EVALUATION OF DOMAIN WALL THICKNESS IN TGS CRYSTALS FROM THERMAL DIFFUSIVITY MEASUREMENTS

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In studies by the present authors on the differences in thermal diffusivity of single- and multi-domain TGS crystals in the three principal crystallographical directions, the behaviour of multi-domain TGS crystals with regard to non-steady thermal processes was shown to resemble that of heterogeneous solid two-phase systems, with one phase consisting of the bulk of the domains and the other of the domain walls. Here, by resorting to numerical values of the anisotropic thermal diffusivity coefficients of single- and multi-domain TGS crystals, we calculate the heterogeneity factor p of the system as well as the thermal diffusivity k^w of the walls, on the assumption of a limited anisotropicity of the latter. The heterogeneity factor of multi-domain crystals is found to amount to $p = 0.09$, and the thermal diffusivity coefficients of the walls at heat propagation in the direction [010] and [100] or [001] to $k^w_{22} = 1.39 \times 10^{-3}$ cm^2/s and $k^w_{11} = k^w_{33} = 0.96 \times 10^{-3}$ cm^2/s, respectively. From p and the known mean width of domains in TGS crystal, the mean wall thickness of domains results as $\bar{d} = 4.5 \times 10^{-6}$ cm.

1. Introduction

The determination of domain wall thickness in ferroelectric crystals is a rather complicated problem. Available model and phenomenological-theoretical considerations, as well as experimental studies, [1–12], lead to a thickness of 180° walls of the order of several lattice constants. The 90° walls occurring in polydirectional ferroelectrics only [13, 14] are somewhat thicker. Wall thickness data are mostly available for barium titanate, potassium phosphate, and Rochelle salt, but hardly at all for TGS. The thickness of 180° domains walls in TGS crystals was determined by Fousek [11] from considerations of Zhirnov [8] as being of the order of 10^{-6} cm whereas Petroff [15], by X-ray topography, obtained a value of about 5×10^{-6} cm.

Thermal diffusivity studies in the three principal directions of single- and multi-domain TGS crystals [16] have shown the presence of walls to affect the diffusivity value quite

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markedly. The behaviour of the thermal diffusivity with regard to an unsteady thermal process is such as to justify the treatment of the multi-domain crystals as heterogeneous systems. Once the diffusivity values of the single- and multi-domain crystals are known for the three principal directions, the heterogeneity factor p as well as the thermal diffusivity of the phase causing the heterogeneity can be calculated. The heterogeneity factor of multi-domain crystals in conjunction with the mean linear dimension of the domains (which is available from microscopic studies) permits evaluations of the mean thickness of the domain walls.

2. *Heterogeneity of multi-domain crystals, and thermal diffusivity of their domain walls*

Thermal diffusivity studies [16] of single- and multi-domain TGS crystals show an increase in number of domains to cause a marked decrease in the numerical values of the coefficients defining the diffusivity. The thermal diffusivity coefficients for the three principal crystallographical directions of TGS crystals determined at + 18°C are listed in Table I.

TABLE I

Numerical values of thermal diffusivity coefficients of single- and multi-domain TGS crystals measured at +18°C, from Ref. [16]

Crystallographical direction	Thermal diffusivity coefficients of:	
	single-domain crystals	multi-domain crystals
[100]	$k_{11}^{s} = 3.08 \times 10^{-3}$ cm²/s	$k_{11}^{m} = 2.57 \times 10^{-3}$ cm²/s
[010]	$k_{22}^{s} = 2.94 \times 10^{-3}$ cm²/s	$k_{22}^{m} = 2.80 \times 10^{-3}$ cm²/s
[001]	$k_{33}^{s} = 2.13 \times 10^{-3}$ cm²/s	$k_{33}^{m} = 1.92 \times 10^{-3}$ cm²/s

The differences in diffusivity *vs* the number of domains prove that, in studies bearing on unsteady processes, multi-domain TGS crystals can be dealt with as heterogeneous solid two-phase systems. A measure of their heterogeneity is conveniently provided by the parameter p, defined as follows:

$$p = \frac{V_w}{V_d} \tag{2.1}$$

where V_w is the volume of a domain wall, and V_d that of a domain. Assuming differences between the heat capacity and density of the bulk and walls of the domains to be negligible, the deficit in diffusivity of multi-domain crystals in comparison with single domain ones has to be attributed entirely to a difference between the thermal diffusivity of the bulk and walls of the domains.

An evaluation of the thermal diffusivity of domain walls can be performed by resorting to a simplified model of multi-domain crystal. In the microscopic pattern of domain structure in TGS crystals shown in Fig. 1, the domain walls visible in the plane (010) have the shape of more or less irregular lines. In our further considerations of heat transfer in such crystals,

and with the aim of simplifying our calculations, we shall assume these walls to represent sets of mutually parallel layers, perpendicular to the crystallographical directions [100] and [001]. Since the heterogeneity due to the presence of domain walls is relatively small, the differences in thermal diffusivity in the directions [100] and [001] will depend essen-

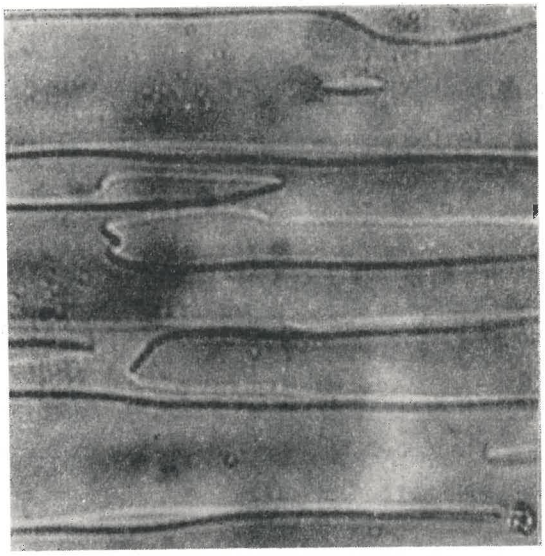

Fig. 1. Pattern of domain structure in TGS crystal observed at room temperature

tially on the presence of walls with surfaces perpendicular to the heat flux direction. The role of walls oriented parallel to the heat flux can be assumed to be negligible. As a further simplification, we shall assume the anisotropy in diffusivity of a wall to be of limited nature. Specifically, we shall assume the diffusivity of a wall in the ferroelectric direction [010] to differ from that of the same wall in the directions [100] and [001]:

$$k^w_{22} \neq k^w_{11} = k^w_{33}. \tag{2.2}$$

In particular, at heat flux parallel to [010] *i.e.* to the sides of the domain, the effective thermal diffusivity of the multi-domain crystal k^m_{22} will be given by the following expression involving the diffusivity of the single-domain crystal k^s_{22}, that of the domain wall k^w_{22}, and the heterogeneity factor p of the system:

$$k^m_{22} = (1-p) \cdot k^s_{22} + p \cdot k^w_{22}. \tag{2.3}$$

On the other hand, at heat flux parallel to [100] or [001] *i.e.* perpendicular to the sides of the domains, the respective thermal diffusivity coefficients take the form:

$$\frac{1}{k^m_{11}} = \frac{(1-p)}{k^s_{11}} + \frac{p}{k^w_{11}} \tag{2.4}$$

and

$$\frac{1}{k^m_{33}} = \frac{(1+p)}{k^s_{33}} + \frac{p}{k^w_{33}}. \tag{2.5}$$

Eqs (2.4) and (2.5) and the relations (2.2) yield, for the numerical diffusivity values k^s_{11}, k^s_{33}, k^m_{11}, and k^m_{33}, listed in Table I, the factor p as:

$$p = 1 - \frac{k^s_{11} \cdot k^s_{33} \cdot (k^m_{33} - k^m_{11})}{k^m_{11} \cdot k^m_{33} \cdot (k^s_{33} - k^s_{11})} = 0.090. \tag{2.6}$$

On inserting into (2.3), (2.4) and (2.5) the numerical value of p and those of the respective anisotropic thermal diffusivity coefficients for single- and multi-domain TGS crystals, we obtain the following values of thermal diffusivities of the domain walls:

$$k^w_{22} = \frac{k^m_{22} - k^s_{22} + p k^s_{22}}{p} = 1.39 \times 10^{-3} \text{ cm}^2/\text{s}, \tag{2.7}$$

and

$$k^w_{11} = k^w_{33} = \frac{p \cdot k^s_{11} \cdot k^m_{11}}{k^s_{11} - k^m_{11} + p \cdot k^m_{11}} = \frac{p \cdot k^s_{33} \cdot k^m_{33}}{k^s_{33} - k^m_{33} + p \cdot k^m_{33}} = 0.97 \times 10^{-3} \text{ cm}^2/\text{s}. \tag{2.8}$$

The calculated numerical values of thermal diffusivity coefficients of the domain walls are smaller by 50÷70 per cent respectively than those of the anisotropic diffusivity coefficients of the single-domain crystals.

3. *Mean domain wall thickness in TGS crystals*

For evaluating the mean thickness of domain walls in TGS crystal, one has to assume a domain shape geometrically simpler than the real shape revealed by direct microscopic observation. The domain structure pattern exemplified by Fig. 1 justifies the assump-

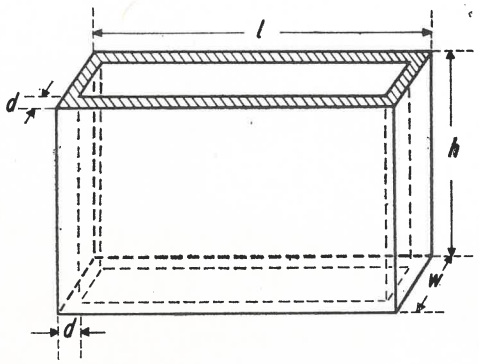

Fig. 2. Simplified model of ferroelectric domain used in the calculations of wall thickness

tion of a model domain in the shape of the perpendicular parallelepiped shown in Fig. 2. The heterogeneity p of this model is given by the expression:

$$p = \frac{w \cdot l \cdot h - (w - 2d)(l - 2d)}{w \cdot l \cdot h} \tag{3.1}$$

with the following notation: l, w, h — respectively length, width and height of the parallelepiped; d — wall thickness. On the realistic assumption of $d^2 \to 0$ and $l \gg w$, we obtain for the thickness d of the domain wall:

$$d = \tfrac{1}{2} \cdot p \cdot w. \tag{3.2}$$

On inserting in (3.2) the value $p = 0.09$ derived from our previous considerations and assuming after others [17–22] the domain width in TGS crystals as amounting on the average to $\bar{w} = 10^{-4}$ cm, we obtain a mean thickness of domain walls in TGS of $\bar{d} = 4.5 \times 10^{-6}$ cm, in accordance with Petroff's result derived by X-ray topography [15].

4. Discussion and conclusions

The relative differences in thermal diffusivity coefficients of single- and multi-domain TGS crystals, $\frac{(k^s - k^m)}{k^s} = \frac{\Delta k^{sm}}{k^s}$, for the conductance directions [100], [010] and [001], amount respectively to 0.17, 0.05 and 0.12. These values prove that the presence of domain walls plays an essential role in heat transfer phenomena in TGS crystals. The smallest differences $\frac{\Delta k^{sm}}{k^s}$ are found when the walls of the domains are parallel to the heat flux, and the largest differences $\frac{\Delta k^{sm}}{k^s}$ — when the heat flux is directed perpendicularly to the walls of the domains. Such large relative differences between the diffusivity coefficients of single- and multi-domain TGS crystals justify our treatment of the multi-domain TGS crystal as a heterogeneous solid two-phase system. This, in fact, was the starting point of the present paper.

According to the direction of heat propagation in the crystal, the values of thermal diffusivity coefficients of the walls are by 50÷70 per cent smaller than those of the anisotropic diffusivity coefficients obtained in single-domain crystals. This is in agreement with the general trend of the changes in thermal diffusivity of the crystals as the number of defects of their crystal lattice increases.

The mean wall thickness $\bar{d} = 4.5 \times 10^{-6}$ cm, evaluated from an analysis of thermal diffusivity data obtained in TGS crystals, results from the assumption of a mean domain width of the order of 10^{-4} cm. The domain structure of TGS crystals depends on numerous factors, in particular conditions of growth, thermal processing, and the state of ageing [20, 21]. In the present work, thermal diffusivity was studied in crystals grown in the paraelectric phase and rejuvenated previous to measurement. Such crystals have a fine domain structure, with a small mean domain width. By etching the surface perpendicular to the direction of the ferroelectric axis [010], the mean width of a domain could be evaluated at 10^{-3} cm. The considerably finer dew method [19] revealed rather numerous domains of a mean width of the order of 10^{-4} cm. The few available reports of domain structural studies in TGS by electron microscope technique have permitted the observation of domains with a mean width of $10^{-4} \div 10^{-5}$ cm [18, 22]. The choice of the best mean

width of domains in TGS crystal thus remains controversial. The real thicknesses of the walls can vary rather widely. This is corroborated, among others, by the results of dispersion studies of dielectric permittivity in TGS crystals in the microwave region. Kaczmarek [23] observed dispersional variations in dielectric permittivity of TGS crystals as a result of resonance vibrations of their domain walls, in accordance with suggestions of Kittel [24]. The resonance vibrations of the walls ranged over a relatively wide interval of frequencies, from 10^9 to 10^{11} Hz, a fact that is accessible to interpretation by differences in thickness of the walls in the crystals under consideration.

The values of wall thicknesses available in the literature are essentially mean values, resulting from indirect studies. In this respect, the method of domain wall thickness evaluation from thermal diffusivity applied by us here, does not differ from earlier methods. However, it is highly plausible that this method, applied to ferroelectric crystals, the domain structure of which is geometrically of a much better defined nature, will permit a more accurate evaluation of the thickness of their domain walls.

REFERENCES

[1] W. Kaenzig, R. Sommerhalder, *Helv. Phys. Acta*, **26**, 603 (1953).
[2] H. M. Barkla, D. M. Finlayson, *Phil. Mag.*, **44**, 109 (1953).
[3] W. J. Merz, *Phys. Rev.*, **95**, 690 (1954).
[4] W. Kinase, H. Takahashi, *J. Phys. Soc. Japan*, **10**, 942 (1955).
[5] W. Kinase, *Progr. Theor. Phys.*, **13**, 529 (1955).
[6] W. Kinase, H. Takahashi, *J. Phys. Soc. Japan*, **12**, 464 (1957).
[7] I. Furuichi, T. Mitsui, *Phys. Rev.*, **80**, 93 (1950).
[8] V. A. Zhirnov, *Zh. Eksper. Teor. Fiz.*, **35**, 1175 (1958).
[9] I. I. Ivanchyk, *Fiz. Tverdogo Tela*, **3**, 3731 (1961).
[10] L. N. Bulaevskii, *Fiz. Tverdogo Tela*, **5**, 3183 (1963).
[11] J. Fousek, *Japan J. Appl. Phys.*, **6**, 950 (1967).
[12] V. Dvorak, V. Janovec, *Japan J. Appl. Phys.*, **4**, 400 (1965).
[13] E. A. Little, *Phys. Rev.*, **98**, 978 (1955).
[14] L. P. Kholodenko, *Fiz. Tverdogo Tela*, **3**, 3142 (1961).
[15] J. F. Petroff, *Phys. Status Solidi*, **31**, 285 (1969).
[16] T. Krajewski, F. Jaroszyk, *Acta Phys. Polon.*, **A43**, 831 (1973).
[17] V. P. Konstantinova, *Kristallografiya*, **7**, 748 (1962).
[18] L. Taurel, F. Gilletta, *Proc. Int. Meeting Ferroelectricity*, Prague, **2**, 43 (1966).
[19] M. Šafrankova, J. Fousek, J. Kaczer, *Proc. Int. Meeting Ferroelectricity*, Prague, **2**, 51 (1966).
[20] J. Stankowska, *Acta Phys. Polon.*, **31**, 527 (1967).
[21] V. P. Konstantinova, J. Stankowska, *Kristallografiya*, **16**, 158 (1971).
[22] B. Hilczer, C. Pawlaczyk (private communication).
[23] F. Kaczmarek, *Acta Phys. Polon.*, **A38**, 393 (1970).
[24] C. Kittel, *Phys. Rev.*, **83**, 458 (1951).