THERMAL CONDUCTIVITY OF TGS CRYSTALS DOPED WITH Fe^{3+} IONS

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The thermal conductivity of single-domain TGS crystals, pure as well as Fe^{3+}-doped at various concentrations, was studied in the three principal crystallographic directions applying the comparative method. Dealing with the doped single-domain TGS crystals in the process of heat transfer as solid two-phase systems, with the one phase consisting of the pure crystal lattice and the other of cubic regions distorted by the presence of Fe^{3+} ions, the magnitude of these regions and their thermal conductivity was evaluated. By comparing the results obtained for thermal conductivity and thermal diffusivity of pure and Fe^{3+}-doped TGS crystals, the relative variations of their specific heat due to the presence of foreign Fe^{3+} ions were determined.

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1. Introduction

Studies of thermal conductivity (ThC) and thermal diffusivity (ThD) in pure and doped TGS crystals [1–11] have shown these quantities to be strongly dependent on the actual domain structure of the crystal and the amount and type of the dopands present in their crystal lattice. Dikant [6] was the first to study the influence of Fe^{3+} ions on the ThD of TGS crystals in the ferroelectric [010] direction. At room temperature, he observed a ca. 20% decrease in numerical value of the ThD coefficient; this, however, was due to the Fe^{3+} ions as well as the multi-domain structure of the crystals investigated. More highly univocal results were obtained with crystals polarized permanently previous to measurement [10]; in this way, it was possible i.a. to evaluate the magnitude of the cubic regions distorted in the TGS lattice by the presence of Fe^{3+} ions.

The simplifying assumption that the specific heat of the pure lattice and the distorted regions is the same is, however, a source of error when evaluating the magnitude of the latter from ThD measurements. In order to determine the degree to which the magnitude

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in question is affected by the specific heat value of distorted regions taken as distinct from that of the pure lattice, we performed a ThC measurements of pure and Fe^{3+} ion doped TGS crystals. The results were then compared with those of earlier ThD studies [10] of the same crystals. The comparison permits, in this case as well, the determination of the relative changes in specific heat of the doped crystals versus the concentration of the foreign ions introduced. With the inhomogeneity coefficient of the two-phase system available, it is also possible to evaluate the specific heat of the distorted regions thus gaining information concerning the degree of their rigidification compared to the surrounding lattice.

2. Preparation of the crystals, and measuring method

TGS crystals were grown from aqueous solutions of the salts by the isothermal method (the ferroelectric phase) at 43°C. Crystals doped with Fe^{3+} ions were obtained from aqueous solutions containing $Fe_2(SO_4)_3 \cdot nH_2O$ at concentrations of 0.5; 1; and 2 percent weight of Fe in the solution. Rods were cut in the three principal crystallographic directions in accordance with the coordinates proposed by Konstantinova et al. [12]. The cylindrical crystal rods, 4 mm in diameter and of a lenght of 15 mm, had two holes bored in them into which copper-constantan measuring micro-thermocouples were introduced. The holes were localized so that the temperature gradient, measured along the axis of the cylinder, was independent of their position [13].

The Fe^{3+} ion concentration in the crystals was determined by the method of absorption spectrum analysis [14]. The Fe^{3+} concentrations obtained with 0.5; 1; and 2 percent weight of iron in the initial solutions amounted to 6; 10; and 18×10^{-4} percent weight, respectively.

ThC was measured by the comparative method [15]. The rod was placed between a plate and a cylinder, made of fused quartz SiO_2. The quartz plate served to determine the magnitude of the heat flux through the crystal studied, and the quartz rod for stationarity control of the flux. The latter was produced by a micro-heater, fixed with adhesive to the quartz plate. The two quartz standards were provided with measuring copper-constantan micro--thermocouples and placed, together with the TGS crystal, inside a modified vacuum holder [16]. The ThC coefficient for the fused SiO_2 used as standard was assumed after Ref. [17].

3. Results and discussion

The ThC coefficient of pure and Fe^{3+}-doped single-domain TGS crystals was determined at 25°C for the three principal crystallographic directions. All crystals were studied in the single-domain state only, subsequent to permanent polarization in an external electric field. With increasing Fe^{3+} concentration, the ThC decreases by $24 \div 26$; $33 \div 38$; and $45 \div 51$ percent respectively for Fe^{3+} ion concentrations of 6×10^{-4}; 10×10^{-4}; and 18×10^{-4} percent weight. The ThC values for the three directions [100], [010] and [001] are given in Table I where, for comparison, the ThC values obtained by Helwig and Albers [4] for multi-domain pure TGS crystals are also given.

TABLE I

Numerical values of the thermal conductivity coefficients λ for pure and Fe^{3+}-doped TGS crystals at 25°C

Fe^{3+} dopands concentration in TGS crystal in percent weight × 10^4	Thermal conductivity coefficients λ [W/m deg] in the crystallographic direction			
	[100]	[010]	[001]	
0	0.628	0.550	0.500	After [4]
0	0.775	0.726	0.714	From this work
6	0.567	0.548	0.540	From this work
10	0.515	0.446	0.439	From this work
18	0.425	0.352	0.345	From this work

All TGS crystals, pure as well as Fe^{3+}-doped, had been grown under identical conditions in the ferroelectric phase. The influence of domain walls on the ThC eliminated by permanent polarization of the crystals in an external electric field. Hence, the changes in ThC of our crystals can be assumed to be due exclusively to the presence of foreign Fe^{3+} ions in the crystal lattice. Studies on the ThC and ThD of doped crystals have shown that the above coefficients depend on the type of the dopands and decrease with increasing concentration of the latter. The relative great decrease of ThC in Fe^{3+}-doped TGS crystals compared to pure ones suggests the possibility of their formal treatment as solid two-phase systems, the one phase consisting of the pure TGS lattice and the other of cubic regions distorted by the presence of Fe^{3+} ions. The ThC of the two phases is, obviously, different. Thus, on this very simple model of a single domain Fe^{3+}-doped TGS crystal, one can proceed to determine the size of the distorted regions from anisotropic measurements of the ThC as function of the Fe^{3+}-ion concentration in the crystal lattice. Assuming, as done in Refs [7, 9, 10], the Fe^{3+} ion distribution as isotropic and the distorted region as cubic, the effective ThC λ^{eff} of the doped crystal can be expressed in the form:

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

with λ^{p} the ThC of the pure crystal and λ^{d} that of a distorted region. The coefficient $x^3 = p = \Delta V/V$ is the ratio of the volume ΔV of all distorted regions and the total volume V of the crystal and, thus, provides a measure of its inhomogeneity. The anisotropy of ThC pure and deped TGS crystals is relatively small, particularly for the directions [010] and [001]. Hence it can be assumed that, in these directions specifically, the distorted regions are isotropic with regard to their ThC. Having available the ThC coefficients $\lambda^{\mathrm{p}}_{22}$ and $\lambda^{\mathrm{p}}_{33}$ of pure TGS crystals and the effective ThC coefficients $\lambda^{\mathrm{eff}}_{22}$ and $\lambda^{\mathrm{eff}}_{33}$ of deped ones, one can determine the value of $x^3 = p$ on assuming $\lambda^{\mathrm{d}}_{22} = \lambda^{\mathrm{d}}_{33}$. The lenght of the edge of a cubic distorted region in TGS is then obtained from:

$$d = \left(\frac{100Ap}{wCN}\right)^{1/3} \tag{3.2}$$

where A is the atomic weight of the dopand, w the specific weight of the crystal, C the dopands concentration in percent weight, and N Avogadro's number. Depending on the Fe^{3+} concentration, the edge of the cubic distorted region was determined as amounting to $d = 9 \div 12$ nm, in agreement with the results obtained for the same crystals from ThD studies [10].

The values of the inhomogeneity coefficient p and edge of the cubic distorted region d obtained by us versus the Fe^{3+} concentration are given in Table II, together with the values obtained for p and d from ThD measurements of the same crystals [10]. The fact that the values compared are in good agreement shows that the two methods of evaluating these quantities from studies of heat transfer phenomena in crystals doped with foreign ions are equivalent.

TABLE II

Numerical values of inhomogeneity parameters p and linear dimensions d of TGS lattice regions distorted by Fe^{3+} ions, calculated from thermal conductivity and thermal diffusivity measurements

Fe^{3+} dopands concentration in TGS crystal in percent weight $\times 10^4$	Inhomogeneity parameter $x^3 = p = \Delta V/V$ obtained from:		Edge length of distorted region d [nm] obtained from:	
	thermal conductivity	thermal diffusivity	thermal conductivity	thermal diffusivity
6	0.20	0.18	12.2	11.8
10	0.27	0.20	11.4	10.3
18	0.29	0.24	9.4	9.0

The ThC coefficient λ and ThD coefficient k are related simply, as follows:

$$\lambda = \varrho c k, \tag{3.3}$$

where c is the heat capacity of the crystal and ϱ its density. With the values of λ, k and ϱ available for pure and Fe^{3+}-doped TGS crystals, we applied Eq. (3.3) to determine c and its dependence on the Fe^{3+} ions admixtured to the crystal. The results, obtained for 25°C, are shown in Table III. A comparison of the c values obtained by Strukov [18] for pure TGS

TABLE III

Heat capacity values c of pure and Fe^{3+}-doped TGS crystals calculated from thermal conductivity and thermal diffusivity measurements

Fe^{3+} dopands concentration in TGS crystal in percent weight $\times 10^4$	Heat capacity $c \times 10^{-3}$ J/kg deg calculated from thermal conductivity and thermal diffusivity measurements:
0	1.27
6	1.08
10	1.00
18	0.82

from calorimetric measurements and our c values calculated from Eq. (3.3) from ThC and ThD measurements shows that the latter are by about 15% smaller than the c measured calorimetrically. The difference is due mainly to the nonstationarity of the Ångstroem method applied in the ThD studies.

The introduction of Fe^{3+} ions causes a rigidification of the TGS lattice. As a result, the heat capacity is lowered compared to that of pure TGS crystal. From the studies performed, the decrease amounts to 15; 20; and 30 percent for Fe^{3+} concentrations of 6×10^{-4}; 10×10^{-4}; and 18×10^{-4} percent weight, respectively. Having available the heat capacity values of the pure and doped TGS crystals as well as the inhomogeneity parameter values p for various Fe^{3+} concentrations, we evaluated the heat capacity of the distorted regions, finding it to be by one order of magnitude lower than that of the pure crystal lattice. This points to a rather strong mechanical rigidification of the distorted lattice regions containing foreign Fe^{3+} ions.

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