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Electric Conductivity of Nd:KGd$(WO_4)_2$ Crystals at Direct and Alternating Current

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Measurements of the electric conductivity at direct and alternating current and the thermally stimulated depolarization current (TSDC) have been carried out for Nd doped KGd$(WO_4)_2$ crystal in the range of 250 ÷ 400 K. Small maximum-like anomaly of TSDC spectrum at 330 K characterizing by the activation energy 1,68 eV can be associated with the structural defects associated with doped Nd^{3+} ions. Reversible character of the small anomaly on the temperature dependence of dielectric permittivity $\varepsilon(T)$ at 330 K shows also that the weak structure transformation takes place in the crystal.

Ключові слова: Nd:KGd$(WO_4)_2$ crystal; direct and alternating current conductivity; thermally stimulated depolarization current.

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I. Introduction

Among the laser crystals pumping by laser diodes, neodymium-doped potassium gadolinium tungstate (Nd:KGd$(WO_4)_2$ or Nd:KGW) [1-3] is known as effective laser medium. At low pumping energy (0.5 ÷ 1 J), the efficiency of Nd:KGW lasers is 3-5 times higher than the yttrium-aluminum garnets (YAG) laser. The 1067 nm Nd:KGW laser radiation is polarized, that is important for further polarization-sensitive nonlinear conversions, for instance second harmonic generation [4]. KGW single crystals can also be used for fabrication of high-efficiency lasers with high output energy. Besides, KGW host has a high nonlinear susceptibility of the third order [5].

KGW single crystals belong to the monoclinic point group of symmetry 2/m at room temperature. Its unit-cell parameters for C2/c space group are the following: a = 10.652 (4), b = 10.374 (6), c = 7.582 (2) Å, β = 130.80 (2)°, Z = 4 [6]. An influence of Nd-doping on the cell parameters of KGW structure was observed. Due to the similar characteristic of Gd^{3+} and Nd^{3+} ions, the doped Nd^{3+} ions are placed in the position of Gd^{3+} in KGd$(WO_4)_2$ crystal. The changes in parameters follow the changes in lanthanide ionic radii: $r(Gd^{3+}) = 93.8$ pm, $r(Nd^{3+}) = 99.5$ pm.

KGW crystal is characterized by the high density 7.27 g/cm^3, wide transmission spectral range 350 ÷ 5500 nm, and relatively high refractive indices $n_g = 2.033$, $n_m = 1.986$, $n_p = 1.937$ for the wavelength $\lambda = 1067$ nm. The values of refractive indices of Nd:KGW crystals differ from the similar magnitudes of KGW no more than 1 ÷ 2% probably due to the close electron-and-optical characteristics of Gd^{3+} and Nd^{3+} ions.

The aim of present investigation was to study the temperature and frequency dependencies of direct and alternating conductivity and depolarization current in Nd:KGW crystals in the temperature range of 250 ÷ 400 K. The results of such investigations can be useful for better understanding of microscopic electric processes in Nd:KGW samples and for the optimization of exploration regimes of this laser material.

II. Experimental

The samples of Nd:KGW studied (4 ÷ 5% of substituted Gd^{3+} by Nd^{3+} ions) were prepared in the form of plane parallel plate of 2 mm thickness. Two opposite planes of the plate were covered by silver electrodes of the square 1.5 cm^2. The direction of polarizing electric field and thermally stimulated depolarization current (TSDC) coincided with N_g principal axis of optical indicatrix for the wavelength $\lambda = 632.8$ nm [7].

The precision LCR-meter HP 4284A was used for the alternating current measurements. The results discussed below were obtained in the frequency range of 0.02 ÷ 1000 kHz for the measuring field of 3 V/cm.

To measure TSDC the sample of Nd:KGW was heated at first to the temperature 400 K. Then, the direct current electric field of 5 kV/cm was applied to the sample to polarize its during 15 minutes. Immediately

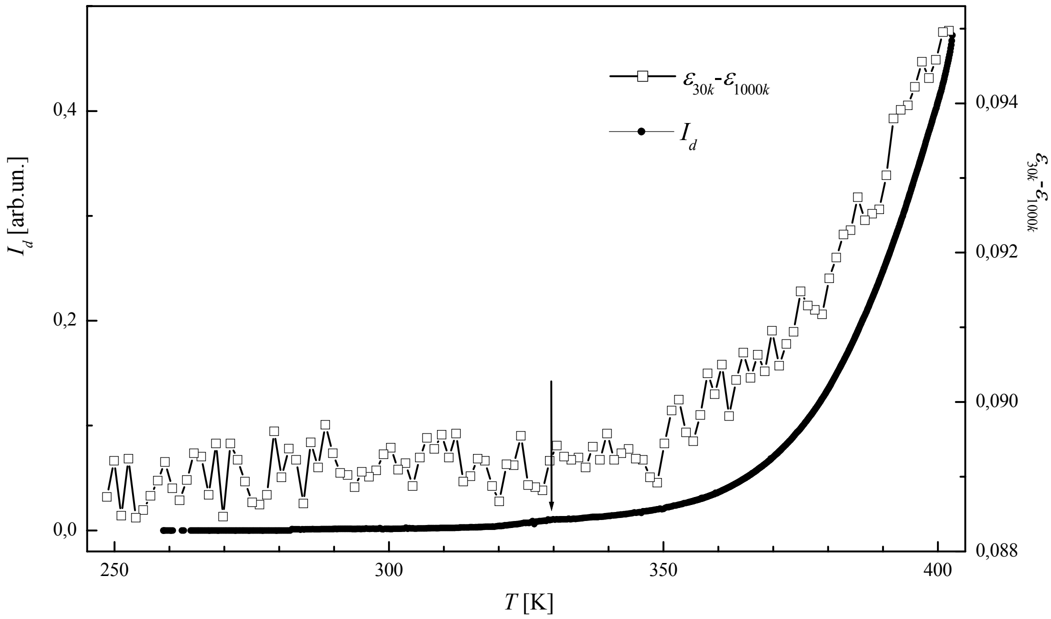

Fig. 1. Temperature dependencies of the depolarizing current I_d in TSDC experiment and the difference of dielectric permittivities ε_{30}-ε_{1000} of $Nd:KGd(WO_4)_2$ crystal for the frequencies 30 and 1000 kHz of electric field along N_g-axis of optical indicatrix.

after that the sample was cooling down to the temperature 240 K by using the liquid nitrogen and the polarization was thus frozen in. The sample was then heated at the constant heating rate 5°K/min and the short-circuit depolarization current was recorded as a function of temperature by the picoammeter connected in series. At these conditions the maximum magnitude of depolarization current was $I_d \sim 10^{-9}$ A. The temperature in chamber was controlled with accuracy not worse than 5×10^{-3} K, and the temperature dependencies of the values measured were stored using personal computer.

The measurements of direct current conductivity of the crystal studied were also performed in similar experimental conditions at the electric field 0.6 kV/cm.

III. Results and discussion

The samples studied are characterized by the direct current specific conductivity $\sigma_1 = 3.39\cdot10^{-15}$ $Ohm^{-1}cm^{-1}$ at the temperature $T_1 = 250$ K and $\sigma_2 = 4.17\cdot10^{-12}$ $Ohm^{-1}cm^{-1}$ at $T_2 = 400$ K. On the basis of these data the activation energy $E_a^{(c)} = 0.41$ eV of the direct current conductivity was calculated using the known Arrhenius law

$$\sigma(T) = \sigma_0 \exp\left(-\frac{E_a^{(c)}}{kT}\right) , \quad E_a^{(c)} = \frac{k \ln\left(\dfrac{\sigma_1}{\sigma_2}\right)}{\dfrac{1}{T_1} - \dfrac{1}{T_2}} \qquad (1)$$

The origin of TDSC current in KGW crystals could be connected with greater ion radius for Nd^{3+} (99.5 pm) than that for Gd^{3+} (93.8 pm). The local distortions (defects) of crystal structure of $Nd:KGd(WO_4)_2$ near Nd^{3+} ions could take place. These distortions can be displayed in the arising of space electric charge redistribution, which could be sensitive to the change of temperature and, therefore, could be displayed in the measurements of temperature dependencies of depolarization current and dielectric properties.

Typical TDSC curve obtained for Nd:KGW crystal is shown in Fig. 1. On the background of monotonous temperature behavior of TDSC $I_d(T)$ the small anomaly at the temperature T = 330 K is seen. In first approximation the temperature dependence of the depolarization current $I_d(T)$ can be described by the relation (2) similar to the relation (1),

$$I_d(T) = I_{d0} \exp\left(-\frac{E_a^{(d)}}{kT}\right) , \qquad (2)$$

where $E_a^{(d)}$ is corresponding activation energy. On the basis of $I_d(T)$ data at the temperatures $T_1 = 250$ K and $T_2 = 400$ K the activation energy $E_a^{(d)} = 0.47 \pm 0.2$ eV was obtained using the relation similar to (1). This magnitude is close to the activation energy of the direct current conductivity $E_a^{(c)} = 0.41 \pm 0.2$ eV. Therefore, the mechanisms of these two temperature activation processes in the range of 250 ÷ 400 K seem to be the same.

The mentioned above anomaly of $I_d(T)$ at the temperature 330 K (Fig. 1.) is clearly seen on the analogous temperature dependence Y(X) in the semi-logarithm scale (Fig. 2). The latter temperature dependence in the range of 359÷400 K is approximated well by the linear dependence shown in Fig. 2 by the dashed line and corresponding equation. The magnitude of activation energy corresponding to this linear dependence is equal to $E_a^{(d)} = 0.75$ eV.

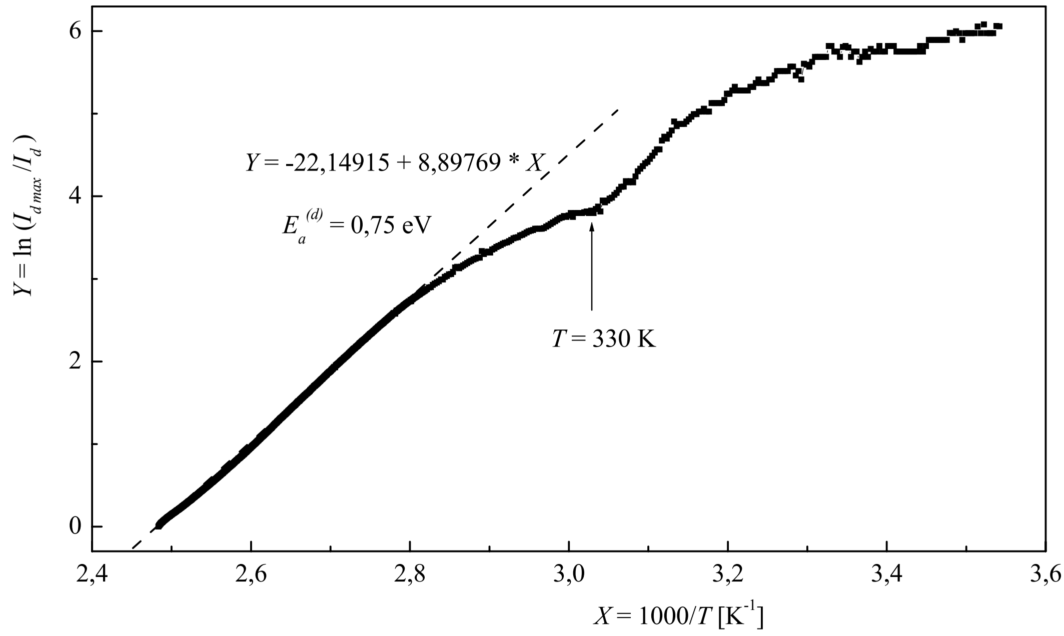

Fig. 2. Presentation of the temperature dependence of TSDC of Nd:KGW crystal in the scales convenient for determination of the corresponding activation energy $E_a^{(d)}$.

The mentioned above linear dependence Y(X) gives possibility to separate the dependence $I_d(T)$ into two parts,

$I_d(T) = I_{d1}(T) + I_{d2}(T)$, (3)

where the dependence $I_{d1}(T)$ corresponds to the mentioned above linear dependence Y(X). The dependence $I_{d2}(T)$ is the experimental dependence $I_d(T)$ from which the high temperature part $I_{d1}(T)$ is eliminated. Such separation gives possibility to analyze precisely the low temperature part $I_{d2}(T)$ of the dependence $I_d(T)$ and especially the corresponding its anomaly at 330°K.

The low temperature part of the dependence $I_{d2}(T)$ in the region of 320 K is characterized by the activation energy $E_a^{(d)} = 1.68 \pm 0.5$ eV (Fig. 3). The magnitude of I_{d2} at the temperature 330 K is five times greater than the corresponding background level; therefore it shows undoubtedly the regularity of this anomaly.

Investigations of the temperature dependence of direct current conductivity have not displayed any

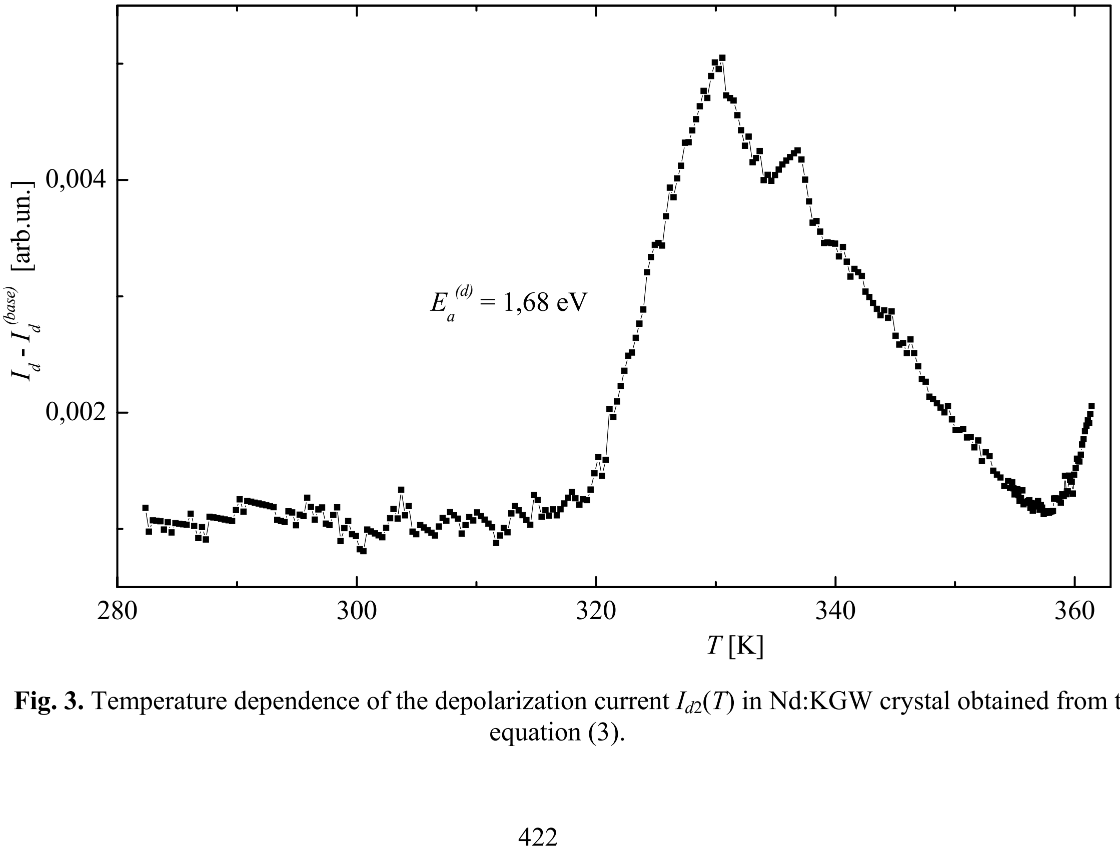

Fig. 3. Temperature dependence of the depolarization current $I_{d2}(T)$ in Nd:KGW crystal obtained from the equation (3).

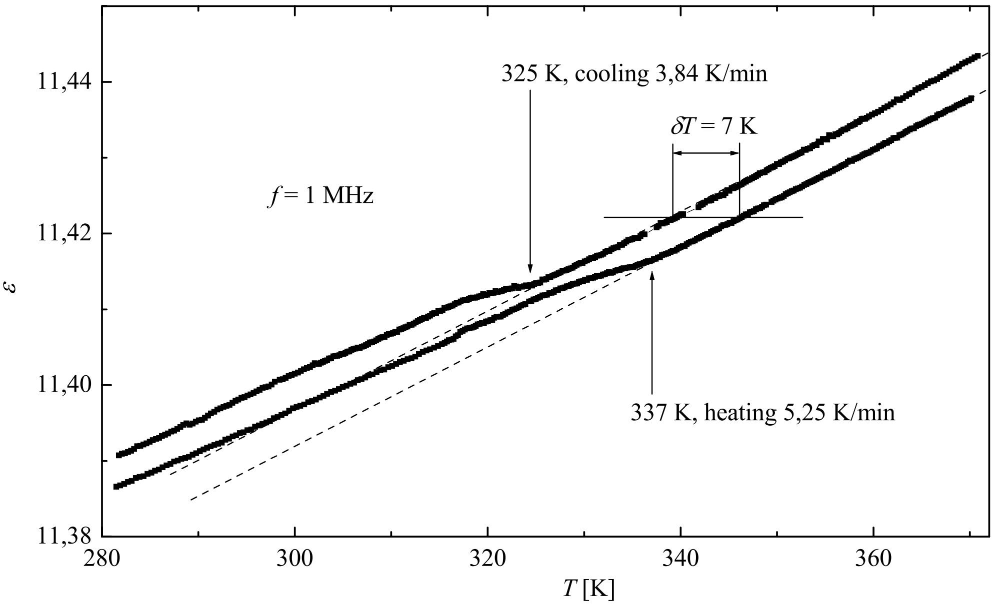

Fig. 4. Temperature dependencies of dielectric permittivity ε (T) of Nd:KGW crystal at cooling and heating run for the frequency 1 MHz of measuring electric field along Ng-axis of optical indicatrix. δT is the temperature shift caused by the instrumental time delay of indication of the sample's temperature.

anomaly at 330 K. This means the relatively small concentration of the depolarization centers which are associated most probably with doped Nd^{3+} ions in Nd:KGW crystal.

For getting more information on the nature of TSDC anomaly centered at 330 K the dielectric measurements with the alternative current have been conducted for Nd:KGW crystal. Clear anomaly is seen on the temperature dependencies of dielectric permittivity ε(T) (Fig. 4.). This anomaly looks like the change of physical value at ferroelectric or ferroelastic phase transition, which are not connected directly with proper order parameter [8]. Moreover the temperature hysteresis of the dependence ε(T) is seen (Fig. 4), ΔT_h = 337 K – 325 K - δT = 5 K, which is characteristic for phase transitions. In view of the small relative magnitudes of the anomaly of physical values at 330 K (Fig. 1, 4), the corresponding phase transformation can be associated most likely with the dopant Nd^{3+} ions than with the units of main matrix of Nd:KGd(WO$_4$)$_2$ crystal.

Additional information about the physical properties of Nd:KGd(WO$_4$)$_2$ crystal can be obtained from the

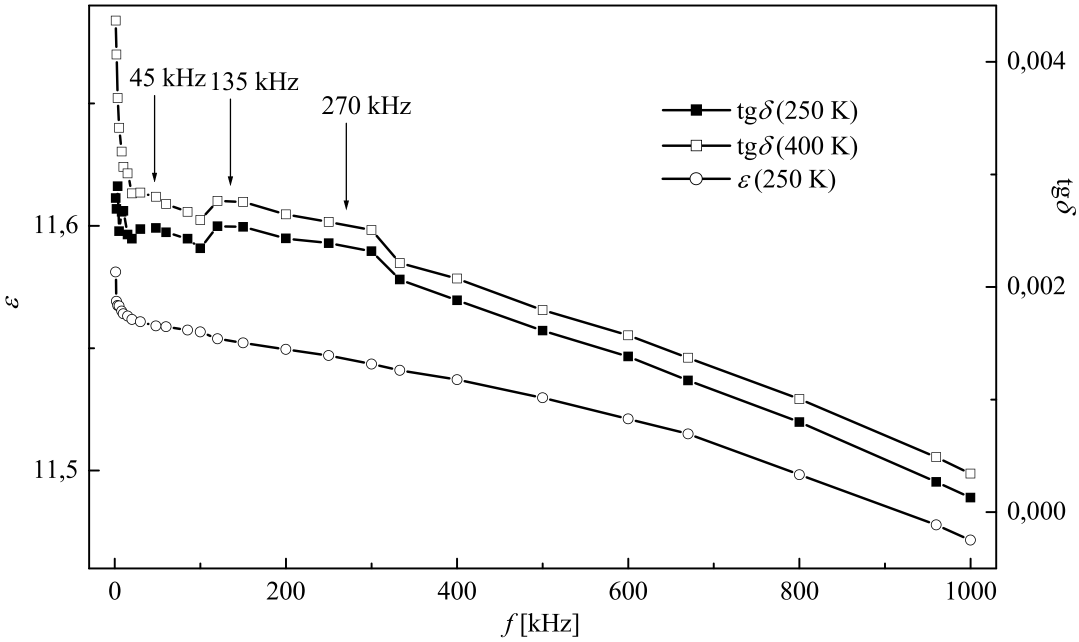

Fig. 5. Frequency dependencies of the dielectric permittivity *ε* at the temperature 250 K and dielectric losses tg*δ* at 250 and 400 K of Nd:KGW crystal for the electric field along N_g-axis of optical indicatrix.

frequency dependencies of dielectric properties (Fig. 5.). The observed quasi monotonous decrease of dielectric permittivity ε and dielectric losses tgδ in the wide range 1 ÷ 1000 kHz is expected as the typical character of frequency dependence of dielectric relaxation. The relative frequency changes of dielectric permittivity Δε/ε are considerably smaller than the corresponding changes of dielectric losses Δ(tgδ)/tgδ (Fig. 5.). Essential maxima of the dielectric losses tgδ are detected for the frequencies 45, 135 and 270 kHz, and the corresponding maxima of the dielectric permittivity ε are almost invisible. It is known that the greater dielectric losses take place in the defect crystals than in the perfect analogs. From the other side, these defects can not change essentially the general dielectric permittivity formed by the all units of crystal. So, the mentioned above maxima of the spectra of dielectric losses (Fig. 5.) are caused most probably by the dopant Nd^{3+} ions. One can take the above mentioned anomalies of the spectra of dielectric losses as the display of small piezoelectric resonances in the crystal, which probably become possible due to the weak distortions of the center symmetry matrix of KGW crystal caused by the dopant Nd^{3+} ions.

Temperature dependence of the additive part of dielectric permittivity (ε_{30}-ε_{1000}) from the frequency range 30 ÷ 1000 kHz is very similar to the analogous temperature dependence of the depolarization current I_d in the wide temperature range 250 ÷ 400 K (Fig. 1.). This peculiarity shows on the common temperature-and-structure origin of these dependencies.

Analysis of the temperature dependencies of the dielectric permittivity ε(T) and dielectric losses tgδ(T) for different frequencies of measuring field shows that the character of these dependencies is similar to the temperature dependencies shown in Fig. 1. The existence of two temperature ranges separated by the temperature 330 K, for which the dependencies of the values studied are somewhat different, is the characteristic feature of this similarity. This can be a result of the weak structural phase transition of the continuous type at 330 K in Nd:KGW crystal.

IV. Conclusions

1. Similar character of the temperature dependencies of TSDC current, direct current conductivity, dielectric permittivity and losses of Nd:KGW crystal in the range of 250 ÷ 400 K show on the common temperature-and-structure origin of these dependencies.
2. Maximum of TSDC spectrum at 330 K can be connected with structural defects associated probably with doped Nd^{3+} ions.
3. Reversible character of the anomaly of temperature dependence of dielectric permittivity ε(T) at 330 K testify for the regular structure transformation of the continuous type in Nd:KGW crystal.
4. Anomalies of the spectral dependencies of dielectric losses tgδ(f) of Nd:KGW crystal can be interpreted as the piezoelectric resonances caused by weak distortions of the center symmetry matrix of KGW due to the dopant Nd^{3+} ions.

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Б. Андрієвський, А. Патрин

Питома електропровідність кристала $Nd:KGd(WO_4)_2$ при постійному і змінному струмі

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Вимірювання питомої електропровідності при постійному та змінному струмі і термічно вимушеному струмі деполяризації (ТВДС) були виконані для кристалу Nd легованого $KGd(WO_4)_2$ в інтервалі 250 ÷ 400 K. Малий максимум подібний аномалії ТВДС спектру при 330 K характеризується енергією активації 1,68 еВ можливо зв'язана із структурними дефектами легованого Nd^{3+} іонами. Реверсивний характер малої аномалії температурної залежності діелектричної сталої $\varepsilon(T)$ при 330 K показує також, що відбувається слабке структурне перетворення в кристалі.