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EFFECT OF NITROANILINE ADMIXTURE ON SELECTED THERMAL PARAMETERS OF TGS CRYSTAL

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Applying the periodic heat wave method, the thermal diffusivity, cooling constant and heat transfer coefficient of TGS crystals, admixtured with para-, meta- and ortho-nitroaniline are measured in the three principal crystallographical directions [100], [010] and [001]. The nitroaniline concentration of the TGS crystal was determined spectrophotocolorimetrically. The mean linear dimensions of the perturbed regions of the TGS lattice were evaluated on two distinct models. Para-nitroaniline admixture is found to perturbate the TGS lattice maximally, compared with m- and o-nitroaniline.

Introduction

The thermal conductivity (ThC) and thermal diffusivity (ThD) of TGS crystal have been the subject of numerous studies [1–9]. Krajewski and Jaroszyk [7], studying ThD in pure single-domain and multi-domain crystals, succeeded in evaluating the mean thickness of the domain walls in TGS [8] as comparable, in order of magnitude, with the value proposed in Ref. [10]. Dikant [11] found a lowering in ThD for TGS crystals containing Fe^{3+} ions. Krajewski and Grzelak [12] confirmed the effect in single-domain Fe^{3+}-doped TGS crystals and evaluated the size of the regions perturbed by the presence of an Fe^{3+} admixture in TGS crystal. The decrease in ThD observed by Dikant [11] was due to scattering of thermal phonons on the defects introduced into the crystals, as well as on domain walls. Krajewski, Jaroszyk and Riad [13, 14] investigated the ThD of TGS crystals doped with Cu^{2+} and Cr^{3+} ions subsequent to their permanent polarisation. In this way, they eliminated thermal phonon scattering by domain walls, and thus obtained results conveying information regarding the influence of admixtures on the ThD of single-domain TGS crystals permitting the evaluation of the mean linear dimensions of the lattice regions perturbed by the admixture ions. Jaroszyk [15], and Jaroszyk and Krajewski [16] elucidated the influence of radiation-induced defects on the ThD, cooling constant (CC) and heat transfer coefficient (HTC) of single-domain TGS crystals. As done by Fletcher et al. [17–19], they dealt with X-ray irradiated TGS crystal as a two-phase system. For such

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a system, they evaluated the mean linear dimensions of spheres, perturbated in the TGS lattice.

The literature contains as yet no data on the influence of dipolar organic admixtures of the type of para-, meta- and ortho-nitroaniline on the ThD, CC and HTC of TGS crystals. We consequently proceeded to investigate the matter, and report our results in the present paper. In our study of the ThD, CC and HTC of TGS crystals admixtured with nitroaniline, we applied Ångström's periodic heat wave method [20, 21] in the version extended by Jaroszyk [15].

1. Preparation of TGS crystals for investigation

TGS crystals, pure as well as doped with nitroaniline, were grown by the dynamical method [22] from saturated aqueous solutions of the salt in ferroelectric phase, at 315 K. The initial material, purified by 5-fold slow recrystallisation of the salt from aqueous solution, contained 0.5% weight of the nitroaniline admixture. All crystals, both pure and doped with nitroaniline, were grown using crystallographically oriented nuclei, cut from TGS crystals containing L-a-alanine molecules at a concentration of 3% weight. Such nuclei, owing to their one-domain state, presumably ensured partial orientation of the dipole moments of the nitroaniline molecules in the TGS lattice in the process of growth. Nitroaniline-doped TGS crystals grown under these conditions were found to exhibit a high reproducibility [23] of the physical parameters measured.

The nitroaniline concentration of the TGS crystals under investigation was determined spectrophotocolorimetrically by having recourse to the considerable difference in solubility of TGS and nitroaniline in distilled water and in ethyl ether. This choice of mutually non-mixing solvents permitted the easy separation of the aqueous solution containing dissolved TGS only from the ethyl ether solution containing practically only the respective nitroaniline. The latter solution was studied spectrophotocolorimetrically. The concentration of the three nitroanilines thus admixtured to the crystal lattice of TGS was found to amount to $3 \times 10^{-3}\%$ weight.

From the crystals obtained, rods were cut in the principle crystallographical directions of the coordinate system proposed by Konstantinova et al. [24]. In the crystal rods, cut in the directions [100], [010] and [001], two small cavities x_1, x_2 were bored into which copper-constantan thermocouples were introduced. The position and depth of the cavities fulfilled the optimal conditions, determined by Green and Cowles [25]. The rods had the shape of cylinders, 0.4 cm in diameter and about 3 cm in length. The distance between x_1 and x_2 was approximately 0.5 cm. A micro-heater and a heat reservoir of high capacity were connected to the ends of the rod with adhesive. The crystal with micro-heater, thermocouples and heat reservoir was then placed inside a vacuum holder (for details, cf. Ref. [26]), in vacuum of 0.7 N/m^2. The heat reservoir was in good thermal contact with the outer shield of the vacuum holder. The temperature of the crystal at thermal equilibrium was measured with an accuracy of ± 0.01 K by the compensation method. The thermocouples were made applying long leads 0.005 cm in diameter to reduce to a minimum the transfer of heat from the crystal.

2. *Results*

The ThD, CC and HTC of TGS crystals, pure as well as doped with para-, meta- and ortho-nitroaniline, were measured at a constant temperature of 298 K. The numerical values of the parameters ThD, CC and HTC were determined in the three principal crystallographical directions [100], [010] and [001] of permanently polarized TGS crystals, thus eliminating any influence of domain walls on the thermal quantities measured. The changes in ThD, CC and HTC measured by us can therefore be attributed to the influence of the dipolar admixtures of nitroaniline $C_6H_4NO_2NH_2$ solely. The dipole moments of para-nitroaniline, meta-nitroaniline and ortho-nitroaniline amount to 6.12 D, 4.85 D and 4.26 D respectively.

Table I, for comparison, gives the values of the thermal diffusivity k, cooling constant β, heat transfer coefficient α and heat loss coefficient G for pure, polarized TGS crystal, at 298 K. Whereas Table II gives k, β, α and G for TGS crystals doped with para-nitroaniline (p-NTGS), meta-nitroaniline (m-NTGS) and ortho-nitroaniline (o-NTGS), at 298 K and admixture concentrations of $3 \times 10^{-3}\%$ weight.

TABLE I

Thermal diffusivity k, cooling constant β, heat transfer coefficient α and heat loss coefficient G of pure one-domain TGS crystals at 298 K

Crystallographical directions	k (cm²/s)	β (s⁻¹)	α (W/cm² · K)	G (W/K)
[100]	$3.9 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$	$4.5 \cdot 10^{-4}$	$1.45 \cdot 10^{-3}$
[010]	$3.65 \cdot 10^{-3}$	$2.4 \cdot 10^{-3}$	$6.3 \cdot 10^{-4}$	$2.05 \cdot 10^{-3}$
[001]	$3.5 \cdot 10^{-3}$	$2.3 \cdot 10^{-3}$	$5.9 \cdot 10^{-4}$	$1.90 \cdot 10^{-3}$

TABLE II

Thermal diffusivity k, cooling constant β, heat transfer coefficient α and heat loss coefficient G of one-domain TGS crystals, admixtured with para-, meta- and ortho-nitroaniline, at 298 K

Admixture	Crystallographical directions	k (cm²/s)	β (s⁻¹)	α (W/cm² · K)	G (W/K)
p-NTGS	[100]	$3.55 \cdot 10^{-3}$	$3.0 \cdot 10^{-3}$	$7.8 \cdot 10^{-4}$	$2.6 \cdot 10^{-3}$
	[010]	$3.25 \cdot 10^{-3}$	$6.2 \cdot 10^{-3}$	$1.6 \cdot 10^{-3}$	$5.2 \cdot 10^{-3}$
	[001]	$3.18 \cdot 10^{-3}$	$4.0 \cdot 10^{-3}$	$1.05 \cdot 10^{-3}$	$3.5 \cdot 10^{-3}$
m-NTGS	[100]	$3.6 \cdot 10^{-3}$	$2.7 \cdot 10^{-3}$	$7.0 \cdot 10^{-4}$	$2.3 \cdot 10^{-3}$
	[010]	$3.3 \cdot 10^{-3}$	$5.1 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$	$4.3 \cdot 10^{-3}$
	[001]	$3.2 \cdot 10^{-3}$	$2.9 \cdot 10^{-3}$	$7.7 \cdot 10^{-3}$	$2.5 \cdot 10^{-3}$
o-NTGS	[100]	$3.7 \cdot 10^{-3}$	$2.5 \cdot 10^{-3}$	$6.5 \cdot 10^{-4}$	$2.1 \cdot 10^{-3}$
	[010]	$3.4 \cdot 10^{-3}$	$3.7 \cdot 10^{-3}$	$9.5 \cdot 10^{-4}$	$3.1 \cdot 10^{-3}$
	[001]	$3.2 \cdot 10^{-3}$	$3.3 \cdot 10^{-3}$	$8.6 \cdot 10^{-4}$	$2.8 \cdot 10^{-3}$

On comparison of Tables I and II one notes that dipolar nitroaniline admixtures cause a decrease in numerical value of the thermal diffusivity k of TGS. Crystals containing nitroaniline exhibit an increase in β and α. The values of β and α are the highest in the case of para–nitroaniline and the lowest in that of ortho–nitroaniline admixture, though in all three cases higher than in pure TGS.

3. *Discussion of the results*

The above, well apparent changes in ThD of nitroaniline admixtured TGS crystals as compared with pure TGS suggests that the doped crystals can be considered to be two-phase systems as done by Krajewski, Riad and Jaroszyk [13, 14] in their study of ThD in TGS admixtured with Cu^{2+} and Cr^{3+} ions. The one phase, in the present case, consists of the unperturbed crystal lattice of TGS and the other of cubic (model *A*) or spherical (model *B*) lattice regions perturbed by the presence of the nitroaniline admixture. The ThD of the two phases is different. On the assumption of model *A* or *B* for the bulk of nitroaniline-admixtured TGS crystal, one is able to evaluate the dimensions of the perturbed regions from the results of ThD studies of pure and admixtured single-domain crystals. The HTC determined in our studies shows i.a. that thermal phonons are scattered geometrically on the lattice defects. The increase in HTC has to be related to the numbers and dimensions of the scattering centres introduced into the crystal.

Assuming an isotropic distribution of the admixture and the same density and specific heat for the two phases, one derives on model *A* the following relation for the effective thermal diffusivity k^{eff} of doped TGS:

$$k^{\mathrm{eff}} = k^{\mathrm{p}}\left[(1-x^2)+\frac{k^{\mathrm{d}}\cdot x^2}{(k^{\mathrm{p}}-k^{\mathrm{d}})\cdot x+k^{\mathrm{d}}}\right], \tag{3.1}$$

with k^{p} — the ThD of the pure crystal, and k^{d}–that of regions perturbed by the presence of dipolar nitroaniline admixture. The parameter $x^3 = p_{\mathrm{c}} = \Delta V/V$ defines the ratio of the volume ΔV of all the perturbed regions to the total volume V of the crystal. In order to determine p_{c} as to its numerical values, which will be necessary to arrive at an evaluation of the size of the perturbed regions, one has to assume some slight anisotropy in ThD of the latter. A criterion of the choice of the crystallographical directions for which this assumption is correct is to be gained from Eq. (3.1). For $k^{\mathrm{d}} \to 0$, the following condition is fulfilled:

$$x^3 = p_{\mathrm{c}} \geqslant \left(\frac{k^{\mathrm{p}}-k^{\mathrm{eff}}}{k^{\mathrm{p}}}\right)^{3/2}. \tag{3.2}$$

In our measurements, the condition (3.2) was fulfilled for the directions [010] and [001]. The ThD ratio $k_{11}^{\mathrm{eff}} : k_{22}^{\mathrm{eff}} : k_{33}^{\mathrm{eff}}$ of TGS crystals admixtured with para-, meta- and ortho-nitroaniline amounted, respectively, to 1.12 : 1.02 : 1.00; 1.12 : 1.03 : 1.00; and 1.15 : 1.06 : 1.00. For the directions [010] and [001], the following relation is fulfilled:

$$k_{11}^{\mathrm{d}} \neq k_{22}^{\mathrm{d}} = k_{33}^{\mathrm{d}}. \tag{3.3}$$

Once the values of k_{22}^{p}, k_{33}^{p}, k_{22}^{eff} and k_{33}^{eff} are known the graphical solution of Eq. (3.1) permits the determination of p_c in the interval of variability $\langle 0,1 \rangle$. Assuming the perturbed region as cubic (model A), the length of its edge is obtained from the relation:

$$d^3 = \frac{p_c \cdot \pi \cdot R^2 \cdot b}{n}, \tag{3.4}$$

where R is the radius and b — the height of the cylindrical crystal rod, and n — the number of perturbed regions. The number n can be calculated from the relation

$$n = \frac{m \cdot c \cdot N}{100 \cdot A}, \tag{3.5}$$

where m is the mass of the crystal, c — the admixture concentration in % weight, A — the molar mass of the admixture, and N — Avogadro's number. With regard to Eqs (3.4) and (3.5) we obtain for d the expression

$$d = \left(\frac{100 \cdot A \cdot p_c}{\varrho \cdot c \cdot N}\right)^{1/3}, \tag{3.6}$$

with ϱ — the density of the crystal.

In the work under consideration we moreover applied the model of spherical perturbed regions (model B) [27, 28] for comparison with the results obtained with model A. The initial assumptions to be made are similar. In this case, the effective thermal diffusivity k^{eff} of the admixtured TGS crystal is expressed as follows:

$$k^{eff} = k^{p}\left[\frac{(2 \cdot k^{p}+k^{d})-2x^3 \cdot (k^{p}-k^{d})}{(2 \cdot k^{p}+k^{d})+x^3 \cdot (k^{p}-k^{d})}\right], \tag{3.7}$$

where k^p, k^d and $x^3 = p_s$ have the same meaning as above. With p_s available, we determine the radius r of a sphere of the TGS lattice perturbed by nitroaniline from the following equation:

$$r = \left(\frac{300 \cdot A \cdot p_s}{4\varrho \cdot c \cdot N}\right)^{1/3}. \tag{3.8}$$

TABLE III

Dipole moments, inhomogeneity coefficients (p_c, p_s) and dimensions of perturbated regions, according to model $A(d)$ and model $B(r)$, in TGS crystals doped with para-, meta- and ortho-nitroaniline

Admixture	Dipole moment (D)	Model A (cubic)		Model B (spherical)	
		p_c	d (nm)	p_s	r (nm)
p-NTGS	6.12	0.08	7.2	0.16	8.2
m-NTGS	4.85	0.07	6.7	0.11	7.3
o-NTGS	4.26	0.06	6.4	0.09	6.8

Table III gives the dimensions (d, r) of the perturbed regions as well as the parameter (p_c, p_s) for the models A and B, respectively. Moreover, we give the dipole moments of p-, m- and o-nitroaniline. The dimensions (d, r) of the perturbed regions in TGS do not differ considerably for the three nitroanilines. One moreover notes a correlation between the parameters d and r and the respective three dipole moments. The molecules of para-nitroaniline have the greatest dipole moment of the three, and perturb the TGS lattice the most strongly.

The numerical values of the linear dimensions of the perturbed regions determined by us applying models A and B are close to those of the perturbed regions in TGS crystals doped with Cu^{2+} and Cr^{3+} ions [13, 14], TGS crystals doped with Fe^{3+} ions [12], and TGS crystals containing radiation defects [16].

4. *Conclusions*

a) TGS crystals with nitroaniline molecules displayed lower values of thermal diffusivity in comparison with those of pure TGS crystals in the crystallographical directions examined.

b) TGS crystals doped with nitroaniline molecules showed increases in the values of the cooling constant, the heat transfer coefficient and the heat loss coefficient in comparison with those of pure TGS crystals.

c) It was found in TGS crystals doped with nitroaniline molecules that there was a relationship between the linear dimensions of the perturbed regions and the dipole moments of the three types of nitroaniline introduced into the crystals. Para-nitroaniline molecules have the greatest dipole moment and disturb the structure of TGS crystals to the greatest extent.

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