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Effect of Doping and Irradiation on Optical Parameters of Triglycine Sulphate Single Crystals

Crystals of triglycine sulphate (TGS) doped with orthonitroaniline (ONA) irradiated with different doses of γ -radiation were used to investigate γ -radiation effect on electrical and optical parameters. The absorption coefficient and the reflectance were measured and hence the extinction coefficient, the optical refractive index and the dielectric constants (ϵ_1' , ϵ_1'') of unirradiated and irradiated TGS crystals were calculated. Values of the allowed indirect optical energy gap E_g^{opt} of TGS doped with ONA were calculated as a function of γ -dose. Value of E_g^{opt} decreases from 4.72 eV to 4.25 eV with increasing γ -doses from 0 up to 3 Mrad. The values of the static dielectric constant $\epsilon_s(0)$ and the effective electrical conductivity σ_0 at room temperature and their dependence on γ -dose were also calculated.

Keywords: ferroelectrics, radiation effects in solids, optical properties

Introduction

Physical parameters of solids were proved to be affected by γ -rays irradiation [DIENES and VINEYARD]. Valuable information about electronic changes taking place in ionic crystals subjected to γ -rays have been gathered [SCHULMAN and COMPTON and FOWLER]. Optical properties, such as absorption and transmission, are useful tools to study the structural bonding between neighbouring atoms in crystalline solids.

Triglycine sulphate (TGS) crystals have been the subject of intensive investigations as a material having superior optical memory [GALUSTIAN] and utilizing pyroelectric effects in camera tubes and because of the observed increase in their infrared parameters after doping with organic molecules [KRAJEWSKI and BREZIEWSKI].

Some physical properties, such as spontaneous polarization, dielectric, pyroelectric, piezoelectric and elastic properties of pure TGS crystals as well as for crystals admixed with metallic ions or organic molecules, were studied by Eisner, Tylczynski, Batra and Mathur and Gaffar [GAFFAR et al. 1988, 1989].

Single crystals of triglycine sulphate grown in the presence of ONA were found to be discriminated by an internal bias which is responsible for changes in ferroelectric behavior in the region of the phase transition. The internal bias has an effect on the Curie constant and the maximum value of the dielectric constant in a way similar to that produced by an external electric bias field [GAFFAR et al. 1989]. However, at low concentration the dopant effect was not enough to create the sufficient bias to alter the whole crystal into a single domain one. Optical properties of TGS crystals doped with ONA have not yet been studied. However, it is known that irradiation of TGS crystals with γ -rays decreases the value of the dielectric constant, greatly affect the shape of the hysteresis loop [ALEMANY et al.], the value of spontaneous polarization and d.c. electrical conductivity [HILCZER and MICHALCZYK; AMIN and MOHSEN]. The phase transition temperature T_c lowered by 6.4 K when TGS crystals

irradiated with 3 Mrad γ -dose and at higher doses (30 Mrad) the anomaly at T_c disappeared [STRUKOV et al.]. The degradation of TGS crystals grown from irradiated seeds was the subject of different studies [MILOVIDOVA et al. 1992,1993]. Recently, the effect of ultraviolet irradiation on the surface potential of TGS crystal admixed with Fe^{3+} was also discussed [DEBSKA and CZAPLA].

The present investigation deals with the study of optical parameters of TGS crystals doped with orthonitroaniline (ONA) and the effect of γ -rays on these parameters. Such a study might be promising since the individual effect of ONA and irradiation on TGS crystals is quite valuable.

Experimental

The starting salt for growing TGS single crystals was synthesized from chemically pure glycine and concentrated sulphuric acid in the molar ratio 3:1 and then the orthonitroaniline (0.2 weight percent of the compound) was added to the triglycine sulphate aqueous solution. The salt for growing TGS crystals was purified by three times slow recrystallization. The process of crystallization were performed in the ferroelectric phase at 318 K by slow evaporation of the solution at constant temperature. Transparent, flawless and well developed planes crystals were obtained in all the cases within about six weeks. Detailed information about the growth conditions and mechanism was given previously [GAFFAR and ABD EL-AZIZ].

From the crystals, plane parallel plates were cleaved perpendicular to the ferroelectric b-axis, then crystal plates were etched in water on a wet piece of soft cloth. The prepared samples were clear, transparent and free from any noticeable defects, i.e. optically perfect.

Samples of TGS doped with ONA were irradiated with γ -radiations at room temperature using ^{60}Co source (Alcyon II CGR, France) at constant dose rate of 0.02 Mrad/h. with different doses ranging from 0.3 up to 3 Mrad.

The optical transmittance of the samples was recorded using unpolarized monochromatic light with Shimadzu UV-VIS-2101 PC dual beam scanning spectrophotometer in the wavelength range 190 - 900 nm. The surrounding medium was air and all the measurements were done at room temperature. The system comprises photometer unit, a microcomputer of the IBM PC/PS2 type and UV-2101 PC personal spectroscopy software package. The reflectance measurements were made using specular reflectance attachment. The relative specular reflectance was measured at an incident angle of 5° , while the sample was placed horizontally facing downward and was illuminated from the bottom.

Results and Discussion

Fig. (1) shows the spectral distribution of the optical absorption coefficient (α) for TGS crystals doped with ONA in the photon energy range 3 - 5.5 eV for different γ -doses. The total absorption coefficient exhibits a long varying tail at low energies. Above 4.8 eV the absorption coefficient steeply increases with energy. In addition to some gaps, an absorption band could be observed near 4.8 eV.

The relationship between absorption coefficient α and photon energy $\hbar\omega$ can be expressed as :

$$\alpha\hbar\omega = A(\hbar\omega - E_g^{opt.})^r \quad (1)$$

where A is a constant nearly independent of photon energy and $E_g^{opt.}$ is the optical energy gap. Here r represents an index that can takes any of the values : $1/2$, $3/2$, 2 or 3 depending

on the type of transition responsible for the absorption. For allowed direct transition $r = 1/2$ while $r = 3/2$ for forbidden direct transition. For allowed indirect transition $r = 2$ and for forbidden indirect transition $r = 3$. The range within which this equation is valid is very small and hence it becomes too difficult to determine exactly the value of the exponent r [COHEN et al.].

The simplest way to deduce the type of transition is to examine the value of r which relates $\hbar\omega$ to $(\alpha\hbar\omega)$ with a straight line relationship. For single phonon absorption process, the absorption coefficient for an allowed indirect transition is given by :

$$\alpha\hbar\omega = A(\hbar\omega - E_g^{opt.} + E_p)^2 \tag{2}$$

where $E_g^{opt.}$ is, in this case, the allowed indirect energy gap and E_p is the phonon energy. The corresponding form for phonon emission is given by :

$$\alpha\hbar\omega = B(\hbar\omega - E_g^{opt.} - E_p)^2 \tag{3}$$

where B is a constant has the same nature as A.

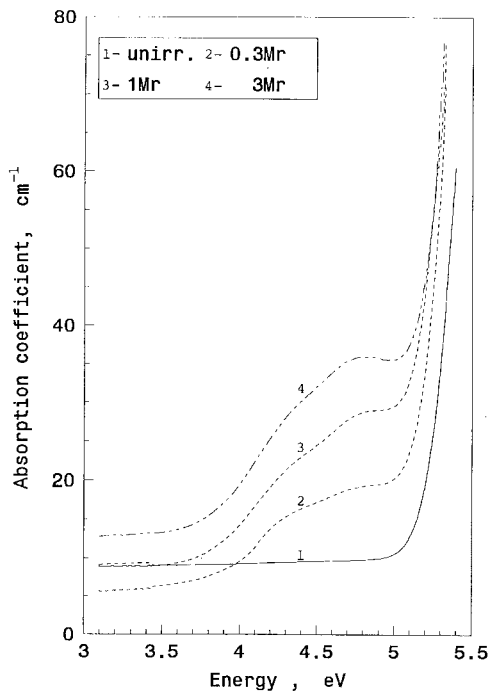


Fig. 1 : Absorption coefficient versus photon energy for unirr. and irradiated TGS crystals doped with ONA.

In a small energy range, the dependence of $(\alpha\hbar\omega)^{1/2}$ on $(\hbar\omega)$ for the unirr. and irradiated samples of TGS doped with ONA is shown in Fig. (2). From the figure, two distinct families of straight lines could be observed in two photon energy ranges, 5.09-5.14 and 5.14-5.29 eV. This indicates that the optical absorption obeys equation (1) with $r = 2$ which means that TGS crystal is an indirect material and the fundamental edge is due to allowed indirect transitions. By extrapolating the straight lines to the value where $(\alpha\hbar\omega)^{1/2}=0$, values of $E_{g1} = E_g^{opt.} + E_p$ and $E_{g2} = E_g^{opt.} - E_p$ could be determined. Regression analysis through the data gives the values of optical energy $E_g^{opt.}$; phonon energy E_p and phonon equivalent temperature T_p listed in Table (1).

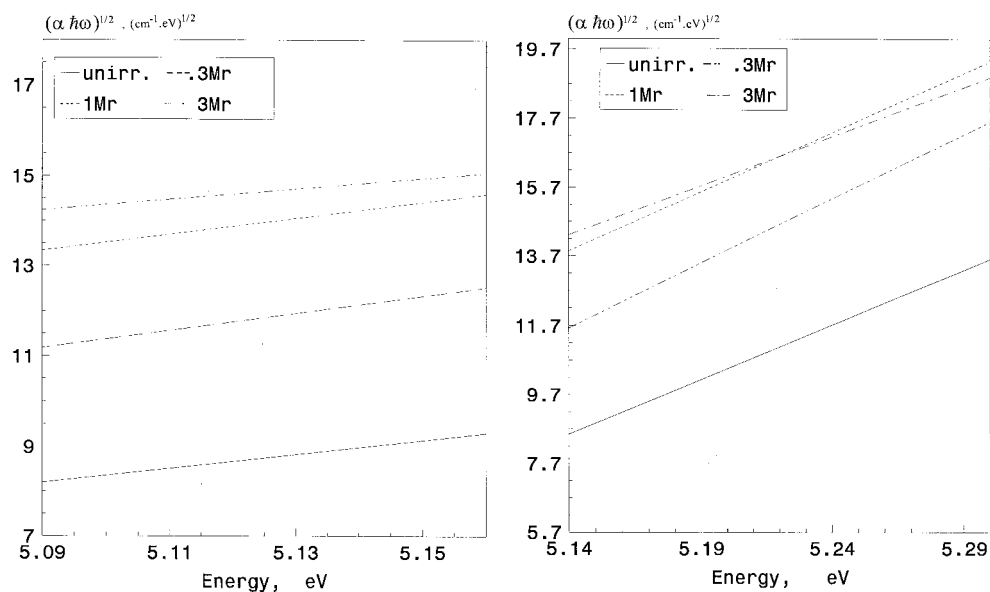


Fig. 2: (a) Relation between $(\alpha\hbar\omega)^{1/2}$ and photon energy in the low-energy range for TGS crystals doped with ONA and irradiated with γ -doses, (b): Relation between $(\alpha\hbar\omega)^{1/2}$ and photon energy in the high-energy range for TGS crystals doped with ONA and irradiated with γ -doses.

Physical quantity	γ -Dose (Mrad)			
	0	0.3	1.0	3.0
Indirect forbidden optical energy gap E_g^{opt} (eV)	4.72±0.01	4.55±0.01	4.63±0.01	4.25±0.01
Phonon energy E_p (meV)	0.15±0.01	0.19±0.01	0.20±0.01	0.39±0.01
Phonon equivalent temperature, T_p (K)	1760±5	2235±5	2355±5	4510±5
Static dielectric constant $\epsilon(0)$	3.05±0.05	3.35±0.05	3.20±0.05	3.70±0.06

Table (1) : Optical constants for unirradiated and irradiated TGS crystals doped with ONA

The following conclusions can be drawn from the spectral distribution of α in the photon energy range 3 - 5.5 eV.

- The cut-off wavelength of unirradiated TGS crystals doped with ONA lies at 225 nm. In case of γ -irradiated samples the cut-off is moved slightly towards the higher wavelength region (at about \approx 235 nm).
- The general level of absorption in TGS crystals increases under the influence of irradiation by γ -rays. This is probably due to the scattering by γ -irradiation-induced defects in the crystal.
- For γ -irradiated TGS crystals, E_g^{opt} was found to be shifted towards lower energy region as the γ -dose increases. This decrease in E_g^{opt} may be attributed to point defects created in TGS during γ -irradiation by direct interaction of Compton electrons with lattice atoms and by multiple collisions.
- The maximal absorption coefficient of the band observed at 310 nm increases with increasing the dose of γ -radiation. This absorption band could be attributed to the free radicals $\text{CH}_2\text{COO}^\cdot$ formed at lattice sites of glycine-I since these radicals are unstable in low irradiation doses [COHEN et al.].

- The two absorption bands observed at 240 nm and 258 nm may be attributed to stable free radicals $\text{NH}_3\text{CH COO}^\cdot$ formed in glycine-II and -III. These two bands are quite similar to those observed by HUEZER and BANLANICKA in TGS crystals doped with Cu^{2+} .

The degree of disorder and defects present in TGS crystals changes due to several factors such as heat treatment and radiation energy. Increased disorder and defects is known to reduce the value of the optical gap. Optical absorption measurements were made by MONTEMEZZANI et al. on Fe^{3+} -doped TGS single crystals and aqueous solutions exposed to ultraviolet irradiation. According to this work ultraviolet photons bleach the Fe^{3+} absorption band centers at about $\lambda = 290$ nm and induce a shift in the absorption edge towards the shorter wavelength. Abass and Al-Eithan indicated that the optical absorption of TGS crystals doped with Cr^{3+} in the absorption edge is due to the transition from valence band to the donor levels. The three valence bands investigated were attributed to the electrostatic energy of the interaction between a dipole of the Cr^{3+} cluster and that of the glycine ion. For γ -irradiated TGS crystals doped with Cu^{2+} -ions HUEZER and BANLANICKA observed absorption bands due to irradiation. This behaviour was attributed to free radicals produced by γ -irradiation in glycine molecules.

Other optical constants were determined using the relations :

$$K = \frac{\alpha\lambda}{4\pi} \quad (4)$$

where K is the extinction coefficient,

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \quad (5)$$

where n is the refractive index and R is the reflectance of the surface.

$$\epsilon_r' = n^2 - K^2, \quad \epsilon_r'' = 2nK \quad (6)$$

where ϵ_r' and ϵ_r'' are the real and imaginary parts of the complex dielectric constant, respectively.

The energy dependence of the refractive index for unirradiated and irradiated with different γ -doses TGS crystals doped with ONA is illustrated in Fig. 3.

The following conclusions can be drawn from figures 1 and 3 :

- The absorption coefficient increases with increasing γ dose.
- The refractive index decreases with increasing γ -dose. For higher γ -doses the values of (n) become close to each other which may be due to a sudden change E_g^{opt} under the influence of the first γ -dose.
- The wavelength at which the anomalous behaviour of the refractive index starts is the same as that at which irradiated TGS crystals exhibits absorption bands. This anomalous behaviour is accompanied by a dispersion, probably because of a large contribution from polarization effects.

The variation of both the extinction coefficient and the imaginary part of the dielectric constant ϵ_r'' with energy preserves the same dependence of the absorption coefficient while the behaviour of ϵ_r' , the real part of the dielectric constant, and the refractive index is the same.

The imaginary part of the dielectric constant ϵ_r'' is related the refractive index with the well known Debye equation [OMAR, P. 392] :

$$\varepsilon_r''(\omega) = \frac{\varepsilon_r(0) - n^2}{(1 + \omega^2 \tau^2)} \omega \tau \quad (7)$$

Here $\varepsilon_r(0)$ is the static dielectric constant, $\omega = 2\pi\nu$ and ν is the measuring frequency and τ is the relaxation time.

At high frequencies where $\omega \tau \gg 1$ [in our case τ has the approximate value 10^{-11} sec. at room temperature (MANSINGH and LIM KOON) and hence $\omega \tau > 10^4$] the above equation reduces to :

$$\varepsilon_r''(\omega) = \{\varepsilon_r(0) - n^2\} / \omega \tau \quad (8)$$

The relation connecting the effective electrical conductivity σ_0 to the imaginary part of the dielectric constant ε_r'' takes the form [OMAR, P.165] :

$$\varepsilon_r''(\omega) = \frac{\sigma_0}{\varepsilon_0 \omega (1 + \omega^2 \tau^2)} \quad (9)$$

where ε_0 is the dielectric constant of free space = 8.854×10^{-12} farad/m. In the high-frequency region $\omega^2 \tau^2 \gg 1$, which corresponds to the visible and ultraviolet regions, equation (9) becomes :

$$\varepsilon_r''(\omega) = \frac{\sigma_0}{\varepsilon_0 \omega (\omega^2 \tau^2)} \quad (10)$$

Substituting and rearranging equations 8 and 10 we have:

$$n^2 = \varepsilon_r(0) - \frac{\hbar^2 \sigma_0}{\varepsilon_0 \tau} \frac{1}{\hbar^2 \omega^2} \quad (11)$$

which represents a straight line with a slope equals to $\hbar^2 \sigma_0 / \varepsilon_0 \tau$ ($= 3.215 \times 10^6 \sigma_0$) and an intercept equals to $\varepsilon_r(0)$. From the intersection and slope one can determine the effective electrical conductivity σ_0 and the static dielectric constant $\varepsilon_r(0)$.

The dependence of n^2 on $1/\hbar^2 \omega^2$ is depicted in Fig.(4) from which values of $\varepsilon_r(0)$ and σ_0 at room temperature are deduced. These values change with the dose of γ -radiation, as shown in Table 1 and Fig. (5). The calculated values of σ_0 agree well with the experimental values measured in our laboratory. The electrical conductivity increases with γ -dose reaching its maximum at 0.3 Mrad. This increase may be due to the lattice defects introduced by γ -radiation which tend to weaken the interaction forces between dipoles. Another factor that may arise is the ionization effects which leads to the appearance of internal bias. This internal bias is responsible for the shift of the phase transition temperature T_c , variations observed in the shape of the hysteresis loop and the value of spontaneous polarization. Further increase of γ -dose decreases the electrical conductivity σ_0 . This decrease is probably due to recombination process of the induced defects formed previously at low doses.

Data presented in Table (1) indicate changes in optical energy gap E_g^{opt} and static dielectric constant $\varepsilon_r(0)$ with γ -dose in agreement with predictions from the equation of Kramers-Kronig [OMAR, P. 405] :

$$\varepsilon_r(0) = 1 + \frac{2}{\pi} \int_{\omega_0}^{\infty} \frac{\varepsilon_r''(\omega)}{\omega} d\omega \quad (12)$$

where $\omega_0 = E_g^{opt.} / \hbar$ is the frequency at the absorption edge.

It worth noticing that expression (12) is valid for $\hbar\omega < E_g^{opt.}$ which is justified in present calculation.

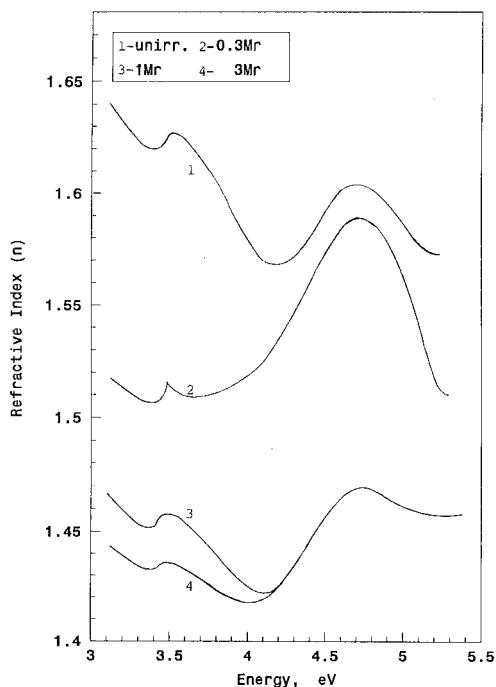


Fig.3 : Refractive index (n) versus photon energy for unirradiated and irradiated TGS crystals doped with ONA

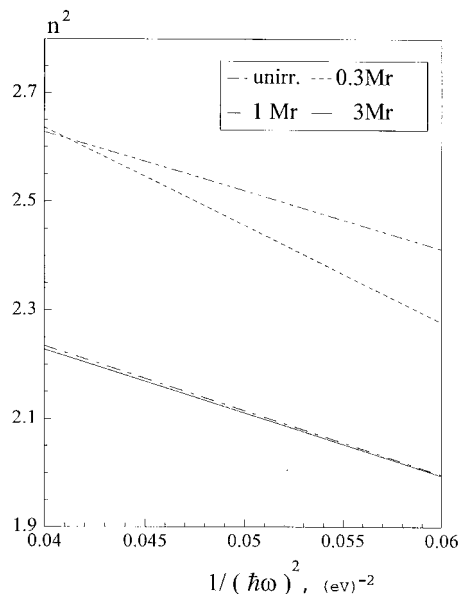


Fig. 4: Relation between n^2 and $(\hbar\omega)^{-2}$ for TGS crystals doped with ONA and irradiated with γ -rays in different doses.

Conclusions

- 1- The allowed indirect optical energy gap $E_g^{opt.}$ of TGS crystals doped with ONA decreases effectively after irradiation with γ -rays. Phonon energy and phonon equivalent temperature and their dependence on the γ -dose were calculated.
- 2- The formation of stable and unstable free radicals of the form $\text{NH}_3\text{CH COO}^\cdot$ and $\text{CH}_2\text{COO}^\cdot$ after irradiating TGS crystals with γ -rays could be the reason for the observed absorption bands in the energy range 3 - 5.5 eV.
- 3- The refractive index of TGS crystals doped with ONA was calculated as a function of γ -dose. Values of the effective electrical conductivity σ_0 and the static dielectric constant $\varepsilon_r(0)$ at room temperature for samples of TGS doped with ONA and irradiated with different γ -doses are estimated from the behaviour of the refractive index as a function of the photon energy and the results are confirmed experimentally.

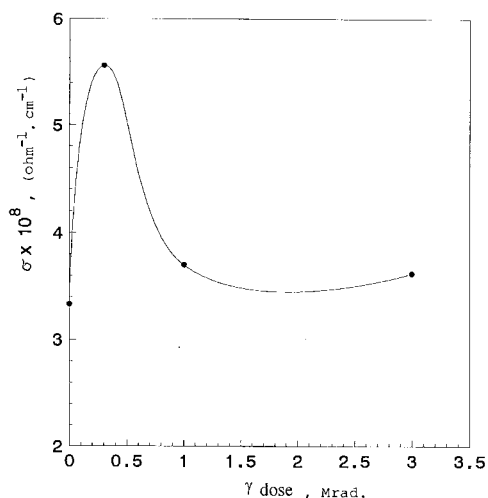


Fig. 5: Relation between σ_0 at room temperature and the γ -radiation dose for TGS crystals doped with ONA.

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