Electrical and dielectric properties of $CdWO_4$ crystals

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Electrophysical investigations of $CdWO_4$ crystals have been carried out by thermo-stimulated polarization and thermoelectret state depolarization in interrelation with temperature dependences 290–550 K of DC conductivity and permittivity at 1 kHz frequency. The depolarization currents are correlated with activation of the dipole defect complex reorientation processes (current peaks at 308, 319, 338 and 365 K) and with development of spatially heterogeneous of the volumetric charge which as a result of localization of the current carriers on capture levels (the wide non-elementary intense maximum at 400–550 K). The basic parameters of the main relaxators and conductivity have been estimated. The explanation of the electrical properties and polarization effects are based on the assumed predominance of intrinsic structural defects that may be probably the cadmium and oxygen vacancies and also defect complex based on these vacancies. The experimental data on conductivity do not contradict to small-polaron theory.

Проведены электрофизические исследования кристаллов $CdWO_4$ методами термости-мулированной поляризации, деполяризации термоэлектретного состояния во взаимо-связи с температурными зависимостями 290–550 K проводимости на постоянном токе и диэлектрической проницаемости на частоте 1 kHz. Токи деполяризации связываются с активацией реориентационных процессов дипольных комплексов дефектов (пики тока при 308, 319, 338 и 365 K) и образованием пространственно неоднородного рас-пределения обьемных зарядов вследствие локализации носителей заряда на уровнях захвата (широкий неэлементарный интенсивный максимум 400–550 K). Оценены ос-новные параметры главных релаксаторов и проводимости. Обьяснения электропровод-ных свойств и эффектов поляризации базируются на допущении доминирования собст-венных дефектов структуры, которыми могут быть вакансии кадмия и кислорода, а также более сложные комплексы дефектов на их основе. Полученные эксперименталь-ные закономерности проводимости не противоречат теории поляронов малого радиуса.

Cadmium tungstate crystals, $CdWO_4$ (CWO) of the wolframite type structure are used widely, in particular as scintillators in tomography and high-energy particle spectrometry [1, 2]. Such materials should meet the appropriate requirements like sensitivity, reliability and stability of their characteristics. The technical characteristics of CWO are defined to a great extent by the structure defects. At present, the nature of point defects in this compound is under discussion.

The electrical properties provide an important information on structural defects and their nature. But such investigations in case of CWO are fragmentary. Several works [3–5] contain experimental conductivity data at temperatures exceeding 650 K for undoped CWO crystals [4, 5] and those doped by different impurities [3]. In [5], it is concluded that as the oxygen pressure is reduced, the CWO electrical conductivity is changed from mixed ion-electron to electron n-type one. In this case, it is just the Cd and O vacancy pairs that must be the dominating defects. The appearance of these vacancies is caused by the deviation

from stoichiometry during the crystal growth. The intrinsic defect concentrations in CWO can be changed by means of the purposeful technology variations [1, 3] (in particular, by controlling CdO evaporation). Electrical parameters in case of such technological variation are sensitive to small change in the defect structure of CWO crystals. These parameters can be used to control the required properties in the improvements of the CWO crystal technology.

In [4–6], the electrical characteristics of CWO ceramics have been studied. In [7], some electrical and dielectric parameters of CWO crystals and other tungstates at room temperature are presented. The photoconductivity of CWO in the 220–400 nm spectral region was observed in [8]. The thermally stimulated polarization (TSP) and depolarization (TSD) currents in CWO were not investigated to date.

In this work aimed at the study of CWO, we investigate the total DC conductivity σ, TSP currents (I_{TSP}), TSD currents (I_{TSD}), and dielectric permittivity ε. The behavior of electrically active defects in undoped CWO crystals of wolframite type is discussed basing on experimental data. The measurements were done in the temperature range 290–550 K. The peculiarities of polarization in CWO, temperature evolution of the active dipolar centers and probable interaction between the defects are established considering the efficiency of the polarization charge accumulation.

The CWO single crystals used for investigation were grown from melt by Czochralski technique using high purity initial components. The obtained crystals were colorless. The level of non-controlled impurities did not exceed 0.001 at. %. The samples were selected from high-quality (free of inclusions, cracks and other macrodefects) single-phase part of the boule. Monoclinic crystals CWO belong to wolframite structure type (space group $P2/c$ [3]). The samples for the investigations were cut along the cleavage plane (010), perpendicular to the crystal growth axis (along axis b). The graphite electrodes with guard ring were deposited on the cleaved surfaces of 0.5 mm thick disc-shaped samples of 10 mm in diameter. Measurements in the thermostatic quartz cell in air were carried out using V7-30 type voltmeter-electrometer. Temperature was varied linearly at the rate of 0.1 K/s both at heating and cooling. The conductivity current, TSP and TSD of thermal-electret states were studied using the

procedure used recently [9] for lead tungstate study. The vector of the external DC electrical field in the experiments was perpendicular to the (010) plane. The efficiency of the polarization charge accumulation was studied by varying the polarization conditions, *i.e.* the polarization voltage U_p, temperature T_p and time τ_p. The polarization nature was established considering the dipole and space-charge mechanisms [10] of charge formation, taking into account the presence of the blocking electrodes. The intensities I_m of the current peaks, their positions in the thermogram (temperature maxima values T_m) and half-widths of TSD peaks in the spatially polarized heterogeneous charge model were analyzed for the investigated crystals.

Simultaneously with the DC investigations, the permittivity was measured in the same temperature range by the capacitor method [11, 12] at 1 kHz frequency using a CLR E7-13 measuring device. The $\varepsilon(T)$ dependences were measured for the initial non-polarized and previously polarized CWO crystals under different polarization conditions. For CWO, in contrast to PWO [11, 12], no additional specific features of the $\varepsilon(T)$ curve were observed. The experimental data processing and the expansion of non-elementary experimental curves into Gaussian components were made using the Origin software. The external DC field value did not exceed of 10^5 V/m, which fall within the linearity range of the voltage-current characteristic.

The investigated CWO crystal at room temperature exhibits low DC conductivity of $\sigma \sim 10^{-15}$ to 10^{-14} $\Omega^{-1} \cdot$cm^{-1}. This corresponds to the Maxwell relaxation time [10] (taking into account the ε values obtained in this work) in the range 10^3 to 10^2 s. The $\sigma(T)$ dependences in the lnσ ($10^3/T$) coordinates are presented in Fig. 1. Typical TSP currents spectra are shown in the inset in Fig. 1. A relatively intense current peak of the TSP curve with maximum at about 360 K is observed upon the first heating of consecutive measuring cycles. At subsequent measurements (Fig. 1b, curve *2*), after thermal removing of relaxation processes, this TSP peak is not observed. The mentioned behavior of TSP currents is typical for solids at the dipole reorientation [13].

Upon the first heating, the ln $\sigma = f(10^3/T)$ dependence in temperature range of TSP current peak differs from the dependences recorded in the next measurement cycles (Fig. 1a). The curve at repeated
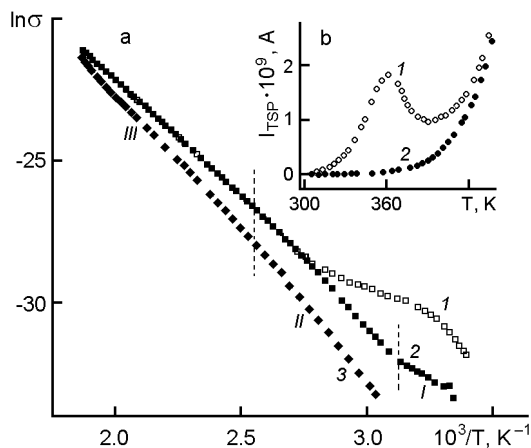
Fig. 1. Temperature dependences of electrical conductivity (a) and thermally stimulated polarization currents (b) for $CdWO_4$ crystal. Curves *1* — measurements upon the first heating, *2* — the same in repeated measurements, *3* — measurements upon cooling. Vertical dotted lines show the points of the $\ln\sigma = f(10^3/T)$ slope changes and relatively separate linear intervals I, II and III.
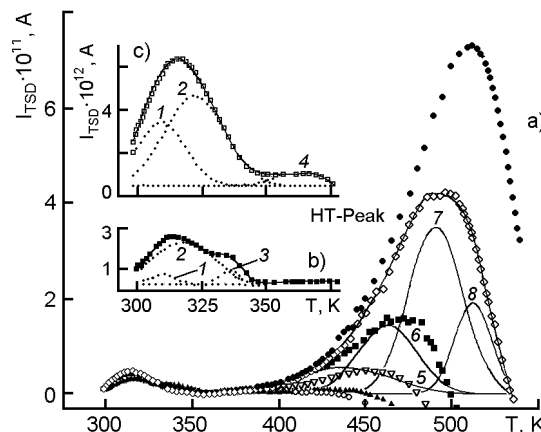

Fig. 2. Thermally stimulated depolarization currents in $CdWO_4$ crystal. Curves (a) show dependence of the full TSD spectra on the polarization temperature: *1* — $T_p = 400$ K, *2* — 420 K, *3* — 440 K, *4* — 470 K, *5* — 500 K, *6* — 520 K; curves (b) — $T_p = 390$ K; curves (c) — $T_p = 360$ K. Dotted line depicts the components obtained after the expansion of non-elementary maxima; solid curves, envelope of the expanded components; dots, experimental points. Tests at $U_p = +50$ V, $\tau_p = 5$ min.

measurements may be approximated by three linear segments in temperature ranges (I) 290–320 K, (II) 320–390 K and (III) at $T > 390$ K. The activation energy values ΔE at corresponding temperatures, derived from $\ln \sigma = f(10^3/T)$ curves and the pre-exponential factor σ_0 values in $\sigma = \sigma_0\exp(-\Delta E/kT)$ dependences (where k is the Boltzmann constant) are presented in Table 1. Experimental points in temperature range III give straight line in the $\ln \sigma = f(10^3/T)$ plot independently from number of heating cycles. The $\ln \sigma = f(10^3/T)$ curve at cooling differs from the same at heating. Values of ΔE and σ_0 for this case are also listed in Table 1. The activation energy at cooling is seen to be higher than that at heating.

The correlation between the charge transfer and polarization effects was investigated by studying the TSD current. The

TSD spectra of CWO crystals in the temperature range 290–550 K are presented in Fig. 2a–c. Optimal values of the voltage and the polarization time were found experimentally and amount $U_p = +50$ V and $\tau p = 5$ min, respectively. At polarization temperatures $T_p > 450$ К, considerable changes occur in the high-temperature region of the TSD curve. As is seen from Fig. 2a, an intense and broad high-temperature TSD peak (HT-peak) is formed in such conditions. Increasing T_p results in linear shift of the HT-peak (Fig. 3d) towards higher temperatures. The $I_m(T_p)$ function (Fig. 3c) is nonlinear and close to the exponential one.

In Fig. 3, the behavior of other CWO TSD current maxima is shown depending on the sample polarization conditions. The evaluated values of main relaxation parameters (maxima 1–8, respectively) are presented in Table 2 as calculated using the well-known relation [10]. To calculate the activation energy, we used the expression $E_0 = 30kT_m$ (column "a" in Table 2) and the "initial increase" method when this was possible (column "b", Table 2). Basing on the criterion of functional dependence maximum (the first derivative should be equal to zero), $d[I_{TSD}(T)]/dT = 0$, the frequency factor was estimated using
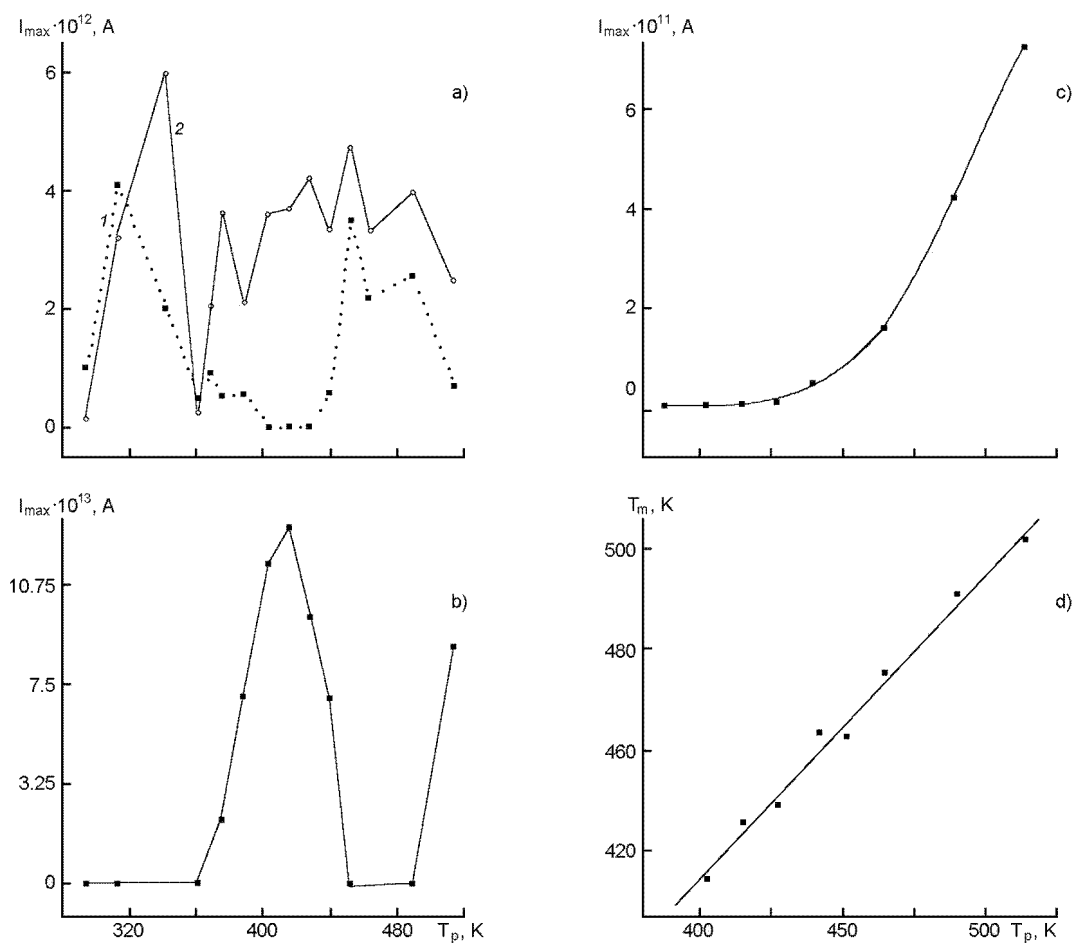
Table 1. Activation energy ΔE and pre-exponential factor σ_0 in various temperature ranges of $\sigma(T)$ dependence for $CdWO_4$ crystals

T, К	ΔE, eV		σ_0, $\Omega^{-1}\cdot cm^{-1}$	
	heating	cooling	heating	cooling
290–320	0.42	–	$6.0\cdot10^{-8}$	–
320–390	0.82	0.95	$1.2\cdot10^{-1}$	1.2
390–550	0.71	0.80	$4.5\cdot10^{-3}$	$1.8\cdot10^{-2}$

Fig. 3. Dependences of thermally stimulated depolarization currents maximum intensity (a–c) and maximum temperature (d) on the $CdWO_4$ crystal polarization temperature. Curves (a) correspond to peaks *1*, *2*; (b) — *3*; (c, d) — high-temperature (HT) peak. The numeration and designation of TSD maxima according to Fig. 2.

Table 2. Temperature of maximum T_m, activation energy E_0 and frequency factor ω for $CdWO_4$ crystals as determined from TSD curves

No. peak	T_m, K	E_0, eV		$\omega \cdot 10^{-11}$, s^{-1}
		(a)	(b)	
1	308	0.80	0.82	1.17
2	319	0.83	0.84	1.03
3	338	0.88	–	0.96
4	365	0.94	0.94	0.89
5	435	1.13	0.62	0.83
6	463	1.20	–	0.73
7	493	1.28	–	0.72

$\omega = (\beta E_0/kT_m{}^2)\cdot\exp(E_0/kT_m)$ expression assuming that quasi-particles of a single type are involved in the elementary relaxation process. Energies E_0 here correspond to the values in the column (a) of Table 2. Thus, when varying the polarization conditions, two main groups of complex maxima have been found in experiment in the TSD curve within 300–390 K and 400–550 K temperature ranges. The TSD current maximum at 365 K is observed in TSP spectra (Fig. 1b).

The efficiency of the polarization charge formation can be connected with the intensity of maxima caused by the respective kind of relaxators. The polarization of the sample without contribution of the electrically active centers corresponds to zero value of I_m. At the dipole polarization, this corresponds to zero concentration of the certain dipole centers or their inactivity at the specified temperature. In the case of space-charge formation mechanism of spatially heterogeneous charge distribution in

the crystal, the $I_m = 0$ value corresponds to the empty charge trapping levels in the region of its localization.

The dependences of peak 1–4 intensity (Fig. 2) on the polarization temperature, their low intensities and small half-widths, the constancy of T_m found in experiments are seen in Fig. 2 and Figs. 3a–b. According to the criteria [10, 13] those facts evidence the dipole nature of the peaks. The high-temperature broad non-elementary peak in the 400–550 K range (Fig. 2a) corresponds to the space-charge polarization mechanism. The dependence of this peak on polarization condition is shown in Figs. 3c–d. The high-temperature complex TSD maximum (HT-peak) can be expanded into components 5–8 (Fig. 2a, curve V). This corresponds to four space-charge trapping levels.

As to peaks 1, 2, some temperature ranges of maximum intensities thereof are seen in Fig. 3a. At $T_p > 425$ K, the I_m values of peaks 1, 2 increase. Peak 3 (Fig. 3b) is in the range $350 \text{ K} < T_p < 450 \text{ K}$. As well as in case of peaks 1, 2, the peak 3 intensity increases at $T_p > 490$ K. A slight scatter of points in the resulting $I_m(T_p)$ curves (Fig. 3a) can be related to the inaccuracy of the complex maximum expansion into Gaussians (closely located components 1 and 2).

In the 290–550 K range, the $\varepsilon(T)$ dependence (Fig. 4) is linear. As in the conductivity case, an insignificant hysteresis in $\varepsilon(T)$ dependences is observed at heating and cooling (Fig. 1). For the investigated CWO crystals at room temperature, $\varepsilon = 17$ (according to [8], $\varepsilon = 14$). A slight linear increase according to the relationship $\varepsilon = 6.5 \cdot 10^{-3} T + 11.2$ gives $\varepsilon = 18$ to 19 at 550 K. Such insignificant changes of ε when the temperature is changed in mentioned ranges may result from crystal conductivity, which increases exponentially with increasing temperature (Fig. 1). The preliminary polarization of the sample, its heating to the maximum temperature of measurements, as well as the cooling conditions (i.e. history of the sample) do not affect the $\varepsilon(T)$ dependence of CWO crystals. In PWO crystals [11, 12], the preliminary excitation by the external DC field has resulted in a non-elementary maximum in $\varepsilon(T)$ curve near 320 K. The ε values in this maximum are one order higher as compared to those at room temperature. The intense relaxation processes were observed in PWO crystals, too. In CWO crystals, such relaxa-
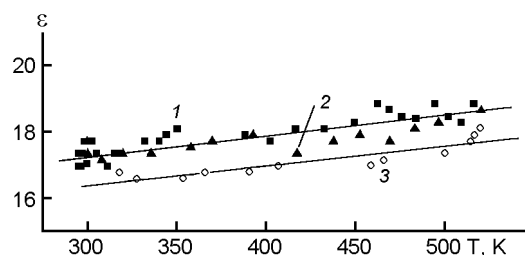

Fig. 4. The temperature dependences of permittivity of $CdWO_4$ crystal. Curves *1*, *2* — the first and following measurements upon heating, respectively, *3* — measurements upon cooling.

tion is absent. Under identical experimental conditions, the respective parameters of the TSD curves in CWO are on the average two orders lower than in PWO. The obtained experimental data suggest some notes on the temperature behavior of electrically active defects in CWO single crystals. Models of intrinsic defects and charge transfer mechanisms in the mentioned temperature range for compounds of such structure are not yet ascertained unambiguously. The main attention of researchers was focused on luminescence and its kinetic and scintillation properties (see, e.g., [1–3, 14, 15]) in CWO, both undoped and doped with various impurities. The CWO local spectral levels were studied using thermoluminescence and thermally stimulated conductivity methods at $T < 300$ K [16, 17].

The CWO crystal electron structure is similar to that of PWO [18, 19]. The distribution of the electron state density near the band gap can be described in the framework of oxygen-tungsten complexes. The valence band is formed mainly by the corresponding states of oxygen while the conductance band, by the tungsten states. The crystal chemistry features of divalent metal tungstates are considered in [20], where it has been shown, in particular, that in PWO (scheelite), the close anionic packing is more "loosened" than in CWO (wolframite). These structural features (in CWO and PWO) would no doubt effect the electrical characteristics of both crystals. We have considered the electrical properties of PWO in detail in [9, 11, 12]. The temperature changes of CWO electrical characteristics, as noted above, are studied insufficiently. In CWO crystals, the low conductivity in the conditions of performed experiments is of a mixed ionic/electronic character. At high temperatures, this was shown in [4, 5].

The weakly bound electrically active charge carriers, which drift in a DC field toward the near-electrode regions, form in these regions spatially heterogeneous space charges. An appreciable efficiency of such processes was observed at $T_p > 400$ К (Fig. 3c). At $T < 400$ К, the re-orientation processes related to the complex defects of the dipole nature are more effective. Basing on the number of TSD maximums, several kinds of dipole centers (TSD peaks 1–4) can be distinguished in CWO crystals.

The relaxation process caused by the dipole centers of type 3 (peak 3), is intensified when T_p changes in 350–450 К range (Fig. 3b). In these conditions, peak 1 is almost absent (Fig. 3a). At $T_p > 490$ К, the first two TSD maxima decrease essentially, and the intensity of the third maximum increases. Such behavior of TSD peaks 1–3 intensities and their relative similarity in the I_m values indicate a close genetic binding of the corresponding dipole center types and the similarity in their nature. Theoretical description of current peaks 1–4 is consistent with the scheme [10, 13] of interacting dipoles and complexes where those are involved.

The low-intensity TSD peak is observed at $T_p > 360$ К. At $T_p > 400$ К, the space-charge polarization predominates. The HT-peak at indicated T_p has a high intensity (Fig. 2a, Fig. 3c), since high temperatures favor an increased mobility and the efficient migration of electron charge carriers.

The energy characteristics of relaxators 1–4, the possibilities of spatial orientation change due to shifts of more mobile component of corresponding dipole center types are different. We can assert that the electronic processes in 290–400 K range influence less on the relaxation polarization, than at $T > 400$ К. At high temperatures ($T > 400$ К), the electrostatic interaction between the dipole center components decreases, but the dissociation of defect complexes predominates. At low temperatures ($T < 400$ К), dipole associates are formed. The indicated features of the ionic/electronic processes cause the slope change of $\ln\sigma = f(10^3/T)$ line with inflection points at 320 and 390 K (see Fig. 1 and Table 1).

The dissociation and association of defect complexes is energy-asymmetrical. This results in hysteresis in $\sigma(T)$ dependence for CWO (Fig. 1) and slightly different course of $\varepsilon(T)$ curves (Fig. 4) at heating and cooling. The relatively low activity of the electron processes does not stimulate noticeable changes in $\varepsilon(T)$ curves for CWO.

It follows from the performed experiments that in the investigated undoped CWO crystal, as well as in PWO [9, 11], the intrinsic defect disordering is dominating. The possible main structure defects are cadmium and oxygen vacancies. At high temperatures, single vacancies predominate. Near room temperature, the dipole complexes are formed due to electrostatic aggregation of vacancies with opposite signs: the vacancy pairs (dipolons) and more complex associates on their base. At the same time, this does not exclude relatively isolated tetrahedral oxygen-tungsten complexes $WO_4{}^{2-}$ and processes of electron charge carrier localization near such complexes on corresponding vacancies.

The quite close coupling of electron charge carriers with the lattice causes the formation of small radius polarons, as is confirmed by the exponential character of the $\sigma(T)$ dependence (Fig. 1) and by the values of charge transfer parameters (Table 1). It is to note that the oscillation series in the energy spectra of charge localization centers in CWO crystals, revealed at the thermoluminescence measurements, is explained [21] as a demonstration of the polaron effect.

Thus, the complex of electrophysical investigations of CWO single crystal (wolframite structure type) has been carried out. For the first time, the TSD currents in CWO along the crystal growth axis [010] were studied. Two series of TSD maxima at 300–390 K and at 400–550 K (see Fig. 2 and Table 2) have been observed in 290–550 K temperature range. These maxima have dipole and space-charge (HT-peak) nature, respectively. The elementary point defects (particularly O and Cd vacancies) tend to form complex associates, that accumulate at temperatures close to RT. A relatively better lattice temperature stability of CWO crystals causes a lowered lability of the electrically active defects as compared to PWO. The preliminary excitation of CWO by external DC electric field does not cause noticeable changes in $\varepsilon(T)$ curves. The electron component of the CWO electrical conductivity may be described in the frame of small-radius polaron theory. More accurate nature definition of charge localization centers and electrically active defects of CWO lattice requires an additional investigations.

It is to note that the proposed methods are sensitive to small changes of structural defect states in CWO crystals. Microscale displacements of more mobile components of defect complexes (the spatial orientation

changes in the selected crystallographic direction, the energy minimization), or their association/dissociation produce noticeable changes in the TSD spectra.

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Електричні та діелектричні властивості кристалів CdWO$_4$

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Проведено електрофізичні дослідження кристалів CdWO$_4$ методами термостимульованої поляризації, деполяризації термоелектретного стану у взаємозв'язку з температурними залежностями 290–550 К провідності на постійному струмі та діелектричної проникності на частоті 1 kHz. Струми деполяризації пов'язуються з активізацією реорієнтаційних процесів дипольних комплексів дефектів (піки струму при 308, 319, 338 та 365 К) та утворенням просторово неоднорідного розподілу об'ємних зарядів внаслідок локалізації носіїв заряду на рівнях захоплення (широкий неелементарний інтенсивний максимум 400–550 К). Оцінено основні параметри головних релаксаторів та провідності. Пояснення електропровідних властивостей та ефектів поляризації базуються на припущенні домінування власних дефектів структури, якими можуть бути вакансії кадмію та кисню, а також складніші комплекси дефектів на їх основі. Отримані експериментальні закономірності провідності не суперечать теорії поляронів малого радіуса.