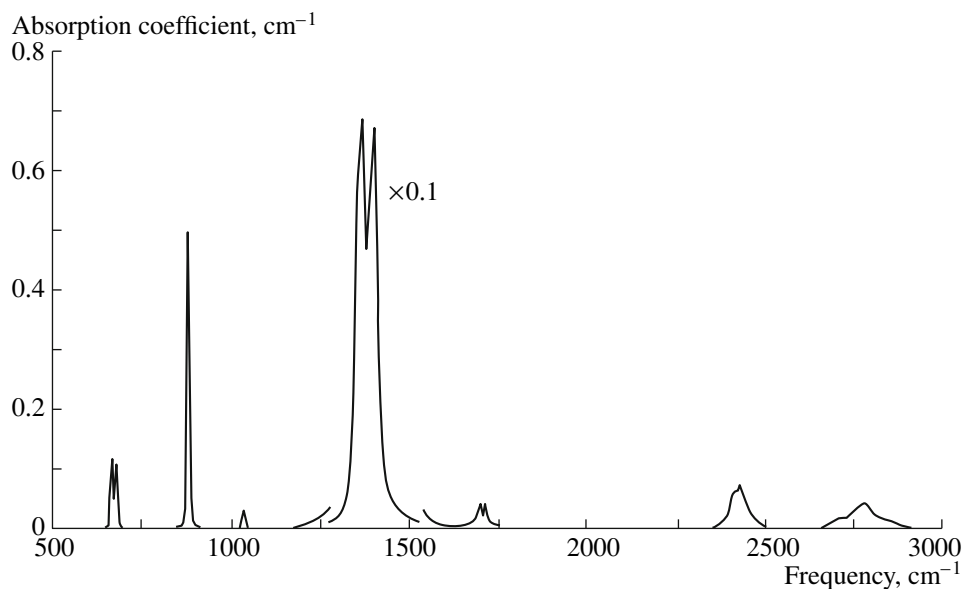


which produces  $\text{HCO}_3^-$  ions and  $F$  centers.

The data of [5] and [7] are obviously contradictory. Because of this, our aim was to identify all absorption bands observed in the vibrational spectra of CsI( $\text{CO}_3$ ) and CsI(Tl,  $\text{CO}_3$ ) crystals prior to and upon irradiation. This enables us to explain radiation-induced transformations of  $\text{CO}_3^{2-}$  ions in the CsI lattice.

### EXPERIMENTAL

The crystals used in our study were grown by the Kyropoulos technique in a platinum crucible in the argon atmosphere. The source CsI salt of ultrahigh-purity grade was preliminarily dehydrated at 200 and 400°C. For doping, we used TII and  $\text{Cs}_2\text{CO}_3$  salts of ultrahigh-purity grade. A number of crystals were grown under conditions of melt hydrolysis. For this purpose, we added damp air in prescribed proportion into the argon atmosphere and, therefore, the resulting crystals contained  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  molecular anions. The thallium concentration in the crystals was (5–9) ×



**Fig. 1.** Absorption spectrum of a  $\text{CsI}(\text{CO}_3)$  crystal with  $\text{CO}_3^{2-}$  ion concentration of  $1.2 \times 10^{-3}$  wt %.

$10^{-2}$  wt %. The presence of oxygen-containing impurities was determined by IR spectroscopy and chemical analysis. Single crystals were irradiated by a  $^{60}\text{Co}$   $\gamma$ -ray source, unfiltered emission of a mercury lamp, and daylight ( $h\nu < 3.8$  eV). The concentration of molecular anions is given in wt %. The IR absorption spectra were recorded on a UR-20 spectrophotometers in the 400–4000- $\text{cm}^{-1}$  frequency range.

## RESULTS AND DISCUSSION

Figure 1 presents the vibrational spectrum of a CsI crystal activated with a  $\text{Cs}_2\text{CO}_3$  impurity, which was thoroughly dehydrated. Because of dehydration, the concentration  $\text{OH}^-$  ions in the crystal was below the sensitivity threshold of the chemical optical techniques ( $< 10^{-4}\%$ ). The concentration of  $\text{CO}_3^{2-}$  ions was rather high ( $1.2 \times 10^{-3}\%$ ), which provided the observation of all characteristic bands in the vibrational spectrum. The experimental IR absorption spectrum of the crystal contained absorption bands with maxima at 667.5, 678.5, 878, 1033, 1362, 1385, 1693, 1705, 2390, 2410, 2690, and 2770  $\text{cm}^{-1}$ .

It is known that a free  $\text{CO}_3^{2-}$  ion is plane and has the  $D_{3h}$  symmetry [9]. In this case, its  $\nu_2$ ,  $\nu_3$ , and  $\nu_4$  vibrations are active in the IR region. In the CsI lattice, the local symmetry of a  $\text{CO}_3^{2-}$  ion decreases down to  $C_{2v}$  because of the effect of an anion vacancy, which is found in the anion site adjacent to the  $\text{CO}_3^{2-}$  ion and counterbalances the excess charge. In this case, the degenerate  $\nu_3$  and  $\nu_4$  vibrations are split, and the totally symmetric  $\nu_1$  vibration becomes active in the IR region

[9, 10]. According to [6], the spectrum of the  $\nu_3$  band represents a superposition of bands with maxima at 1355, 1365, 1385, and 1410  $\text{cm}^{-1}$ . The bands at 1355 and 1410  $\text{cm}^{-1}$  are assigned to valence vibrations of a  $\text{CO}_3^{2-}$  ion, which substitutes for an anion in a regular lattice site, and the bands at 1365 and 1385  $\text{cm}^{-1}$  are assigned to the impurity–vacancy dipole  $\text{CO}_3^{2-} - \text{V}_a^+$ .

Table 1 presents the identification of fundamental and composite vibration frequencies of  $\text{CO}_3^{2-}$  ions in the CsI lattice, which is based on calculations made

**Table 1.** Identification of fundamental and combined vibration frequencies for  $\text{CO}_3^{2-}$  ions in unactivated CsI crystals

Vibration frequency	Relative absorption coefficient at the absorption band maximum	Identification
1033	0.065	$\nu_1$
878	1	$\nu_2$
1362	13.6	$\nu_3$
1385	13.2	
667.5	0.264	$\nu_4$
678.5	0.229	
1693	0.0911	$\nu_1 + \nu_4$
1705	0.1	
2390	0.0903	$\nu_1 + \nu_3$
2410	0.1334	
2690	0.0175	$2\nu_3$
2770	0.0678	