

Influence of Bi doping and high-temperature annealing on optical and dielectric properties of CdWO₄ crystals

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Received September 12, 2019

The effect of Bi doping and annealing in hydrogen on the optical and dielectric properties of CWO crystals is investigated. It has been found that transmission of crystals decreases significantly in the region of 300–900 nm under the influence of the annealing and doping. In the temperature range of 80–290 K, a significant increase in the intensity of TSC and TSL of CWO crystals doped with Bi has been found. At the same time, there is no clear correlation between the maxima of the TSC and TSL curves, as well as there is the simultaneous emission of the red and blue luminescence bands at the maxima of the TSL curves. Under the influence of annealing and doping with Bi, a significant change in the complex dielectric constant of the CWO samples has been found in a wide frequency range.

Keywords: CdWO₄ crystal, crystal doped with Bi, annealing in hydrogen, complex dielectric constant.

Исследовано влияние легирования Вi и отжига в водороде на оптические и диэлектрические свойства кристаллов CWO. Установлено, что под воздействием отжига и легирования пропускание кристаллов значительно снижается в области 300–900 нм. Обнаружено значительное увеличение интенсивности ТСП и ТСЛ кристаллов CWO, легированных Вi, в интервале температур 80–290 К. При этом отсутствует четкая корреляция между максимумами кривых ТСП и ТСЛ, а также отмечается высвечивание в максимумах кривых ТСЛ одновременно красной и синей полос люминесценции. Установлено существенное изменение комплексной диэлектрической проницаемости образцов CWO в широком интервале частот под воздействием отжига и легирования Вi.

Вплив домішки Вi і високотемпературного відпалу на оптичні та діелектричні властивості кристалів CdWO₄. *О.М.Чугай, І.А.Тупіцина, О.О.Волошин, С.В.Олійник, І.В.Луньов*

Досліджено вплив легування Вi і відпалу у водні на оптичні та діелектричні властивості кристалів CWO. Встановлено, що під впливом відпалу і легування пропускання кристалів значно знижується в області 300–900 нм. Виявлено значне збільшення інтенсивності ТСП і ТСЛ кристалів CWO легуваних Вi в інтервалі температур 80–290 К. При цьому відсутня чітка кореляція між максимумами кривих ТСП і ТСЛ, а також відзначається висвітлення у максимумах кривих ТСЛ одночасно червоної і синьої смугами люмінесценції. Встановлено істотну зміну комплексної діелектричної проникності зразків CWO у широкому інтервалі частот під впливом відпалу і легування Вi.

1. Introduction

CdWO₄ (CWO) crystals are widely used as scintillators for detecting ionizing radiation. It was found in numerous researches that the luminescent properties of these crystals substantially depend on the point defects of their structure. Therefore, traditionally, these properties are controlled by introducing dopants into the crystal. It was previously established [1–3], that doping of CWO crystals with trivalent impurities, in particular Bi³⁺, causes the more significant change in the optical and scintillation characteristics of the crystals in comparison with doping with ions of a different valence. In this case, the compensation of the excess charge formed by the impurity ion plays an important role. However, the mechanism of such compensation, as well as the influence of high-temperature annealing in hydrogen on the properties of these crystals is still insufficiently studied. In this regard, the need to expand the arsenal of methods for researching the properties of crystals is obvious. In particular, dielectric spectroscopy is of particular interest, since intrinsic defects and dopants have a decisive influence on the dielectric response of crystals of different compositions [4–6]. In view of the foregoing, the purpose of this article is to research the effects of the dopant Bi³⁺ and high-temperature annealing in hydrogen on the optical and dielectric properties of CWO crystals.

2. Experimental

The investigated CWO crystals were grown by the Czochralski method in a platinum crucible with high-frequency heating. Impurity Bi₂O₃ was added to the mixture in the amount of $2.5 \cdot 10^{-2}$ mass %. Table 1 shows the results of the analysis of the content of cationic impurities in the grown crystals obtained by atomic absorption spectroscopy.

Table 1. Impurity composition of CdWO₄ crystals

10 ⁻⁴ mass. %									
Fe	Cu	Ca	Na	Al	Mo	Si	Bi	Pb	Mn, Mg, Ni, Cr, Bi, Ti, Sn
Undoped									
<2	<0,5	<10	<2	<2	<20	<20	<0,5	<1	<1
Bi-doped									
<2	<0,5	<10	<2	<2	<20	<20	10	<1	<1

Round plate shaped samples ($\varnothing = 12$ mm, $h = 3$ mm) were obtained by cleaving the plane (010).

When measuring thermally stimulated luminescence (TSL) and thermally stimulated conductivity (TSC), the sample placed in the cryostat was cooled with liquid nitrogen to a temperature of 80 K. Subsequent irradiation of the sample was performed using an X-ray source RUP-200 ($E = 100$ – 200 kW, $I = 1$ – 4 mA, Mo anticathode, dose rate 2 R/s, exposure time 1–10 min.). After cessation of irradiation, the sample was heated to room temperature at a speed of 1.5–5 deg/min. The constant heating rate (± 0.5 %) was provided by an electronic thermostat UTL-01. Sample radiation reaches an MDR-3 monochromator, and then the photomultiplier FEU-106. In this case, thermoluminescence was recorded in the wavelength range of 200–800 nm. In the case of a weak TSL signal, the monochromator was not used, and the radiation was measured by one of two photomultipliers equipped with appropriate filters. This ensured the registration of thermoluminescence both integrally over the spectrum and separately in any of the luminescence bands.

The dependence of the TSC was measured in the above temperature range according to the scheme with a guard electrode. Silver films evaporated in vacuum were used as electrodes. An electrometric amplifier was used with current sensitivity of 10^{-14} A. The radiating surface of the sample was the film-free part separating the guard and the measuring electrodes.

A spectrophotometer SHIMADZU 1240 (wavelength range of 300–900 nm) was used to measure the optical transmission spectrum. Real-valued ϵ' and imaginary ϵ'' parts of dielectric constant ϵ^* were measured in the frequency range of 12 – 10^5 Hz by a capacitive method using an immitance meter LCR 819 (firm Instec, Taiwan). The voltage on the sample was 1 V.

Additional heat treatment of the samples was carried out in a hydrogen atmosphere for 1.5 h at a temperature of 500°C.

3. Results and discussion

3.1 Optical properties

Fig. 1 shows the transmission spectra of nominally pure and doped CWO crystals, measured before and after annealing in hydrogen. As we see, as a result of annealing, the transmittance spectrum of the nominally pure crystal practically did not change, unlike the crystal doped with bismuth, the spectrum of which is characterized by a significant decrease in transmittance in almost the entire studied spectral region. This, in our opinion, suggests that bismuth atoms activate the reduction processes in CWO crystals during annealing in hydrogen. It should be noted that the defects formed during such processing of the crystals are similar to defects of the radiation nature [7].

Looking ahead, we note that, in contrast to the processes of optical absorption, the thermally stimulated processes in the crystals studied are extremely sensitive to point defects. Fig. 2 shows the spectra of thermally stimulated luminescence and thermally stimulated conductivity, confirming this statement. Thus, the TSC curves of pure samples in the temperature range studied (Fig. 2a) contain six to seven maxima. In this case, in the same temperature range, the TSL curves contain a slightly smaller (five to six) number of maxima in the wavelength ranges of red (620 nm) and blue (495 nm) spectral regions. Further in the text and in the caption to Fig. 2, these spec-

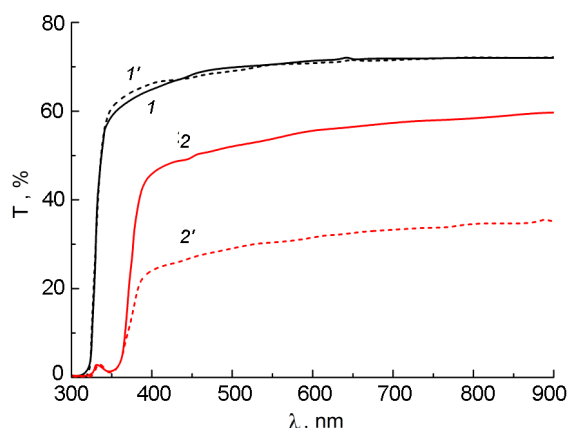


Fig. 1. Transmission spectra of CWO crystals: 1, 1' — nominally pure; 2, 2' — Bi-doped; 1, 2 — before and 1', 2' — after annealing in hydrogen.

tral ranges are called "R-" and "B-bands", respectively. We note, that in the temperature range $T < 160$ K the B-band maxima prevail in intensity; while in the temperature range $T = 160-230$ K, R-band maxima of thermally stimulated luminescence are predominant.

To establish the nature of the defects responsible for the maxima of the TSC and TSL curves of the investigated crystals, the corresponding activation maxima E_a were determined. In this case, the method of initial rise of maxima was used. These data are shown in Table 2.

The TSC maxima observed in the temperature range $T < 180$ K coincide with the TSL maxima, but only for the B-band. Therefore, these thermo-luminescence maxima can be associated with recombination processes involving the main charge carriers

Table 2. Characteristics of the TSC and TSL maxima for CWO crystals

Dopant	TSC		TSL			
			B-band		R-band	
	T , K	E_a , eV	T , K	E_a , eV	T , K	E_a , eV
Nominally pure	87	—	85	—	94	—
	120	0.44	120	0.44	124	0.34
	150	0.26	150	0.26	152	0.35
	179	0.24	175	0.24	—	—
	200	—	—	—	196	0.49
	245	0.58	—	—	230	0.9
	270	—	—	—	250	—
Bi	—	—	94	—	94	—
	195	—	182	0.45	182	0.45
	276	0.52	290	0.52	290	0.52

Dashes mean the absence of a maximum or the inability to calculate E_a with sufficient accuracy by the indicated method.

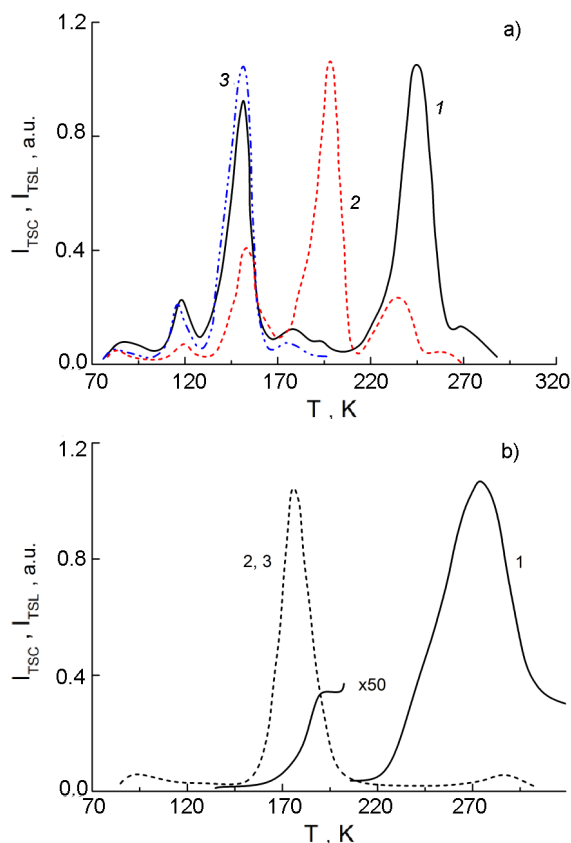


Fig. 2. Curves of TSC (1) and TSL (2, 3) for nominally pure (a) and Bi-doped (b) CWO crystals. Curves 2 and 3 for pure crystals correspond to *R*- and *B*-bands of thermoluminescence.

(most likely electrons) and "defective" centers. It is possible that these defects occur when exposed to X-rays and are in close proximity to the original defects.

An essential feature of the TSL (both in the *R*- and *B*-bands) and TSC curves at temperatures $T > 180$ K is a weak correlation of the maxima of these curves (see Fig. 2a). Therefore, the activation energies of the TSL maxima in the *R*-band and TSC maxima at these temperatures differ significantly (see Table 2). On this basis, it can be assumed that in this case, the TSL is due to the radiative capture of delocalized holes, the mobility of which is significantly lower than the mobility of free electrons. As a result, the intensity of the corresponding (hole) TSC maxima turns out to be low in comparison with the observed electronic maxima, which are somewhat biased with respect to the hole maxima. This conclusion is not consistent with the data of [8], where, on the contrary, the TSL maxima in the temperature range of 210–240 K are explained by the recombination of free electrons.

Doping of the investigated crystals with Bi atoms causes drastic changes in the TSC and TSL curves (Fig. 2b). In particular, these curves are not characterized by relatively narrow maxima observed on pure crystals (see Fig. 2a, b). At the same time, almost the entire light sum is contained in two characteristic wide TSL maxima observed at temperatures of 180 K and 290 K. Moreover, in this case, the thermoluminescence band of 540 nm is dominant. There is no correlation between TSC and TSL maxima. Attention is drawn to the fact that the number of such maxima and the corresponding activation energies are relatively small. Note that the activation energy of 0.52 eV is the same for the maxima of both TSL and TSC. In addition, for the maxima of the TSL of doped crystals, an activation energy of 0.45 eV is typical, the same as for the *B*- and *R*-bands of thermoluminescence.

In all likelihood, doping of CWO samples with Bi^{3+} ions leads to the transformation of the entire structure of shallow traps and luminescence centers, which determine the processes of TSC and TSL. This is evidenced by the following: a significant (by two or three orders of magnitude) increase in the intensity of TSC and TSL; the lack of a clear correlation between the maxima of these curves (see Fig. 2b) and the simultaneous emission of the *R*- and *B*-bands at the TSL maxima, which is not typical for the luminescence of nominally pure samples.

The special role of Bi^{3+} ions in the formation of the described properties, in our opinion, consists also in the formation of donor-acceptor pairs by these ions, which include a luminescence center with $E_a \approx 2.3$ eV and a shallow trap with activation energy $E_a = 0.45$ eV. In accordance with this assumption, the maximum of TSL at 180 K is due to intracenter transitions.

3.2 Dielectric properties

Figures 3 and 4 show the frequency dependences of the values ϵ' and ϵ'' for the crystals studied, measured before annealing in a hydrogen atmosphere, after annealing, and after storage in normal conditions for one and a half years. The figures show significant differences in the curves $\epsilon'(f)$ and $\epsilon''(f)$ depending on the presence of the dopant, as well as the history of the crystals. We point out the difference in the nature of certain dependencies. So, initially, both parts of ϵ^* for undoped crystals (see Fig. 3) are practically independent on fre-

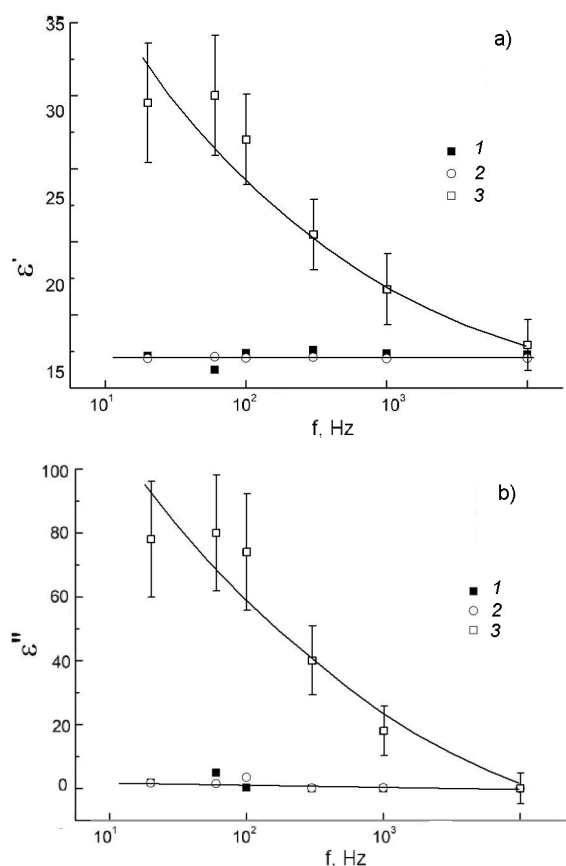


Fig. 3. Frequency dependences of real (a) and imaginary (b) parts of the dielectric constant of nominally pure CWO crystals, measured before (1), after (2) high-temperature annealing, and also after long-term storage.

quency. This value (14) is consistent with the value (16–18) obtained in [9] for undoped crystals. However, there are no data on the value for the studied crystals in the literature. Electrical conductivity σ for the crystals we studied is about 10^{-11} (Ohm-cm) $^{-1}$, which is three to four orders of magnitude greater than the values given in this work.

One of the reasons for this difference is that in our case, the measurements were made not in a constant but in an alternating electric field. The calculations used a known ratio

$$\sigma = \varepsilon_0 \omega \varepsilon'', \quad (1)$$

where ε_0 is the electric constant, ω is the circular frequency. Frequency value of 1 kHz was used. It is important that annealing in hydrogen leads not only to a significant increase in both parts of ε^* but also to a change in the nature of the dependence of these quantities on frequency (curves 1 and 3, Fig. 3). However, as a result of pro-

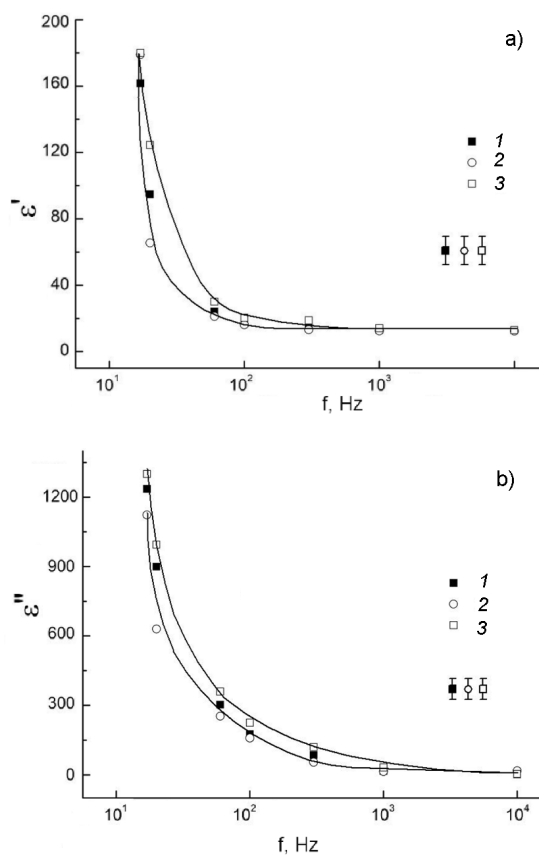


Fig. 4. Frequency dependences of the real (a) and imaginary (b) parts of the dielectric constant of nominally pure Bi-doped CWO crystals, measured before (1), after (2) high-temperature annealing, and also after long-term storage.

longed storage of the crystals, the frequency dependence ε'' and especially ε' become close to the original. A distinctive feature of Bi-doped CWO crystals is the strong frequency dependence of both the parts, regardless of the thermal history of the sample (see Fig. 4). In this case, as in the case of undoped crystals, annealing in hydrogen causes an increase, and prolonged storage — a decrease in ε' and ε'' . However, these changes are relatively small. We emphasize that the electrical conductivity of the crystals under consideration is 6–7 orders of magnitude higher than in the case of undoped crystals.

The key point in explaining the strong dependence of ε' and ε'' on frequency for some CWO crystals consists in the fact that in some cases these dependences contain a linear section (Fig. 5). We are talking about dependencies for crystals doped with Bi, as

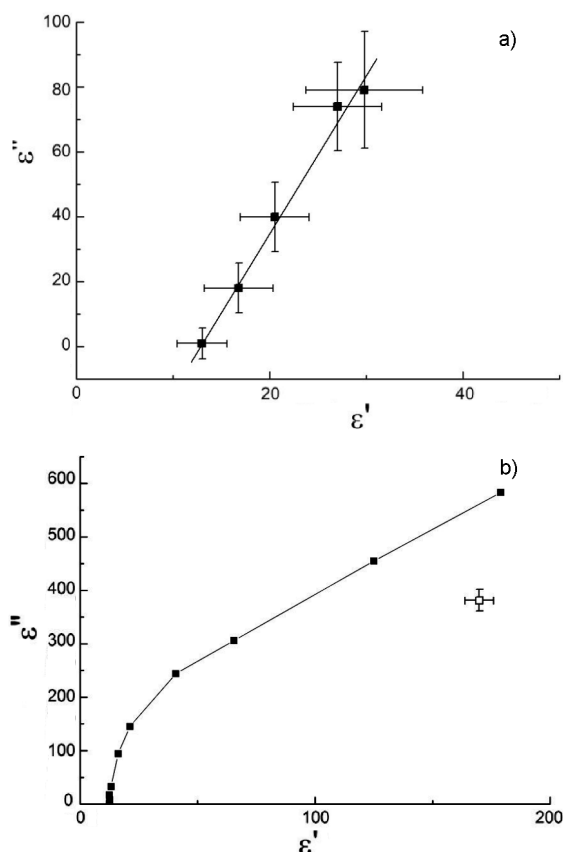


Fig. 5. Cole-Cole diagrams typical for nominally pure and annealed (a) and Bi-doped (b) CWO crystals.

well as for undoped crystals annealed in hydrogen. The specified dispersion feature of ϵ^* can be explained in terms of Jonscher's universal dielectric response model [10]. In this model, the polarization of a crystal under the action of an alternating electric field is associated with carrier jumps from one localized state to another. The field resulting from a separate jump is screened due to lattice relaxation. In this case, the ratio

$$\frac{\chi''(\omega)}{\chi'(\omega)} = \frac{W_1}{W_2} = \text{ctg}\left(\frac{n\pi}{2}\right) = \text{const}, \quad (2)$$

wherein $\chi'(\omega)$, $\chi''(\omega)$ are real and imaginary parts of the dielectric susceptibility, W_1 and W_2 are, respectively, the values of lost and stored energy during the period of the electric field, n is some parameter. The value of this parameter depends on the following factors: the spatial and energy distribution of localized states, and the radius of their wave functions. Taken together, these factors determine the multiplicity of jumps, i.e. the number of links in the chain

of jumps [11, 12]. And the smaller value of the parameter corresponds to a higher jump multiplicity. Our estimates have shown that for undoped and doped CWO crystals, the value of this parameter is 0.1 and 0.2, respectively.

It is natural to assume that, due to annealing in hydrogen, the concentration of intrinsic defects, namely, oxygen vacancies V_O , in undoped CWO crystals increased so much that such defects formed clusters. Moreover, some of the defects in the cluster are different from each other by the charge state and, as a result, by the activation energy. For example, clustering is possible in WO_{3-x} ; the clusters are formed during the reduction of tungsten to the pentavalent state after annealing in hydrogen. This assumption is consistent with a decrease in transmission in the visible region after annealing due to the formation of scattering centers, as well as the presence of several centers responsible for the TSL with different activation energy. Therefore, under the action of an electric field applied to the crystal, charge carriers jump between defects within the cluster, which manifest themselves in the polarization of the crystal. Moreover, with a fixed circular frequency of the field ω , the greatest contribution to the polarization is made by those clusters, the transfer of carriers within which takes place during the time of the order of the half-period of the field $\sim \omega^{-1}$. Prolonged storage in air certainly leads to a decrease in the concentration of oxygen vacancies V_O and, as a result, to the disappearance of the clusters formed with their participation. As a result, the dependence of ϵ' and ϵ'' on frequency disappears (see Fig. 3), their values become close to the initial ones.

A characteristic feature of Bi-doped CWO crystals is that the clusters of intrinsic point defects in them are generated by impurity atoms. As a result, vacancies occurring during hydrogen annealing V_O do not have a significant impact on the size of the clusters. This is confirmed by the absence of a significant effect of annealing and subsequent long-term storage on the frequency dependences of the ϵ' and ϵ'' values, as well as by the noted difference of the parameter n for doped and undoped crystals.

4. Conclusions

Thus, the transmission of light in the visible region of the spectrum, the processes of low-frequency electric polarization, ther-

mally stimulated luminescence, and the conductivity of CdWO₄ crystals are determined by their own defects, also by doping Bi atoms. In this case, defects and doping atoms give rise to electron traps with different activation energies. In the case of a high concentration of point defects, clusters are formed with their participation. Electronic jumps between the point defects in the cluster cause an anomalously high polarizability of the crystals, which we observed for the first time.

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