Thermal prehistory and electrical properties of tungstate crystals

V.N.Shevchuk, I.V.Kayun

I.Franko Lviv National University, Department of Electronics,
50 Dragomanov St., 79005 Lviv, Ukraine

The temperature and time depended changes of electric and dielectric parameters of AWO_4 (A = Ca, Cd, or Pb) single crystals have been experimentally studied. The dielectric properties were measured along [001] in $PbWO_4$ single crystals (scheelite structure type) and show some quasi-periodicity during approximately 20 h time cycle of free relaxation. The connection between these periodic phenomena and thermodielectric effect is proposed to associate with structural and point defects dynamics and their interactions and creation/rebuilding of complex defects (during the relaxation processes). The main role in these phenomena is attributed to oxygen and lead vacancies. No thermodielectric effect was observed in $CdWO_4$ (wolframite structure type) perpendicular to cleavage face (010) at temperatures up to 500 K.

Экспериментально исследованы температурно-временные изменения электрических и диэлектрических параметров монокристаллов AWO_4 (A = Ca, Cd или Pb). Диэлектрические свойства, измеренные вдоль направления [001] в монокристалле $PbWO_4$ (структура типа шеелита), показали определенную квази-периодичность с временной цикличностью близко 20 ч свободной релаксации. Связь этого явления периодичности и термодиэлектрического эффекта предлагается ассоциировать с динамикой структурных и точечных дефектов и их взаимодействием и/или формированием/перестройкой комплексов дефектов (в течение релаксационного процесса). Главная роль в таких явлениях отводится вакансиям кислорода и свинца. В $CdWO_4$ (структура типа вольфрамита) перпендикулярно плоскости скола (010) при температурах до 500 К термодиэлектрический эффект не наблюдается.

1. Introduction

The tungstate crystals AWO_4 (here A is Ca, Cd or Pb) are intensively studied as effective self-activated scintillation materials with short afterglow time [1]. The luminescence properties of the AWO_4 single crystals and their time characteristics depend on the crystal structural and point defects, of complex and not established unambiguously nature. The electrical and dielectric studies of these compounds are fragmentary and insufficient, in spite of the fact that such data are highly informative as to the defects and their state changes under the crystal heat treatment. Therefore, electrical and dielectric proper-ties are considerable in performance of scintillation crystals [2].

Our previous works [3–5] on the studies of $PbWO_4$ crystals using electrical conductivity σ currents, thermal stimulated polarization, and depolarization currents within the temperature range of 290–550 K have revealed a series of local energy levels and relaxation processes of different nature. The studies [3, 4] of the permittivity ε under variations of the $PbWO_4$ crystal temperature T within the 290–550 K range have shown a close connection of such dependences with the depolarization processes in this compound.

In this work, the electrically active defects in the AWO_4 and their influence on characteristics of crystals are investigated taking into account of thermal prehistory of crystals (maximal heating temperatures, polarization time of samples, and times of free crystal relaxation). The dependences $\sigma(T)$ and $\varepsilon(T)$ and thermally stimulated polarization/depolarization were considered in the undoped AWO_4 crystals with the purpose to elucidate the regularities of defect formations, defect interactions, and ion-electron processes.

2. Experimental

Undoped AWO_4 crystals obtained using the Czochralski technique were studied. The measurements on $CaWO_4$ and $PbWO_4$ ($C_{4h}^6-I4_1/a$ space group) samples were performed parallel to the growth axis [001] and perpendicular to cleavage face (010) of the $CdWO_4$ crystal ($C_{2h}^4-P_2/c$ space group). Fig. 1 illustrates the details and crystallographic features of experiment geometry for AWO_4 crystals. Here, shown are some crystallographic elements (basal, cleavage planes, depicted by the suitable *hkl*-symbols, intersections of planes, structural elements of unit cells, coordinating polyhedra of the atoms in investigated tungstate structures), too. The samples prepared were $10 \times 10 \times 0.4$ mm^3 size. The aquadag or Ag-paste was used as the contact. A quartz temperature-controlled measuring cell was used in the investigations (with the temperature control accuracy of better than ± 1 K). The ε values for assumed small edge effects were calculated using the well-known relation for a flat capacitor $\varepsilon = Cd/\varepsilon_0 S$ (C is the measured capacitance of the sample; d and S are its thickness and area, respectively, and ε_0 is the permittivity of free space). The capacitance of a sample was recorded using a CLR E7-13 measuring unit (operation frequency, 1 kHz). The root-mean-square value of the voltage drop on a measured object did not exceed 0.2 V. To obtain correct results, the capacitance of the connection system was taken into account. The temperature was measured using a standard chromel-alumel thermocouple. All other experimental details, in particular, the electrical conductivity measurements were the same as those described before in [3–5].

The measurements in the linear heating or cooling regimes at a rate of 0.1 K/s in
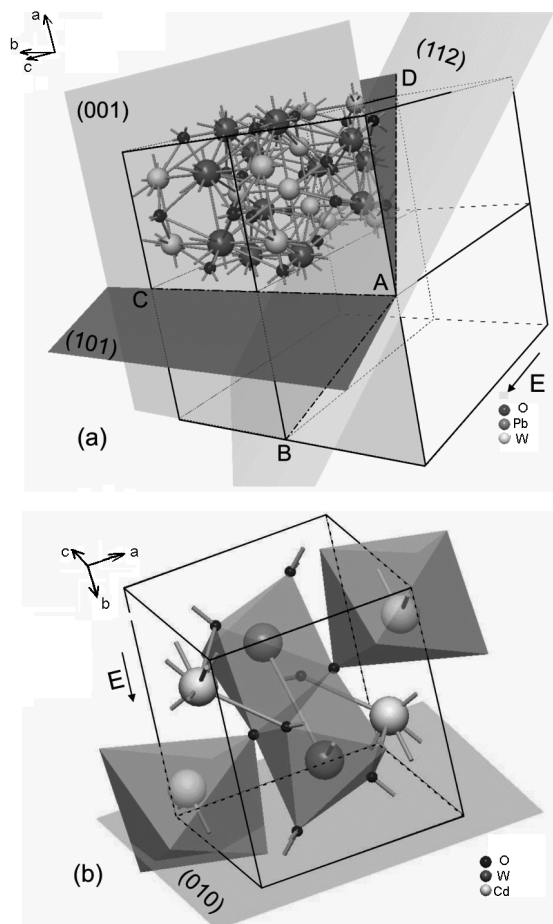

Fig. 1. Clinographic projection of $PbWO_4$ (a) and $CdWO_4$ (b) crystal unit cells. The some elements of structure presented in the frame of one unit cell. The *hkl*-symbols depicted the respective slip planes. Section of the planes depicted by the AB, AC, and AD lines. External electric *dc* field applied parallel to the vector *E*.

the temperature range $T = 290-550$ K were performed. Relaxation of a sample to the quasi-equilibrium state at room temperature after high-temperature heating was controlled by measuring the sample capacitance in certain time intervals t. In order to study the effect of preliminary excitation in an external *dc* electric field E, we applied a *dc* voltage (up to 50 V) to a crystal over a time $t_P = 5-15$ min at different fixed temperatures T_P. The model of space-heterogeneous charge the same as previously [3, 4] under assumption of blocking electrodes was proposed. The experimental data were processed using the standard Origin software package.
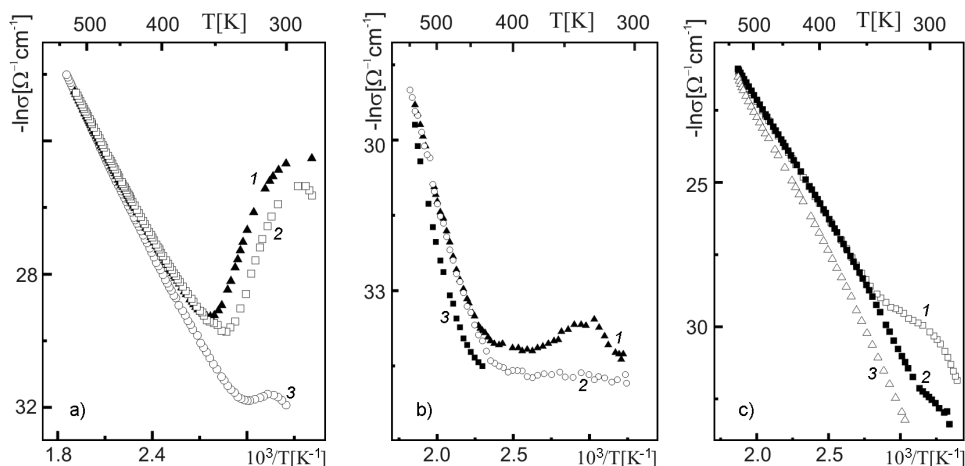
Fig. 2. Temperature dependences of electrical conductivity for $PbWO_4$ (a), $CaWO_4$ (b), and $CdWO_4$ (c) crystals in the air at direct applied electrical field. The curves *1*a, b, c are obtained upon first heating; *2*a, b, c — measurements upon second heating; *3*a, b, c — upon cooling.

3. Results and discussion

Figs. 2 illustrate in the $\ln\sigma - 10^3/T$ plot the typical temperature dependence of the AWO_4 crystals direct conductivity. At the detailed consideration of the $\ln\sigma(10^3/T)$ curves, they can be approximated by several linear segments depicting the corresponding different activation energy values [5]. As Fig. 2 show, the $\sigma(T)$ curves are characterized by low-temperature "structural-sensitivity" and high-temperature segments. At low temperatures, the values of activation energy are low (0.01–0.10 eV). The $\sigma(T)$ curves in low-temperature range are strongly dependent on thermal prehistory of crystals, thermal treatment, and other experimental conditions. At high temperatures, the values of activation energy for the AWO_4 crystals are 0.6–1.1 eV.

The dependences of $\varepsilon(T)$ curve pattern on maximal temperature heating T_h of the sample $PbWO_4$ and $CdWO_4$ are presented in Fig. 3 (a–d) and in Fig. 3e, respectively. Here, shown is the trend of curves in successive heating-cooling cycles. The temperature T_h for the $PbWO_4$ crystals was chosen in accordance with earlier investigations on thermally stimulated currents [4, 6, 7]. Using the thermal depolarization method, under certain conditions, we observed series of depolarization current peaks in the temperature ranges 290–350 K (the range *A*), 350–380 K (*B*), and 400–600 K (*C*). We assumed that these peaks are related to dipole polarization (ranges *A*, *B*) or to space charges produced by equilibrium carriers in a sample (range *C*) [4, 6, 7].
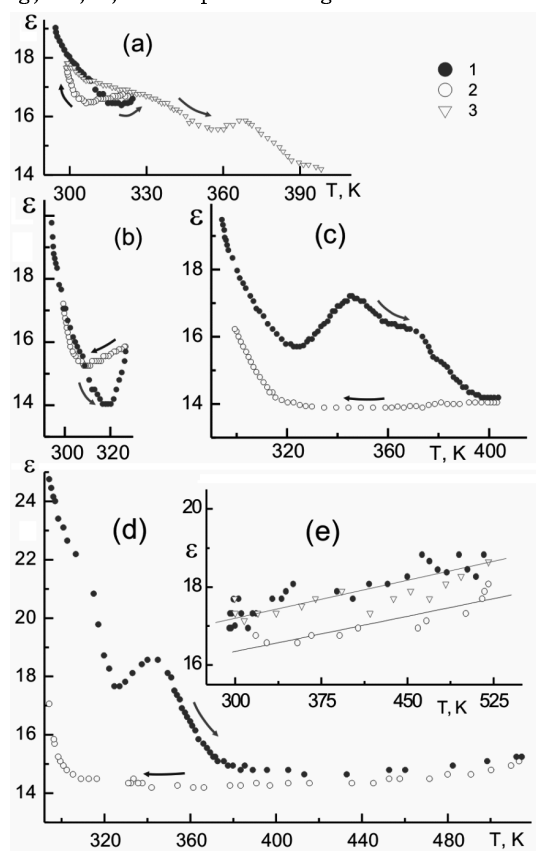

Fig. 3. Temperature dependences of the permittivity of $PbWO_4$ (a–d) and $CdWO_4$ (e) crystals on (1) heating and (2) cooling for different maximum measurements temperatures T_h in one heating-cooling cycle. (3) Heating of the sample at once after the first measurement cycle represented by curves *1* and *2*. T_h values: (a) 325, (b) 335, (c) 405, (d) 515, and (e) 530 K. Measurements in each cycle in (a–d) cases were performed after keeping the sample under room conditions for longer than 24 h.

In Fig. 3(a–d), we see that, in ranges *A* and *B*, probable polarization effects strongly affect the ε(*T*) curves. In the range 400–520 K, conventional shape of the ε(*T*) curves is observed (curve *1* in Fig. 3d). A nonlinear increase in ε at high temperatures is caused by an exponential increase in conductivity with activation energies of 0.7–0.9 eV [6, 7] in the corresponding temperature intervals. In the range 290–400 K, the ε(*T*) curves measured in the heating mode exhibit closely spaced complex maxima that grouped in two rather narrow temperature regions 290–330 and 330–400 K (curve *3* in Fig. 3a and curve *1* in Figs. 3c, 3d).

The ε(*T*) curves measured on heating and cooling differ in shape. Thermal hysteresis appears for $T_h \geq 400$ K, where the values of ε measured on heating are higher than those on cooling. In the cooling mode, no maxima are observed in the ε(*T*) curve. In repeated experiments, the ε(*T*) curves measured on heating remain nonlinear irrespective of T_h or of the sample exposure duration to normal conditions prior to measurements. At $T_h \geq 400$ K (Figs. 3a, 3b), the values of ε measured on cooling are greater than on heating for the same temperatures.

At room temperature, the values of ε usually lie in the interval 25–30. These values agree with the data obtained for $PbWO_4$ in [8, 9]. To establish quasi-equilibrium values of ε after high-temperature heating, the sample must be kept for about 24 h under room conditions. The initial conductivity of crystal is recovered in the same time period [7].

At heating conditions of measuring in the range 400–470 K, the function ε(*T*) for $PbWO_4$ is linear and can be approximated by the relation $\varepsilon = 10.72 + 1.67 \cdot 10^{-3} T$. On cooling (range 470–320 K), function ε(*T*) is also linear: $\varepsilon = 10.71 + 9.07 \cdot 10^{-4} T$. For temperatures $T > 470$ K, the experimental ε(*T*) curves deviates from a linear dependence. This deviation is typical of most materials and is possibly connected with electrical conductivity processes [6].

In case of $CdWO_4$ crystal, the ε(*T*) dependence is linear in the range 290–550 K (Fig. 3e). For $CdWO_4$ at room temperature, ε = 17. These values agree with the given data for $CdWO_4$ in [10] (ε = 14). A slight linear increase take place according to the relationship $\varepsilon = 11.20 + 6.50 \cdot 10^{-3}$ T.

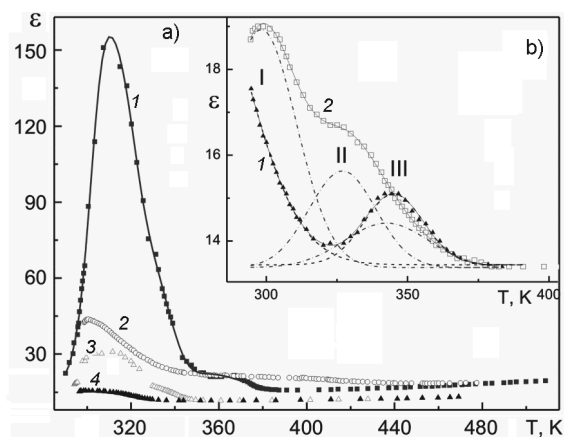At the heating and cooling the ε(*T*) curves hysteresis practically is not ob-

Fig. 4. Temperature dependences of permittivity (a) of (*1*) an initially polarized $PbWO_4$ crystal (T_p = 300 K, t_p = 10 min) and (*2*) the same sample during subsequent heating (T_p = 500 K, t_p = 5 min). (*3*, *4*) Measurements for a non-polarized sample during two successive heating cycles, respectively. In the inset (b) presented the experimental curves of ε(*T*) measured at first heating (*1*), after several heating-cooling cycles and relaxation of investigated sample at the room conditions (*2*). A dashed and dash-dotted line shows elementary components I–III of curves *1* and *2* respectively, solid lines are the sum of deconvolution components.

served. The previous polarization of $CdWO_4$ crystal does not make changes in the ε(*T*) dependence.

In Fig. 4(a–b) are shown the external electric field *E*, temperatures T_P, and thermal treatment influence on the ε(*T*) curves for the $PbWO_4$ crystal, respectively. The results of investigations of the effect of an external dc electric field on the ε(*T*) dependence in $PbWO_4$ are shown in Fig. 4 (curves *1*, *2*). For comparison, Fig. 4 also shows data for a non-polarized sample (curves *3*, *4*). As the field was switched off at 290 K, fast relaxation processes were observed corresponding to ε decreasing in time. The ε(*T*) function was measured after the end of the fast relaxation. The experiments show that, in the range 290–430 K, several maxima are observed in the ε(*T*) curve in the case of polarized samples. The maxima near 320 K form a dominant, rather narrow peak. During the first measurement in the heating mode, this peak was found to be a few times higher than the corresponding peak in the case of a non-polarized sample. The intensities of peak decrease after several heating-cooling cycles and free relaxation of the sam-
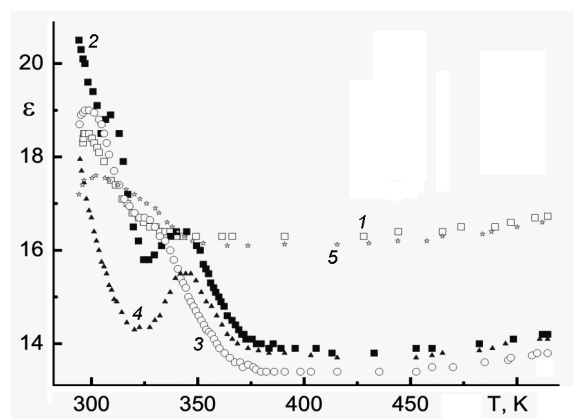
Fig. 5. Experimental function $\varepsilon(T)$ in dependence on thermal prehistory of PbWO$_4$ crystals. Curve (*1*) correspond to the $\varepsilon(T)$ obtained at first measurement; (*2*) — after 24 h; (*3*) — 48 h; (*4*) — 72 h; (*5*) — 96 h.

Fig. 6. Time evolution of ε values measured at different selected temperatures: *1* – 302, *2* – *310*, *3* – 320, *4* — 345, *5* — 400, *6* — 500 K.

ple under room conditions over 4–5 days. A sample polarized at $T_P = 300$ K and not heated retains high values of $\varepsilon = 150$–200 at room temperature for a long time.

For nonpolarized samples at $T \geq 420$ K, ε slowly increases with T. The polarization of a sample results in a faster increase in ε in the range 400–550 K as compared to that for a nonpolarized sample. After one or two cycles of heating to $T > 400$ K and subsequent cooling to room temperature, a nonpolarized sample returns by two-stage way [3] to the quasi-equilibrium state with the initial value of ε.

The $\varepsilon(T)$ spectrum changes caused irreversible transformation in PbWO$_4$ crystal during high-temperature heating shown in Fig. 4b. Curve *1* was taken for the original sample with initial concentration ratio of electrically active defects, previous models are considered in [3]. Under heating to a temperature $T > 500$ K, this ratio changes by reducing of possible associate numbers of defects and charge redistribution between different sorts of interacting capture centers. Curve *2* (Fig. 4b) shows the dependence $\varepsilon(T)$ function for a sample subjected to such heating. In the subsequent cycles of heating the intensity components (see Fig. 4b, curve *1*) decrease. The component II in this case is not observed, and the third component remains nearly unchanged. Only the components I and III are obtained by deconvoluting of the curve *2* (Fig. 4b). Reducing of the curve *2* in Fig. 4b is due to long-term relaxation processes (retention interval over 24 h under room conditions).

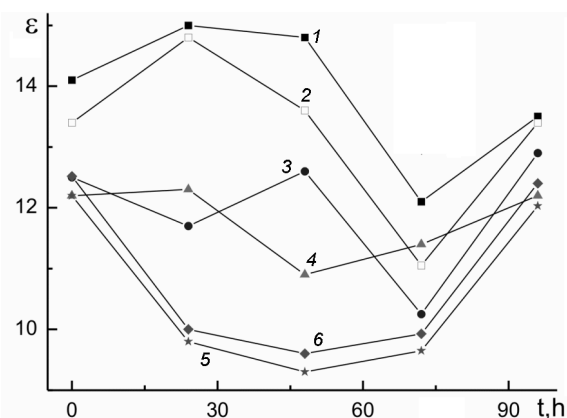Time evolution of the $\varepsilon(T)$ function and the values of ε for PbWO$_4$ at different

stated temperatures are shown in Fig. 5 and Fig. 6, respectively. Curves *1–5* (Fig. 5) are taken under the same conditions at regular intervals (24 h) of free sample relaxation at room temperature. The experiments testify about non-equilibrium of the sample and show that the ratios of the concentrations of certain types of electrically active defects are changed under room conditions due to interactions and quasi-chemical transformations of a complex dipole defects. In these conditions, the temperature difference of $\varepsilon(T)$ curves progress is observed. Time change in the sample show (Fig. 6) quasi-periodicity of ε values. This is illustrated by curves $\varepsilon(T)$ for selected T below 400 K.

The obtained experimental data testify about sharp distinctions in electrical characteristics of the AWO$_4$ crystals and their behaviour with change of temperature, thermal prehistory, and other experimental conditions. In principle, these distinctions are connected with structural features of investigate crystals (see Fig. 1). The PbWO$_4$ crystal having the cleavage plane (001) cleave easily along (101) and (112) planes under crack propagation [11]. The CdWO$_4$ crystal has the perfect cleavage face (010) [12]. The presence of indicated planes are causes the determination/limitation of the displacement ways of vacancy defects and capture the latter by edge dislocations or other structural linear defects. In the tungstate crystals grown by the Czochralski method, dislocations are present in a large number. So, in AWO$_4$ crystals the dislocation density is about 10^3–10^6 cm^{-2} [13, 14].

Edge dislocations are charged, as known from the paper [15]. The migration of the dislocations at elevated temperatures and

external applied *dc* field (as shown in Fig. 1) is not excluded.

Interaction the latter with vacancies form the irregular distribution of charge in the crystal, local deformation instability, and results in changes dependences of ε values and other characteristics of sample induced by temperature and time. In conditions of such processes, the characteristic relaxation times of the sample will also change and establishing of thermodynamic equilibrium can be quasi-periodical character. At repeated heating-cooling cycles, the processes will evolve towards the formation of micro-pores until the cracks in the crystal. The latter was observed in our $PbWO_4$ measuring as a result of multiple thermal cycles. In $CdWO_4$ crystal at the experiment conditions, the relaxation processes are poorly expressed or not observed.

Another additional mechanism of $\varepsilon(T)$ function change can be due to a dipole moment modification of defect complexes in the process of thermal evolution [3]. Here, the determinant factor of change in the sample is non-stoichiometry, its role in cracking tungstate crystals was studied in [16].

4. Conclusions

In the AWO_4 crystals are observed short- and long-term relaxation processes that can monitored by measurement of electrical characteristics. The scheelite structure type of $PbWO_4$ in comparison with the wolframite structure type is "more advantageous" to lability of electrical active defects. In the $PbWO_4$ crystal at measurement temperatures up to 400 K are experimentally detected quasi-periodical change of ε values and the thermo-dielectrical effect in the pre-excited sample by electric field at elevated temperatures.

References

1. M.Nikl, V.V.Laguta, A.Vedda, *Phys.Stat. Sol.(b)*, **245**, 1701 (2008).
2. V.B.Mikhailik, H.Kraus, *Phys.Stat.Sol.(b)*, **247**, 1583 (2010).
3. V.N.Shevchuk, I.V.Kayun, *Phys.Solid State*, **47**, 632 (2005).
4. V.N.Shevchuk, I.V.Kayun, *Radiat.Meas.*, **42**, 846 (2007).
5. V.N.Shevchuk, I.V.Kayun, *Acta Phys.Polonica A*, **117**, 150 (2010).
6. V.N.Shevchuk, I.V.Kayun, *Phys.Solid State*, **45**, 1898 (2003).
7. V.N.Shevchuk, I.V.Kayun, *Functional Materials*, **10**, 229 (2003).
8. H.Huang, W.Li, X.Feng, P.Wang, *Phys.Stat. Sol.(a)*, **187**, 563 (2001).
9. H.Huang, X.Feng, T.B.Tang et al., *Phys.Stat. Sol.(a)*, **196**, R7 (2003).
10. M.V.Mokhosoev, Zh.G.Bazarova, Complex Oxides of Molybdenum and Tungstate with I–IV Group Elements, Nauka, Moscow (1990) [in Russian].
11. I.P.Babiychuk, V.N.Baumer, V.G.Bondar et al., *Functional Materials*, **10**, 224 (2003).
12. L.N.Dem'yanets, V.V.Ilyukhin, A.V.Chichagov, N.V.Belov, *Inorgan.Mater.*, **3**, 1938 (1967).
13. S.Ganesamoorthy, I.Bhaumik, A.K.Karnal, V.K.Wadhawan, *J.Cryst.Growth*, **264**, 320 (2004).
14. B.P.Nasarenko, V.N.Baumer, E.F.Dolzhenkova, M.B.Kosmyna, *Inorgan.Mater.*, **41**, 1114 (2005).
15. N.A.Tyapunina, E.P.Belozerov, *Uspekhi Fizicheskich Nauk*, **156**, 683 (1988).
16. Sangeeta S.C. Sabharwal, *J.Cryst. Growth*, **310**, 2899 (2008).

Термічна передісторія та електричні властивості кристалів вольфраматів

В.Н.Шевчук, І.В.Каюн

Експериментально досліджено температурно-часові зміни електричних та діелектричних параметрів монокристалів AWO_4 (A = Ca, Cd або Pb). Діелектричні властивості, виміряні вздовж напрямку [001] у монокристалі $PbWO_4$ (структура типу шеєліту), показали деяку квазі-періодичність з часовою циклічністю близько 20 год. вільної релаксації. Зв'язок цього явища періодичності та термодіелектричного ефекту пропонується пов'язувати з динамікою структурних та точкових дефектів і їх взаємодією та створенням/перебудовою комплексів дефектів (протягом релаксаційного процесу). Головна роль у таких явищах відводиться вакансіям кисню та свинцю. У $CdWO_4$ (структура типу вольфраміту) перпендикулярно до площини сколу (010) при температурах до 500 К термодіелектричний ефект не спостерігається.