EFFECT OF GROWTH CONDITIONS ON THE THERMAL DIFFUSIVITY AND THERMAL CONDUCTIVITY OF TGS CRYSTALS

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Angström's temperature wave method is applied for measuring thermal diffusivity in the three principal crystallographical directions [100], [010] and [001] and temperature range from $+18°C$ to $+70°C$, of TGS crystals grown in the ferroelectric and paraelectric phases. The conditions of growth are found to have a decisive influence on the thermal diffusivity value. The highest diffusivity was found in permanently polarized single-domain TGS crystals grown in the paraelectric phase, and the lowest in multi-domain ones grown in the ferroelectric phase. In the temperature of phase transition, all TGS crystals exhibited a sharp minimum of thermal diffusivity, independent of growth conditions. On resorting to the known specific heat values c_p for TGS crystals, thermal conductivity coefficients were calculated for the temperature range investigated and then compared with the data available in the literature. This comparison provided information on the properties of the TGS crystals studied by others. The present thermal conductivity studies, in conjunction with measurements of ultrasonic wave velocities in the TGS crystals under investigation, permitted the determination of possible reasons for the difference in mean free path of phonons arising from different growth conditions.

1. Introduction

In recent years, studies on the thermal diffusivity and thermal conductivity of ferro-electrics have become more and more numerous [1–22], since the phenomenological study of the two quantities is a source of interesting information of an integral nature, advantageously supplementing the results of lattice dynamics studies obtained by methods of neutron spectroscopy. Phenomenological investigation is directed primarily at the anomalous temperature-dependent changes in these two quantities exhibited by ferro-electrics at very low temperatures as well as in the temperature region close to the point

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of phase transition. Most of the papers cited above deal with ferroelectrics of the type of $BaTiO_3$, KH_2PO_4 and $NaNO_3$. In rarer cases, they contain data on TGS crystals, of a more highly complicated structure [4, 8, 9, 11, 19, 21].

When subjected to a comparison, the available results of thermal diffusivity and thermal conductivity measurements obtained by various authors in TGS crystals are found to lead to rather strongly divergent numerical values of the diffusivity and conductivity coefficients and to reveal a by far not univocal behaviour of their variations in the phase transition region. The reasons for this are as yet unknown, and incite to further studies.

It is well known that the conditions of growth of TGS crystals are quite decisive in determining the numerical values of certain of their dielectric parameters [23] as well as the domain structure of the crystals [24]. Quite naturally, this led us to expect a similar influence of the growth conditions on the values of their thermal diffusivity and conductivity. We consequently proceeded to an investigation of the thermal diffusivity of TGS crystals grown in the paraelectric and ferroelectric phases, using Angström's method of temperature waves, with regard to its high degree of accuracy [25–27]. The thermal conductivity of the crystals was determined from the known thermal diffusivity, density, and specific heat.

2. Preparation of the crystals, and measuring device

TGS crystals for thermal diffusivity studies were grown from aqueous solutions by the isothermal method in the ferroelectric phase at + 43°C and in the paraelectric phase at + 55°C. The raw materials used for synthesis of TGS salt were of chemical purity. For growing the crystals, we used salts purified by three-fold slow recrystallisation from aqueous solutions. The crystals were cut into rods of square cross-section, oriented for thermal diffusivity studies in the directions [100], [010] and [001] in accordance with the crystallographical reference system proposed for these crystals by Konstantinova, Silvestrova and Aleksandrov [28]. In each rod, two holes were bored for the introduction of copper-constantan thermoelements at points fulfilling the optimal condictions with respect to the upper surface of the rod as defined by Green and Cowles [29]. The rods were then processed to cylinders 0.4 cm in diameter, of a length of 2.2 cm. In order to ensure minimal heat outflow from the crystal cylinder through the thermoelement, the latter was made of sufficiently long wires, 0.005 cm in diameter, which were then wound into spirals. Using Degussa "liquid silver", a micro-heater was glued to one of the frontal surfaces of the cylinder whereas a copper heat recipient of large heat capacity was attached to the other. The crystal with micro-heater, thermoelements, and heat recipient was then placed inside a modified vacuum holder, the details of which have been published elsewhere [30]. The construction of the heat recipient ensured good thermal contact of the crystal and outer shield of the vacuum holder, the temperature of which was varied continuously by means of a Hoeppler thermostat. The temperature of the crystal at thermal equilibrium was measured with the copper-constantan thermoelement by the compensation method with an accuracy of ± 0.01 °C.

For thermal diffusivity measurements on single-domain crystals, the TGS crystalline rods were permanently DC field polarized in the paraelectric phase in the direction [010] and cooled slowly to room temperature in the same DC field. On achieving permanent polarization of the crystal, the polarizing field was switched off. For permanent polarization of rods oriented in the [010] direction, a polarizing field was set up between an electrode contacting the micro-heater, and the copper heat recipient. For permanent polarization of cylinders oriented in the directions [100] and [001], a special system of electrodes closely adhering to the mantle of the cylinder was used after their ferroelectric [010] direction had been established. In crystals oriented in this manner, the two holes for the thermoelements were bored in directions perpendicular to [010] and [001], or respectively to [010] and [100].

A block diagram of the device used in the present thermal diffusivity studies of TGS crystals is shown in Fig. 1. The time-variable temperature field in the crystal was obtained by means of a periodically varying supply to the micro-heater. The temperature waves
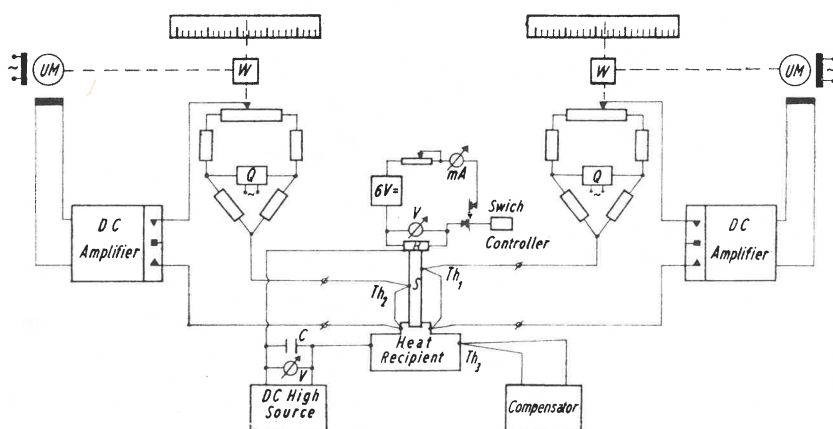

Fig. 1. Block diagram of device used in measuring the thermal diffusivity of TGS crystals by Angström's temperature wave method

propagating in the crystal caused thermoelectric forces, varying with time, in the working circuits of the measuring thermoelements Th_1 and Th_2. The voltage signals from the thermoelements were supplied to the inputs of two DC amplifiers, of identical transducing parameters. The amplified electric signals were recorded by two single-channel EZ-4 devices. The curves defining the time temperature-variations of the crystals were further processed by graphical Fourier analysis, the results of which served for computing the thermal diffusivity coefficients of the TGS crystals by means of an ODRA 1204 computer. The amplitudes of the recorded temperature variations in the upper and lower points of measurement amounted to $0.5°C$ and $0.3°C$ respectively.

With the aim of checking the measuring device used in the present work involving Angström's method, measurements of the thermal diffusivity coefficient of KCl crystals

grown by Bridgman's method [31] were performed. The numerical values obtained in these measurements coincided with the data in the literature [32] to within experimental error, of the order of 2 per cent.

3. Results of measurements

The curves of Fig. 2 show the temperature-dependence of the thermal diffusivity coefficients k of TGS crystals grown in the ferroelectric phase, for the propagation directions [100], [010], and [001]. Void measuring points denote k-values obtained while heating the crystals, whereas full measuring points denote k-values obtained at cooling. From
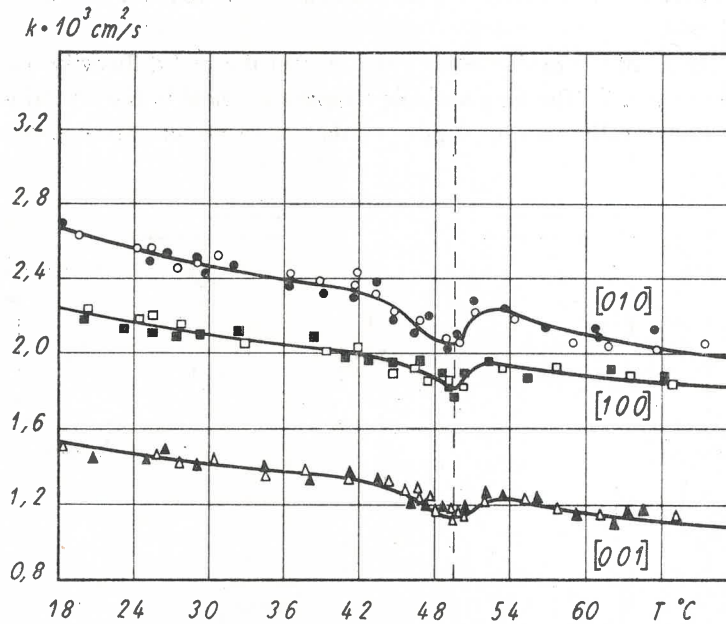

Fig. 2. Temperature-dependence of the thermal diffusivity coefficients k of multi-domain TGS crystals grown in the ferroelectric phase, for the crystallographical directions [100], [010] and [001]

the curves of Fig. 2, the thermal diffusivity of the TGS crystals is seen to decrease nearly linearly with growing temperature in the temperature region investigated exhibiting a marked minimum at the phase transition point for all three principal crystallographical directions of these crystals. In the range of room temperatures, the largest and lowest thermal diffusivities occur in the ferroelectric [010] direction and the [001] direction respectively, pointing to a strong anisotropy of this physical property in TGS crystals. The largest anomalous variations in thermal diffusivity at the phase transition point are observed in the ferroelectric [010] direction.

The curves of Fig. 3 (the markings are those of Fig. 2) show the temperature-dependence of thermal diffusivity for TGS crystals grown in the paraelectric phase, for the three principal crystallographical directions [100], [010], and [001]. A comparison of Figs 2 and 3 shows that the trend of the variations exhibited by the thermal diffusivity in all
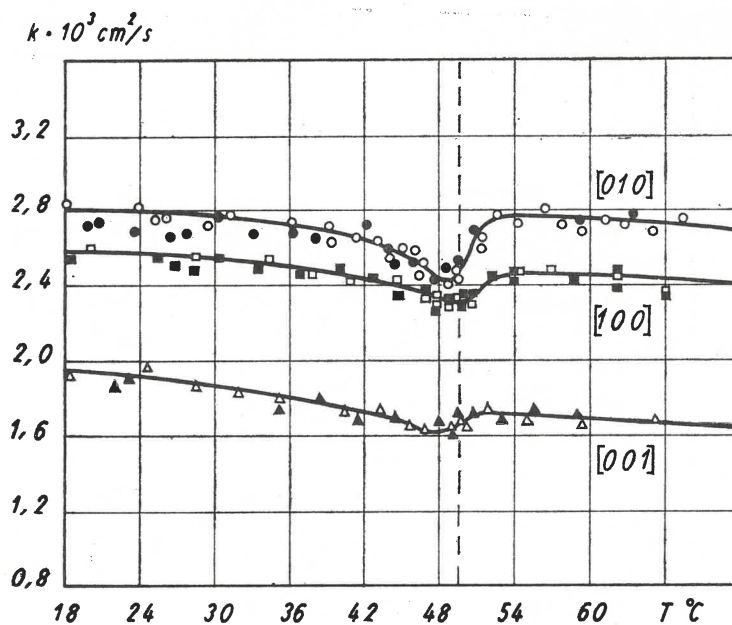
Fig. 3. Temperature-dependence of the thermal diffusivity coefficients k of multi-domain TGS crystals grown in the paraelectric phase, for the crystallographical directions [100], [010] and [001]
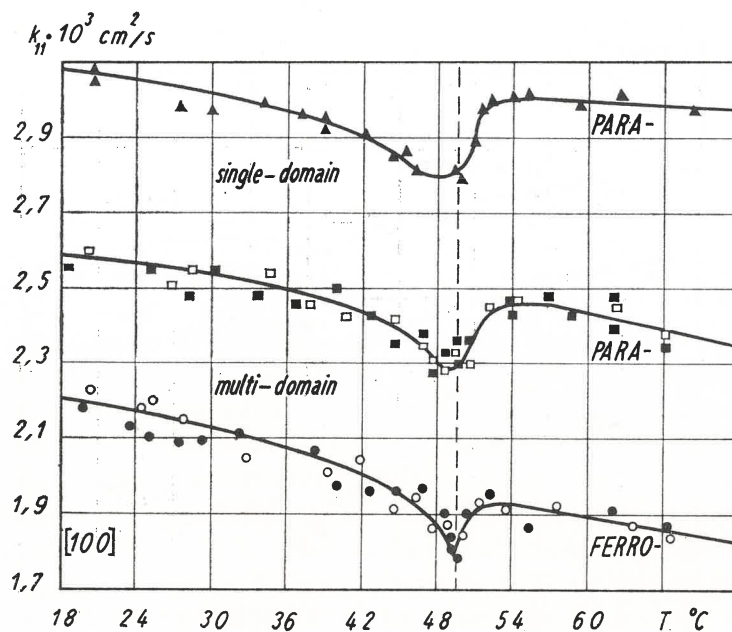

Fig. 4. Temperature-dependence of the thermal diffusivity coefficients k_{11} of multi-domain TGS crystals grown in the ferro- and para-electric phases and of permanently polarized single-domain crystals, for the direction [100]

Fig. 5. Temperature-dependence of the thermal diffusivity coefficients k_{22} of multi-domain TGS crystals grown in the ferro- and para-electric phases and of permanently polarized single-domain crystals, for the direction [010]
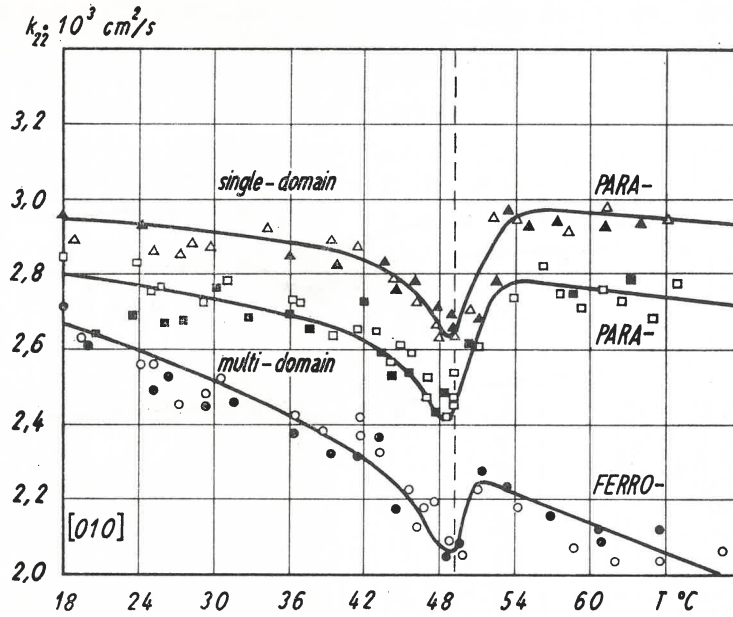

Fig. 6. Temperature-dependence of the thermal diffusivity coefficients k_{33} of multi-domain TGS crystals grown in the ferro- and para-electric phases and of permanently polarized single-domain crystals, for the direction [001]
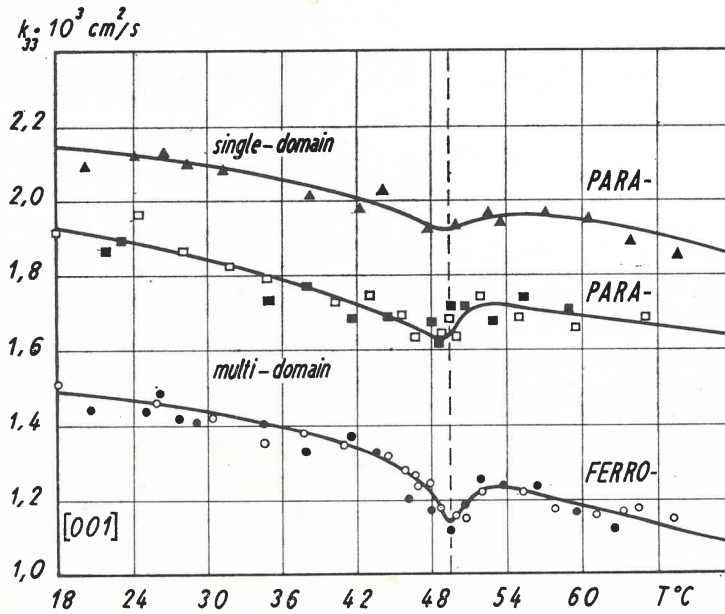
three principal directions remains the same despite the difference in growth conditions of the crystals.

The curves of Figs 4, 5 and 6 show the temperature-variations of the k-values of multi-domain crystals grown in various conditions in the ferro- and para-electric phases as well as of single-domain TGS crystals obtained by the method of permanent polarization, for the propagation directions [100], [010] and [001]. Multi-domain crystals grown in the ferroelectric phase are seen to have a lower thermal diffusivity than ones grown in the paraelectric phase. The largest thermal diffusivity, independently of the direction in which the crystal is cut, is exhibited by single-domain crystals. The k-values of paraelectrically grown crystals exceed at room temperature those of ferroelectrically grown ones by 19%, 4% and 26% respectively for the directions [100], [010], and [001]. The k-values of para-
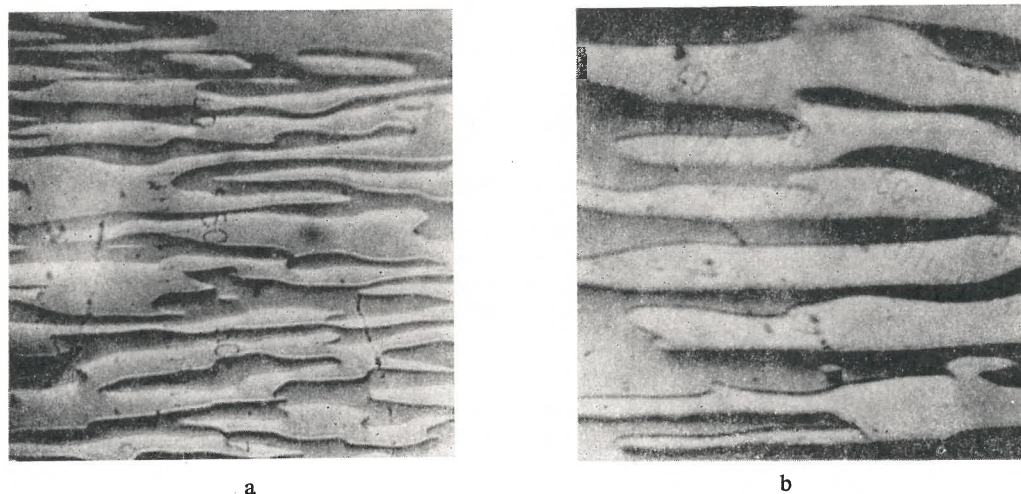

| a | b |

Fig. 7. Pattern of domain structure in TGS crystals grown in the ferroelectric phase (a) and paraelectric phase (b), observed at room temperature

electrically grown permanently polarized crystals exceed at room temperature those of ferroelectrically grown ones by 44%, 10% and 40% respectively for the directions [100], [010], and [001].

For a fuller investigation, patterns of the domain structure of TGS crystals were obtained at room temperature for growth in ferro- and para-electric phases. Etching technique was applied [33]. The pictures of Figs 7a, b show the domain configuration in the ferroelectric (7a) and paraelectric (7b) cases. The well noticeable differences in number of domain walls are due solely to the different conditions of growth.

4. Discussion of the results

The variations in thermal diffusivity coefficient k of TGS crystals observed by us corroborate the initially made assumption of an influence of growth conditions on the thermal diffusivity of these crystals.

Domain patterns of the TGS crystals used show a finer structure in ferroelectric-grown crystals, Fig. 7a, than in ones grown in the paraelectric phase, Fig. 7b. The domain walls in TGS crystals in the ferroelectric phase cause a marked scattering of the phonons, as results from a comparison of the curves of Figs 4, 5, and 6. As the number of domain walls increases, so does phonon scattering. A measure of phonon scattering is provided by their mean free path length $\bar{l}$. The thermal diffusivity coefficient can be expressed as follows:

$$k = \tfrac{1}{2}\bar{v} \cdot \bar{l} \tag{3.1}$$

where $\bar{v}$ is the mean velocity of the phonons corresponding to the mean propagation velocity of elastic waves in the crystal, and $\bar{l}$ is the phonon free path, averaged over all phonons. In order to obtain the most reliable numerical values of $\bar{l}$, ultrasonic wave velocities were measured in the TGS crystals at room temperature. Table I contains

TABLE I

Numerical values of the mean ultrasonic-waves velocities $\bar{v}$ and of the mean free path lengths $\bar{l}$ of phonons (at room temperature) in the three principal crystallographic directions for TGS crystals grown in the ferro- and in para-electric phases

Crystallographic directions	Mean velocities of ultrasonic waves in TGS crystals grown in:		Mean free path lengths of phonons in TGS crystals grown in:	
	ferroelectric phase $\bar{v}$ [cm/s]	paraelectric phase $\bar{v}$ [cm/s]	ferroelectric phase $\bar{l}$ [cm]	paraelectric phase $\bar{l}$ [cm]
[100]	4.98×10^5	5.12×10^5	1.36×10^{-8}	1.49×10^{-8}
[010]	4.30×10^5	4.34×10^5	1.89×10^{-8}	1.93×10^{-8}
[001]	4.00×10^5	4.02×10^5	1.16×10^{-8}	1.29×10^{-8}

the numerical values of $\bar{v}$ obtained for 6 MHz ultrasonic waves propagating in the directions [100], [010], and [001], as well as mean free paths, calculated for these directions from Eq. (3.1). The mean free paths $\bar{l}$ of phonons are found to be larger in TGS crystals grown in the paraelectric phase and shorter in ones grown in the ferroelectric phase. The largest differences in $\bar{l}$ are observed in the directions [100] and [001], whereas in the direction [010] the difference is negligibly small. A numerical comparison of the $\bar{l}$-values points primarily to a stronger scattering of phonons in crystals grown in the ferroelectric phases than in paraelectrically grown ones. The cause of these differences in $\bar{l}$ surely resides in the different numbers of domain walls in crystals grown in different conditions. The relatively large differences in mean free path of the phonons in the directions [100] and [001] may be due, in addition to the different number of domains, to the different geometry of the domains in the different crystallographical directions.

The occurrence of a varying thermal diffusivity in the paraelectric phase, in which domain walls are naturally absent, proves that the lattice defects previously localized in the walls subsist in the paraelectric phase. In the paraelectric range of temperatures, these defects are still a decisive factor of the different thermal diffusivity k of TGS crystals grown in different conditions. The presence in the paraelectric phase of defects stemming from

the domain walls of the ferroelectric phase is corroborated by the phenomena of TGS crystal repolarization at cooling from the paraelectric to the ferroelectric phase in the absence of an external electric field [34], residual pyroelectricity above the Curie point [30], and second harmonic voltage generation in nonlinear dielectric studies of these crystals in the paraelectric phase [35].

The present investigation and discussion permit the conclusion that the thermal diffusivity of TGS crystals is, at the least, indirectly dependent on the conditions of their growth, but is directly dependent on the number and geometry of domain walls present in the ferroelectric phase and the number and type of defects present in the paraelectric phase. The discrepancies of the numerical k-values reported in multi-domain TGS crystals according to the domain structure and defects suggest to us the thermal diffusivity k of
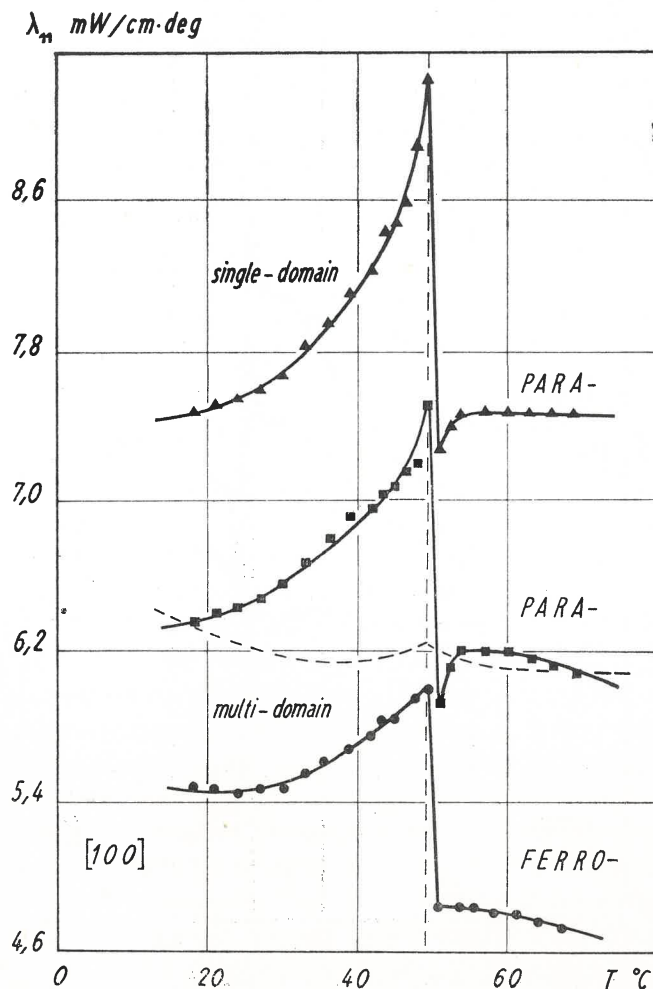

Fig. 8. Temperature-dependence of the thermal conductivity coefficient λ_{11} of multi-domain TGS crystals grown in the ferro- and para-electric phases and of permanently polarized single-domain crystals, for the direction [100]. The dashed line shows the results of Helvig and Albers [21]

single-domain crystals as the most reliable quantity for describing unsteady thermal processes in TGS. In the situation under consideration, multi-domain crystals should be considered as a physically heterogeneous material. The heterogeneity, in the ferro-electric phase, is due to the presence of domain walls having a structure and physical properties differing from those of the bulk of the domain.

Hitherto, investigations of unsteady processes in TGS crystals dealt chiefly with the thermal conductivity λ. For the sake of a comparison with the existing literature [8, 9, 17, 21], we calculated λ for our crystals from the relation:
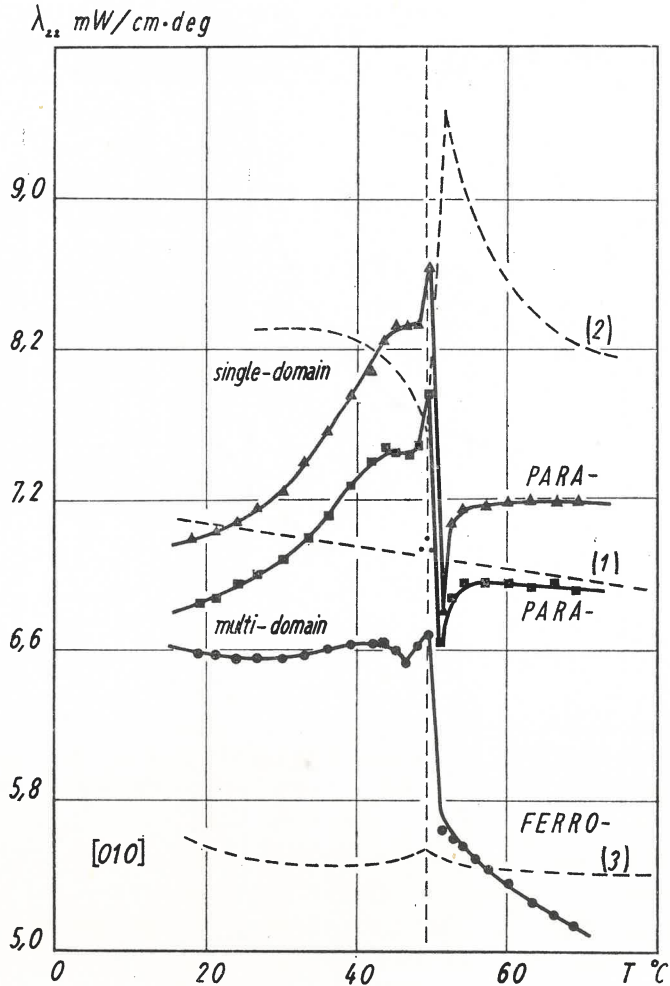
$$\lambda = k \cdot c_p \cdot \varrho \tag{3.2}$$

Fig. 9. Temperature-dependence of the thermal conductivity coefficient λ_{22} of multi-domain TGS crystals grown in the ferro- and para-electric phases, and of permanently polarized single-domain crystals, for the direction [010]. The dashed lines (1) and (2) show the results of Dimarova and Poplavko [8, 17]. The dashed line (3) shows those of Helvig and Albers [21]

where c_p is the specific heat of the crystal and ϱ its density. Numerical values of c_p, and its temperature-dependence, were taken from a paper by Strukov [36]. Curves showing the temperature-dependence of λ for conductivity in the directions [100], [010] and [001] are plotted in Figs 8, 9 and 10 respectively (continuous curves), where the results of Dimarova and Poplavko [8, 17] as well as of Helvig and Albers [21] are also plotted (dashed
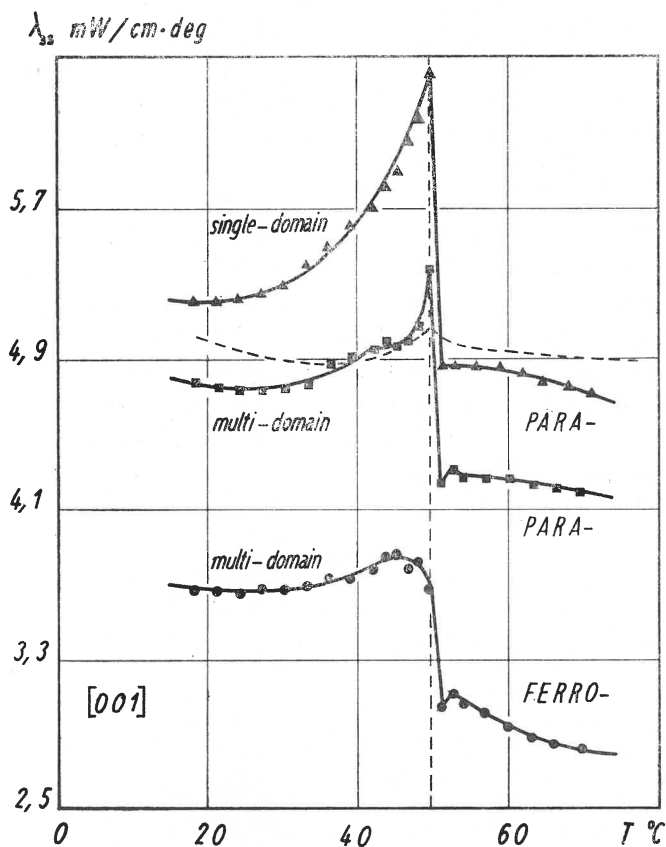

Fig. 10. Temperature-dependence of the thermal conductivity coefficients λ_{33} of multi-domain TGS crystals grown in the ferro- and para-electric phases, and of permanently polarized single-domain crystals, for the direction [001]. The dashed line shows the results of Helvig and Albers [21]

curves). The results of these authors diverge rather considerably, but can be brought to agreement by taking into account the effect of growth conditions and existing domain structure on the λ-value of TGS. The results obtained by Helvig and Albers [21] suggest that they must have been working on quite exceptionally aged crystals with a small number of domains. Those of Dimarova and Poplavko [8] show the authors to have performed their earlier work on TGS crystals grown in the paraelectric phase or at a temperature close to the phase transition point of TGS. More recent results of the same authors [17] suggest that they were using largely polarized crystals. Comparisons like these help to

clarify the source of discrepancies between the numerical λ-values reported for TGS, and prove the necessity of taking into consideration the conditions of growth of the TGS crystals as well as the configuration of their domains when defining numerical values of parameters representative of the physical properties of TGS crystals.

5. Conclusions

The results of the present study of the thermal diffusivity of TGS crystals grown in the ferro- and para-electric phases permit the conclusion that the conditions of growth are decisive in defining the thermal diffusivity and conductivity of the crystals. Independently of growth conditions, TGS crystals exhibit in the point of their phase transition a strongly marked and sharp minimum of thermal diffusivity in the three principal crystallographical directions. The differences in thermal diffusivity of TGS crystals and differences in mean free path of phonons in the ferrolectric phase are due both to a strong variability in number of domains according to the conditions of growth and to a different geometry of the walls according to the crystallographical direction. The variations in thermal diffusivity and in mean free path of phonons in the paraelectric phase are due to a varying concentration of defects, produced chiefly in the domain walls in the ferroelectric phase of the crystal.

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