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OPTICAL CONSTANTS OF THE TGS SINGLE CRYSTAL IRRADIATED BY POWER PULSED ELECTRON BEAM

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The investigation of polarized infrared reflectivity spectra with electric vector $\mathbf{E} \parallel a \sin \beta$ axis and c axis directions in the region 100–2000 cm^{-1} of the triglycine sulphate $(NH_2CH_2COOH)_3 \cdot H_2SO_4$ (TGS) single crystal plate irradiated by a high-current pulsed electron beam with different doses at room temperature is presented in this paper. The parameters of electron beam produced by accelerator facility as a source were: energy $E = 250$ keV, current density $I = 1000$ A/cm^2, pulse duration $\tau = 300$ ns. The real $\varepsilon'(\nu)$ and imaginary $\varepsilon''(\nu)$ parts of permittivity as well as oscillators strength value were obtained by using the Kramers–Kronig dispersive relations. The possible mechanisms of pulsed electron irradiation effect in TGS are discussed.

Приводятся результаты исследования инфракрасных спектров отражения плоскопараллельной пластины кристалла триглицинсульфата $(NH_2CH_2COOH)_3 \cdot H_2SO_4$ (ТГС) в области 100–2000 см$^{-1}$ в поляризованном свете с электрическим вектором падающей световой волны $\mathbf{E}$, параллельным $a \sin \beta$- и c-осям, облученной сильноточным импульсным электронным пучком различными дозами при комнатной температуре. Параметры пучка: энергия $E = 250$ кэВ, плотность тока $I = 1000$ А/см^2, длительность импульса $\tau = 300$ нс. На основе дисперсионных соотношений Крамерса–Кронига получены зависимости реальной $\varepsilon'(\nu)$ и мнимой $\varepsilon''(\nu)$ частей диэлектрической проницаемости от частоты, а также изменение сил соответствующих осцилляторов. На основе полученных данных сделаны некоторые предположения о механизме воздействия сильноточного импульсного электронного облучения на ТГС.

INTRODUCTION

Triglycine sulfate $(NH_2CH_2COOH)_3 \cdot H_2SO_4$ (TGS) and its isomorphic form is an important group of room temperature ferroelectrics. Single crystals of TGS are considered to be the most suitable materials for developing detectors of infrared radiation, environmental analysis monitors, earth observation cameras, astronomical telescopes, military systems and target faces vidicons based on the pyroelectric effect [1, 2]. TGS crystallizes in the monoclinic system, and has a phase transition at about $49\,°C$. Above this temperature, it belongs to the centrosymmetrical point group 2/m. Below the transition point it is ferroelectric and belongs to the point group 2 of monoclinic system [3]. The spontaneous polarization takes place along the monoclinic b axis, the crystal is nonpiezoelectric in paraelectric state. Ferroelectric properties of TGS crystals have been found to change strongly under the action of different kinds of irradiation [4–6] as well as of admixtures [7, 8]. The introduction of defects by irradiation and the admixture of ions provides the essential means of modifying the structure [9, 10].

Radiation defects damage the glycine molecules and produce stable, free radicals [11]. For example, irradiation of TGS crystals with γ-rays decreases the value of the dielectric constant, greatly affects the shape of the hysteresis loop [9, 11], and shifts it with doses, the critical point becomes diffuse, and all delayed processes occurring on polarization reversal become slower, increasing the value of the coercive field [12]. The degradation of TGS crystals, grown from irradiated seeds, was the subject of different studies [14]. Above-considered radiation effects [4–12] are attributed by many authors to an appearance of the internal field in γ- and X-rays irradiated TGS crystals [15], which leads to the pinning of domain walls [16]. This model assumption seems to be more appropriate, since it explains the hindering of the motion of domain walls with the irradiation dose or with defects. Similar results are obtained by the introduction of paramagnetic admixtures into TGS [17, 18].

Therefore, studies dealing with the influence of irradiation as well as of doping TGS crystal on their physical properties are of particular interest. In recent years, the interest in studying pure, irradiated and doped TGS crystals has increased because of their promise in various devices. However, we are unaware of any works that deal with the investigations of the physical properties of TGS under the action of high-current pulsed electron beam. Information obtained from such investigation is not only of great interest to fundamental researches but also of a subject of interest for applied studies.

The aim of this work is to study the effect of pulsed electron beam irradiation on optical properties of TGS single crystal. One of the most effective and informative methods to investigate the nature of the pulsed electron beam interaction with a sample is IR spectroscopic study. This method allows us to obtain not only the most completed information about the lattice transformation, but also lattice dynamics in polar nanoregions.

1. EXPERIMENTAL PROCEDURE

The single crystals of triglycine sulfate $(NH_2CH_2COOH)_3 \cdot H_2SO_4$ (TGS) were produced by solution growth from powder using constant temperature evaporation method. Good optical quality crystals were obtained. TGS samples for the IR spectroscopy investigations were cleaved perpendicular to the polar b axis (two-fold screw axis) from clear regions far from the seeding area, polished to a 0.3 mm thickness and then etched. IR reflectivity measurements in the spectral range 100–2000 cm^{-1} were made using Bruker IFS66v Fourier transform-spectrometer operating at a resolution of 1 cm^{-1} at room temperature. The parameters of electron beam produced by accelerator facility as a source were: energy $E = 250$ keV, current density $I = 1000$ A/cm^2, pulse duration $\tau = 300$ ns.

2. EXPERIMENTAL RESULTS AND THEIR ANALYSIS

The polarized infrared reflectivity spectra of TGS single crystal plate with the electric vector $\mathbf{E} \parallel a \sin \beta$ axis (Fig. 1) and c axis (Fig. 2) directions, respectively, perpendicular to the ferroelectric b axis at the room temperature were obtained in the region 100–2000 cm^{-1} for unirradiated and irradiated by 10, 70 and 150 pulses TGS single crystal. Our IR reflectivity spectra for TGS single crystal agree fairly well with those obtained in Refs. [13, 14]. The
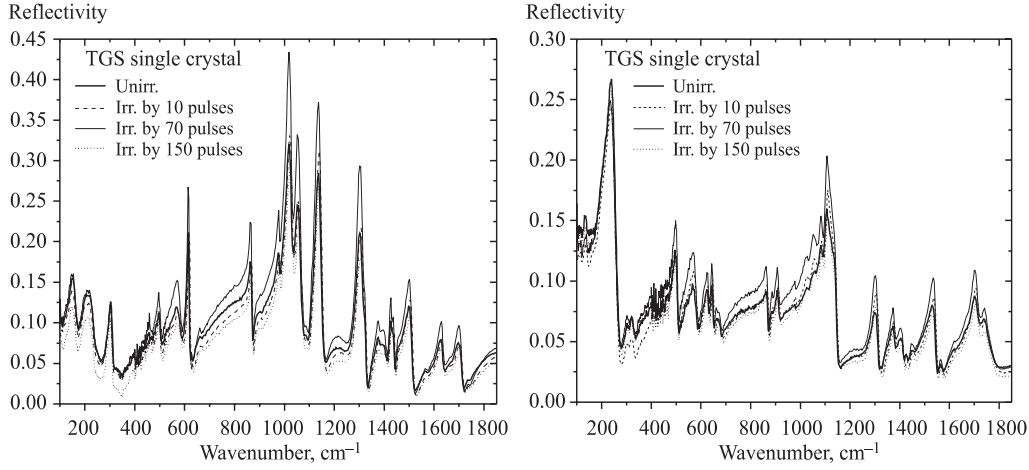
Fig. 1. IR reflectivity spectra $\mathbf{E} \parallel a \sin \beta$ axes before and after irradiation with different doses of the TGS crystal at room temperature

Fig. 2. The same as in Fig. 1, but for $\mathbf{E} \parallel c$ axes

reflectivity spectra were fitted with the well-known formula [15]

$$R(\omega) = \left| \frac{\sqrt{\varepsilon^*(\nu)} - 1}{\sqrt{\varepsilon^*(\nu)} + 1} \right|^2,$$

where $\varepsilon^*(\omega)$ denotes complex dielectric permittivity, which is equal to

$$\varepsilon^*(\omega) = \operatorname{Re} \varepsilon(\nu) + \operatorname{Im} \varepsilon(\nu).$$

To determine the real and imaginary dielectric permittivity, the Kramers–Kronig dispersive relations have been used. In case of lattice reflection the maxima in $\nu \operatorname{Im}(-\varepsilon^{-1}) = f'(\nu)$ and $\nu \operatorname{Im}(\varepsilon) = f''(\nu)$ dependence corresponds to the longitudinal (LO) and transverse (TO) phonon modes, respectively, and $\Delta\varepsilon = \nu_{\mathrm{LO}j} - \nu_{\mathrm{TO}j}$ belongs to the oscillators strength. The resulting $f''(\nu)$ spectra with $\mathbf{E} \parallel a \sin \beta$ axis (Fig. 3) and $\mathbf{E} \parallel c$ axis (Fig. 4) as well as oscillators strength $\Delta\varepsilon$ demonstrate the calculated dependencies from IR reflectivity spectra for the unirradiated and irradiated by different doses TGS crystal, respectively. The fitted mode parameters for the same sample are listed in table. The assignment of «normal» mode spectrum in TGS crystal has been achieved from [19, 20]. On the base of Fig. 3 and table, one can get that the frequency 575 cm^{-1} related with deformational vibrations of N–C–C skeleton of the glycine molecule [20] as well as the SO$_4^{2-}$ ion bands in the range of 500–700 cm^{-1} on the whole is slightly shifted towards the higher wavelength region about 5–10 см$^{-1}$ as the dose increases up to 70 pulses, whereas irradiation of TGS by 150 pulses gives rise to the partial restoration of the phonon mode value, in comparison with unirradiated one. Moreover, it is interesting to note that the increase of oscillators strength with dose up to 70 pulses takes place (see Table). The significant change of intensity of above-mentioned

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Fig. 3. Imaginary part of dielectric permittivity $\mathbf{E} \parallel a \sin \beta$ axes before and after irradiation of the TGS crystal obtained from the fit of IR reflectivity

Fig. 4. The same as in Fig. 3, but for $\mathbf{E} \parallel c$ axes

Mode parameters obtained from the fit of reflectivity spectra with $\mathbf{E} \parallel a \sin \beta$ axes and c axes using Kramers–Kronig dispersive expressions of unirradiated (Unirr.) and irradiated (Irr.) by 10, 70 and 150 pulses TGS single crystals. All mode parameters are expressed in cm^{-1}. The error of IR spectroscopy experiments corresponds to $\pm 1 \ \mathrm{cm}^{-1}$

$\mathbf{E} \parallel a \sin \beta$ axes								$\mathbf{E} \parallel c$ axes							
Unirr.	$\Delta\varepsilon$	10	$\Delta\varepsilon$	70	$\Delta\varepsilon$	150	$\Delta\varepsilon$	Unirr.	$\Delta\varepsilon$	10	$\Delta\varepsilon$	70	$\Delta\varepsilon$	150	$\Delta\varepsilon$
143	23	143	23	143	23	143	23	238	42	236	42	234	42	237	42
200	50	200	50	200	50	200	50	302	57	302	57	302	57	302	57
300	45	299	44	302	44	298	44	567	60	569	60	569	60	567	60
499	19	499	20	500	22	499	20	623	82	623	82	624	82	623	82
575	**25**	**577**	**27**	**585**	**31**	**578**	24	863	7	864	8	862	10	862	9
615	**34**	**618**	**36**	**624**	**39**	**617**	35	907	12	908	14	907	15	908	13
866	9	868	10	872	12	866	10	1082	9	1085	10	1083	10	1084	10
975	5	980	7	987	8	980	5	1105	42	1107	43	1106	43	1107	43
1011	17	1017	19	1024	20	1015	16	1299	24	1302	24	1300	24	1302	24
1047	27	1050	30	1058	29	1051	27	1370	17	1373	14	1371	15	1372	16
1125	**28**	**1130**	**33**	**1137**	**35**	**1131**	**30**	1402	24	1403	23	1402	24	1403	23
1296	32	1301	33	1306	34	1300	33	1530	24	1535	23	1535	23	1534	22
1427	19	1430	19	1430	23	1429	19	1703	22	1704	23	1702	24	1704	23
1492	29	1496	30	1501	32	1495	28	1740	28	1741	29	1742	29	1741	28
1627	30	1632	29	1639	31	1632	29								
1697	25	1701	27	1708	29	1702	24								

mode can be obviously related to an essential increase of «hardness» of the SO_4^{2-} ion and, as a consequence, leads to the increase of action between sulfate ion and both glycine and glyciniy molecules [21]. The increase of asymmetrical $\nu_3(F_2) = 1125$ cm^{-1} frequency (about 12 cm^{-1} value [22] with the dose (Fig. 3), related with the weak «stiffness» of the SO_4^{2-} group, has been observed. Besides, the shift of latter frequency to the «high» was found E. K. Galanov and his coauthors to be proportional to square of the spontaneous polarization value. It should be noted that behavior above considered vibrations as well as its intensity is sensitive to the phase transition $P \leftrightarrow F$ [23]. It is interesting to note that in case $\mathbf{E} \parallel c$ axis (Fig. 4) no essential changes of phonon modes value occurs, whereas intensity and the corresponding oscillators strength in mid-IR range increases. As is seen from Figs. 3, 4, the intensity of the external glycine molecules vibrations, lattice one, and the oscillators strength locating in far-IR range under the action of high-current pulsed electron beam with $\mathbf{E} \parallel a \sin \beta$ axis and $\mathbf{E} \parallel c$ axis has no essential change.

3. DISCUSSION

We have observed essential changes in intensity, shifts of phonon modes, as well as change of oscillators strength in IR reflectance spectra of TGS after irradiation by power-pulsed electron beam. In literature there is a lack of data on high-current pulsed electron irradiation of ferroelectrics [23]. However, there are many articles devoted to different kinds of investigations of ferroelectrics by using stationary irradiation sources [24, 25]. They do not show similar results as obtained by using the high-current pulsed electron beam. Summarizing the results mentioned above: it is possible to suppose that this effect of pulsed electron action relates in value to the power density $W \approx 2.5 \cdot 10^8$ W/cm^2 per pulse of high-current pulsed electron beam which is much more intensive then stationary electron irradiation. In addition, the transfer of energy $E_e = 250$ keV per pulse with duration $\tau = 300$ ns leads to powerful adiabatic heating (see below) within penetration depth of pulsed electrons beam in the sample. Taking into account the value of current density $I_e = 1000$ A/cm^2, duration of pulses $\tau = 300$ ns the density of electrons is equal to about $F_e \approx 5 \cdot 10^{15}$ electrons/cm^2 per pulse. It has been calculated by us, that the penetration depth of the pulsed electrons with beam energy $E = 250$ keV and density of TGS crystal $\rho \approx 1,66$ g/cm^3 is equal to $R_e \approx 400$ μm. It should be noted that value of temperature within the penetration depth of the pulsed electrons in the sample could be calculated by the equation

$$T = \frac{2W}{RCS\rho},$$

where S is the square of irradiated surface; C and ρ are the heat capacity and density of sample, respectively.

Taking into consideration the heat capacity value $C \approx 1.53$ J/g $\cdot$ K at room temperature and the square of irradiated surface $S \approx 4$ cm^2, the temperature value (1) within the affected zone (AZ) corresponds to about $100\,^\circ$C per pulse that is some less than the melting temperature magnitude for TGS crystal $T_f \approx 130\,^\circ$C. Thus, we may conclude that an action of high-current electron pulsed beam on TGS may lead to significant structural transformations of material and variation of the properties in AZ, such as surface hardening due to fast heating up to temperature approximately equal to the melting one, and appearance of damage under

the action of a stress wave (shock wave). In our case, the former mechanism is obviously prevailing for TGS irradiated by 10, 40 and 70 pulses. It is characterized by spatial quasi-repetitive hardening of crystal as well as redistribution of lattice ions and formation of more ordered structure obviously associated with the annealing of point (10^{18} $1/cm^3$) defects within the heat action range. The latter assumptions correlate well with the obtained above shift of the bands (Fig. 3) in the mid-IR range towards the high wavenumber region, an increase of intensity value of SO_4^{2-} groups as well as the growth of oscillators strength with dose. The rise of intensities of these modes can be related to certain hardness increase of sulfate ion which leads to the growth of the deformation action of sulfate groups on the glycine II, glyciniy III and on the glyciniy I ions especially. The latter mechanism is prevailing for TGS irradiated by 150 pulses. It could be related to the damage (appearance of free and stable radicals) of hardened TGS structure caused by very fast heating (10^{10} K/s) which leads obviously to an appearance of stress and deformation waves (shock wave) within depth penetration of pulsed electrons. These assumptions are supported by the shift of bands in mid-IR range towards the lower wavenumber region and the decrease of this intensity values as well as of the oscillators strength magnitudes caused obviously by essential intrinsic irradiation-induced bias fields in TGS crystal.

In order to reveal the nature of the high-current electron pulse radiation on TGS and other ferroelectrics in details, the studies, including X-ray and neutron diffraction experiments as well as UV-visible, IR, Raman, EPR spectroscopy and extended investigation of dielectric properties, are in progress.

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