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Thermal Diffusivity of Pure and Doped TGS Crystals

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ABSTRACT. The thermal diffusivity of pure and doped TGS crystals is measured from 30 to 80°C. The effect of heat treatment upon the thermal diffusivity of pure crystals exemplified the necessity of sample annealing before carrying out any measurements. The main features of the temperature dependence of thermal diffusivity in both ferroelectric and paraelectric phases are discussed. It is found that the valency and ionic radii of the dopant have a considerable effect on the obtained results.

The available experimental data of thermal diffusivity of TGS crystals are scarce. Previous studies of thermal diffusivity of pure and doped TGS crystals have shown this parameter to be strongly dependent upon the condition of growth (Krajewski and Jaroszky 1973a), the actual domain structure of the crystal (Krajewski and Jaroszyk 1973b), and the concentration of foreign ions in the crystal (Dikant 1973 and Krajewski and Riad 1975).

In the present investigation thermal diffusivity measurements were made on two groups of doped TGS crystals as well as on pure ones from 30 to 80°C. The first group was doped with one of the following divalent ions: Ni^{2+}, Co^{2+} and Cu^{2+}. The second group was doped with one of the trivalent ions Fe^{3+} and Cr^{3+}. This was done in the hope of shedding light on the effect of ionic radii and the valency of the dopant upon the thermal diffusivity of TGS crystals.

Experimental

Samples

Pure and doped TGS crystals, for the present study, were grown by the authors (Gaffar and Abu El-Fadl 1984a) from aqueous solutions using continuous

slow cooling technique in ferroelectric phase at ~44°C. All crystals were multidomain single crystals. The concentration of foreign ions in doped crystals was 200 ± 20 ppm. The lattice parameters and the density of pure as well as doped TGS crystals are given in Table 1.

Table 1. The lattice parameters and the density of pure and doped TGS crystals.

Sample	a, (Å) ± 0.001	b, (Å) ± 0.001	c, (Å) ± 0.001	β, ° ± 0.01	ρ Measured density, (g/cm^3) ± 0.001
Pure TGS	9.167	12.640	5.729	105.58	1.689
TGS + Ni^{2+}	9.132	12.634	5.727	105.97	1.691
TGS + Co^{2+}	9.162	12.642	5.717	105.60	1.674
TGS + Cu^{2+}	9.174	12.638	5.714	105.72	1.685
TGS + Cr^{3+}	9.182	12.638	5.727	105.82	1.672
TGS + Fe^{3+}	9.171	12.633	5.723	105.59	1.698

Samples of approximate dimensions $10\times10\times2.5$ mm^3 with the short dimension parallel to one of the three principal crystallographic axes, a, b and c were cut from the grown crystals. Each sample was provided with a copper constantan thermocouple carefully adhered in a small scratch on one surface of the specimen. To enhance the absorption of thermal radiation the other surface was painted black by a thin layer of aquadag solution.

Measurements

The thermal diffusivity (α) of TGS crystals has been measured using the plane temperature wave technique. The apparatus and experimental procedure were described elsewhere (Gobrial *et al.* 1977). In pure crystals, measurements were carried out along the principal crystallographic axes, a, b and c. On doped crystals the measurements were restricted to the ferroelectric polar axis (b-axis).

The thermal diffusivity results obtained on a painted specimen agree well with those for an unpainted one, showing that the painting layer had - almost - no effect on thermal diffusivity of the bulk material. The maximum error in the thermal diffusivity measurement was less than 3%.

Results and Discussion

Pure TGS Crystals

Initial measurements of thermal diffusivity were made at temperatures increasing from 30 to 80°C. Subsequent measurements with decreasing temperature gave thermal diffusivity values different from those obtained initially. Typical behaviour of thermal diffusivity values along the b-axis when taken through heating and cooling cycle is shown in Fig. 1. The total time taken over a heating and cooling cycle was typically about 50 hr. As the temperature of the TGS crystal is raised through the Curie temperature (T_c) the thermal diffusivity passes through a pronounced λ shaped minimum. As seen from Fig. 1 the diffusivity values

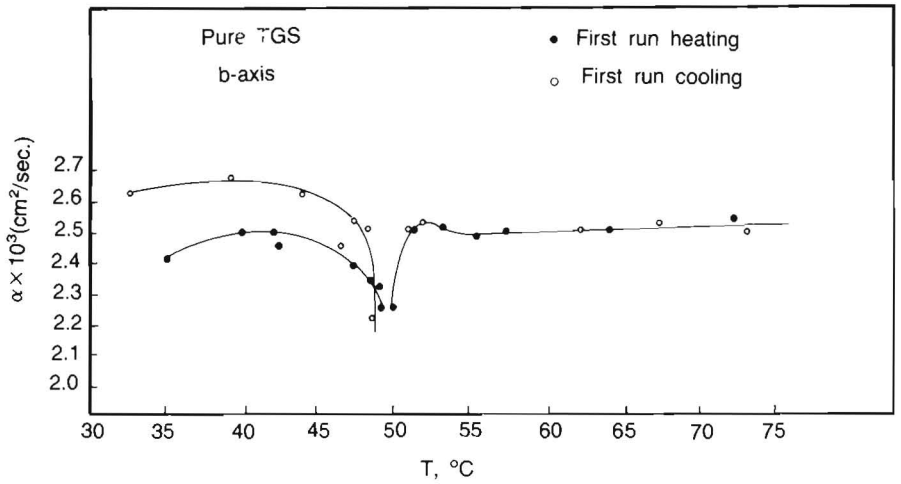

Fig. 1. Typical behaviour of thermal diffusivity of TGS crystals. The values given were taken along the b-axis through heating and cooling cycle.

measured upon cooling are different from those masured prior during heating. The difference is significant (more than 10%) in the ferroelectric phase, while it is within the experimental error in the paraelectric phase. Furthermore, in the ferroelectric phase, α(T) values obtained during cooling are higher than those obtained during heating. This behaviour may be attributed to the induced strains. It was reported that the occurrence of these strains increases the thermal diffusivity, due to the increase of the internal energy of the sample (Mebed *et al.* 1981). It is interesting to mention that the same behaviour was also observed

during the measurements of electrical conductivity and dielectric constant (Gaffar and Abu El-Fadl 1984b). With repeated heating and cooling cycles the reproducibility of the obtained results was satisfactory.

A temperature hysteresis effect was noticed when the sample was heated through the phase transition temperature T_c. It was observed that the transition temperature was shifted towards higher or lower temperatures when the crystal was heated or cooled respectively through the transition. In our opinion this shift, which does not exceed 0.6°C, may be attributed to the fact that cooling through the transition could produce strains in the lattice which would not anneal out at lower temperatures. With repeated heating and cooling cycles the minimum depth became progressively lower and less sharp. In addition, the magnitude and the direction of the shift remained unchanged.

Figures 2, 3 and 4 show the temperature dependence of (α) along the principal crystallographic axes, a, b and c respectively. Smooth curves were drawn through

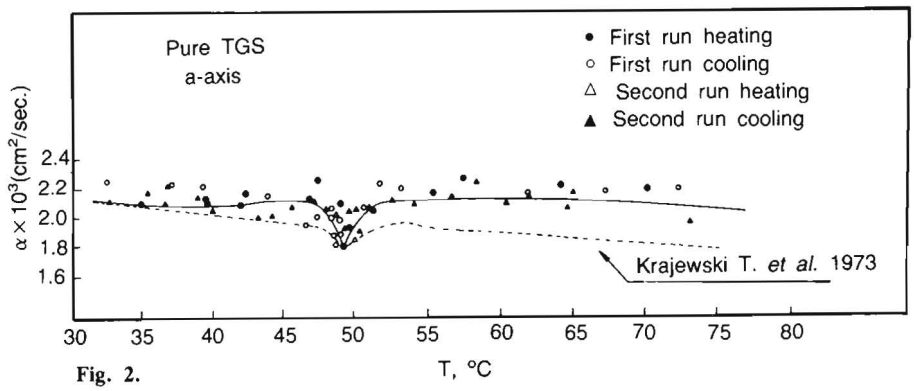

Fig. 2.

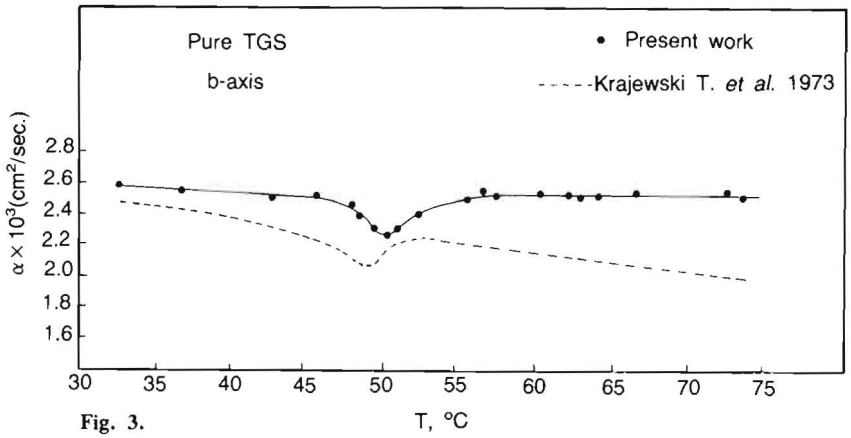

Fig. 3.

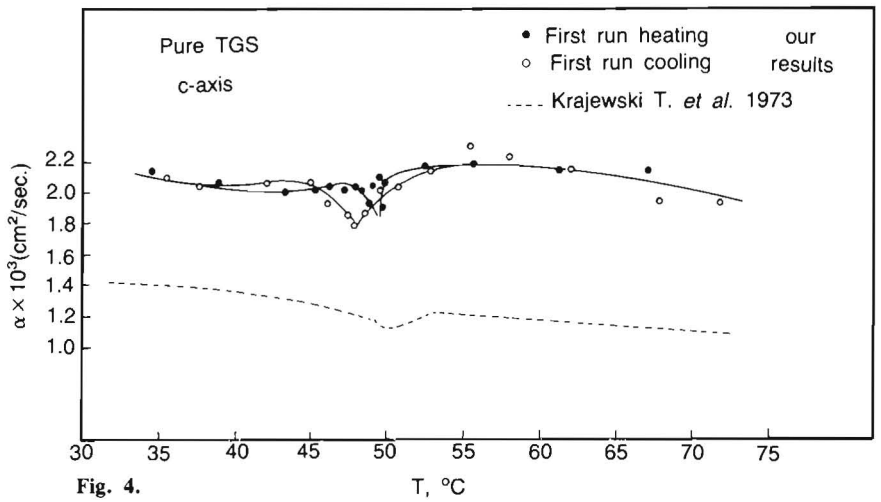

Fig. 4.

Figs. 2,3 and 4. The temperature dependence of thermal diffusivity of a pure TGS crystal along the three principal crystallographic axes, a,b and c.

all points obtained for each sample with maximum point scattering 2% from the curve. All curves exhibit a similar behaviour near the transition temperature.

An initial search in the literature revealed only one set of thermal diffusivity results on multidomain TGS crystals. Curves representing these values (due to Krajewski and Jaroszyk 1973a) is included in Figs. 2,3 and 4 for sake of comparison. It is clear that our $\alpha(T)$ values are, in general, higher than those of Krajewski. This behaviour may be attributed to the differences in either impurity concentration levels or thermal histories between the crystals. Nevertheless the results for our crystals along a and b axes below T_c agree roughly with the Krajewski curves for crystals with various thermal histories and growth conditions.

Regarding the c-axis, the difference between our results and those of Krajewski is surprisingly large and obviously cannot be related to inaccuracy of the experiment. In our opinion, the samples used by Krajewski were impure. Therefore the non uniform distribution occurring by localized preferential incorporation of the impurities along this axis might provide a possible explanation (Loiacono and Kostecky 1981).

Doped TGS Crystals

The temperature dependence of thermal diffusivity of TGS crystals doped with one kind of the following ions Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+} and Cr^{3+} are shown in

Figs. 5,6 and 7 respectively. Shown therein are our results of pure crystals along the b-axis for comparison. There are three features to be noted from our results.

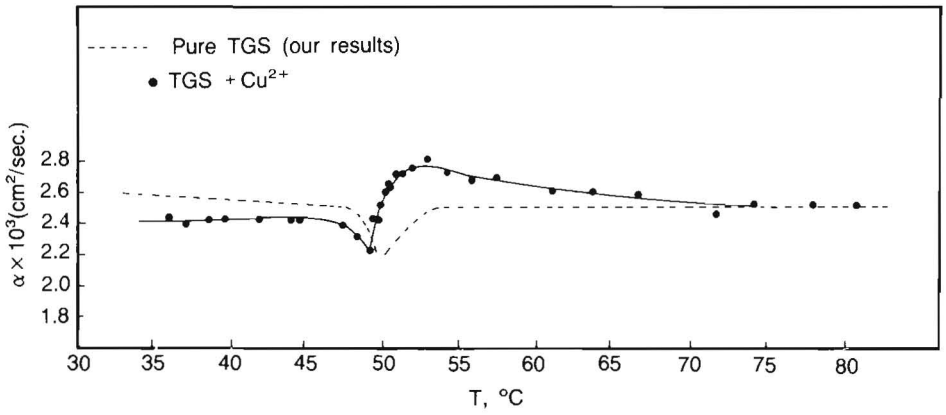

Fig. 5. The temperature dependence of thermal diffusivity of a TGS crystal doped with Cu^{2+} ions.

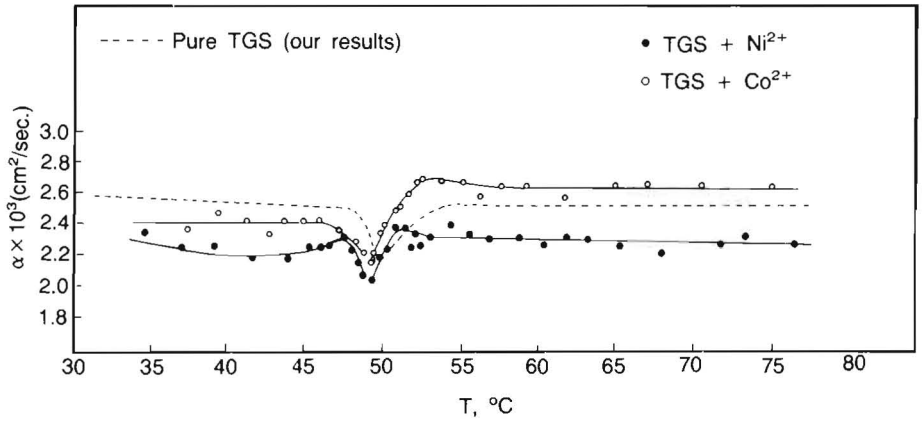

Fig. 6. The temperature dependence of thermal diffusivity of TGS crystals doped with either Ni^{2+} or Co^{2+} ions.

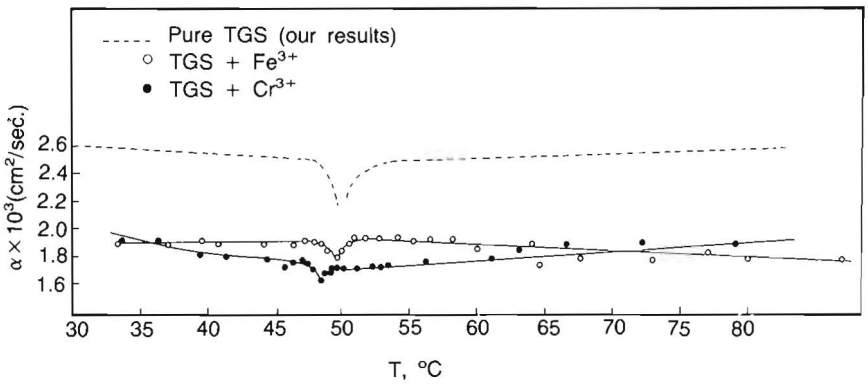

Fig. 7. The temperature dependence of thermal diffusivity of TGS crystals doped with either Fe^{2+} or Cr^{+3} ions.

a) All curves exhibit a similar temperature dependence near T_c. The decrease of the transition temperature due to the presence of foreign ions is easily seen. This behaviour is qualitatively in accordance with the observations of Stankowska (1967) and Polovinko *et al.* (1980).

b) In the ferroelectric phase the thermal diffusivity results of all doped TGS crystals are lower than those of pure crystals. It is clear that trivalent ions reduce the diffusivity more than divalent ions. Similarly albeit a larger decrease in thermal diffusivity values was reported previously for TGS crystals doped with either Cu^{2+} ions (Krajewski and Riad 1975) or Fe^{3+} ions (Dikant 1973). The concentration level of foreign ions in these crystals was higher than in ours. Therefore a quantitative comparsion is not useful.

c) In the paraelectric phase, the thermal diffusivity values of TGS crystals doped exclusively with Co^{2+} or Cu^{2+} ions are higher than those of pure one. The reason for this behaviour is not clear. Nevertheless, this behaviour seems to suggest a relation between the thermal diffusivity and the bonding forces of the foreign ions with the crystal lattice.

The lattice of the doped crystals could be considered as a two phase system. The first phase is predominant and consists of the unperturbed lattice of TGS. The second is composed of perturbed regions due to the presence of foreign ion admixtures. Using the model of spherical perturbed regions (Maxwell 1973, Carslow and Jeager 1959 and Jaroszyk 1980), the average length (d) of these distorted regions could be calculated from the relation:

$$d = \left(\frac{100\ A.P_c}{\rho.\ C.N.}\right)^{1/3} \quad (1)$$

where A is the molar mass of the admixture,
N is Avogadro's number,
C is the admixture concentration,

$$P_c = \frac{\alpha_{pure} - \alpha_{doped}}{\alpha_{pure}} = \triangle\alpha/\alpha_{pure}$$

The calculated "d" values for doped TGS crystals in the ferroelectric phase at 40°C are tabulated in Table 2.

Table 2. The calculated "d" values for doped TGS crystals in the ferroelectric phase at 40°C.

The dopant ion	Admixture concentration C	Ionic radii of the dopant (Å)	$\triangle\alpha/\alpha_{pure}$	(d) (Å)
Cr^{3+}	200 ± 20 ppm	0.63	0.315	200
Fe^{3+}	,,	0.64	0.291	198
Ni^{2+}	,,	0.69	0.140	7.4
Cu^{2+}	,,	0.72	0.040	1.1
Co^{2+}	,,	0.72	0.040	1.1

It can be seen, from Table 2, that the ratio $\triangle\alpha/\alpha_{pure}$ decreases with a slight increase of the ionic radii of the dopant. This result is not expected, since it is plausible to assume that at fixed concentration level of foreign ions in TGS, the smaller the ionic radii of the dopant the smaller the size of the distorted regions and consequently the smaller the variation in the ratio $\triangle\alpha/\alpha_{pure}$. Furthermore, the scattering of phonon waves (wave length $\geqslant$ 200 Å) is relatively small in crystals doped with Cu^{2+}, Co^{2+} or Ni^{2+} ions when compared with crystals doped with Cr^{3+} or Fe^{3+} ions. It seems, therefore, likely to attribute the observed variations in thermal diffusivity values to the differences in valence and ionic radii of the dopant.

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الانتشارية الحرارية لبلورات كبريتات ثلاثي الجليسين نقية وأخرى مطعمة بالشوائب

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يعالج هذا البحث تأثير إضافة بعض الأيونات ثنائية وثلاثية التكافؤ بتركيز صغير إلى بلورات كبريتات ثلاثي الجليسين على الإنتشارية الحرارية لهذه البلورات.

تم إنماء البلورات التي استخدمت في هذه الدراسة من محلول مائي في طور الفروكهربية بطريقة التخفيض المستمر لدرجة حرارة المحلول بدءاً من ٤٤ درجة مئوية تقريباً. اتخذت العينات التي جرت عليها القياسات شكل متوازي مستطيلات أبعاده ٢,٥×١٠×١٠ مليمتر مكعب بحيث يكون البعد الأصغر في اتجاه أحد المحاور البلورية الأساسية الثلاث. ثبت ازدواج حراري على أحد الوجهين الكبيرين للعينة بينما غطى الوجه الآخر لها بطبقة رقيقة من محلول الإكواداج لزيادة قدرة العينة على امتصاص الإشعاع الحراري وقد ثبت أنه لا تأثير لوجود هذه الطبقة على النتائج العملية للبلورات.

استخدمت طريقة الموجات الحرارية المستوية في قياس الانتشارية الحرارية حيث أجريت القياسات في الاتجاهات البلورية الثلاث في حالة العينات النقية بينما اقتصر القياس على إتجاه المحور القطبي في حالة العينات المطعمة بالشوائب.

أظهرت النتائج أن السلوك العام للانتشارية الحرارية للبلورات النقية مماثل لما تعطيه الأبحاث السابقة بينما يكون هناك اختلاف في القيم العددية يرجع إلى الإختلاف في درجة نقاء العينات المستخدمة والمعالجات الحرارية التي أجريت لها، والظروف التي خضعت لها عملية الإنماء البلوري، بالإضافة إلى الإختلاف في تركيب المناطق الفروكهربية من عينة إلى أخرى. لوحظ أيضاً أن قيم الانتشارية الحرارية تختلف في الإتجاهات البلورية الثلاث، الأمر الذي يعتبر منطقياً. يظهر بوضوح

الانتقال الطوري حيث تتغير قيمة الانتشارية الحرارية بطريقة مماثلة لتغير خواص التوصيل والعزل الكهربي لهذه البلورات عند درجة حرارة الانتقال الطوري.

أثبتت النتائج العملية أن المعالجات الحرارية التي أجريت للعينات المستخدمة في هذه الدراسة ضرورية لتكرار الحصول على نفس القيم للانتشارية الحرارية في التجارب المتعاقبة. لوحظ وجود عروة تخلف حراري عرضها حوالي ٠,٦ درجة قد يعزى وجودها إلى الإجهادات التي تنشأ عند تبريد العينة مروراً بدرجة حرارة الانتقال T_c.

لوحظ اختلاف درجة حرارة الانتقال وانخفاض قيمة الانتشارية الحرارية في طور الفروكهربية في حالة العينات المطعمة بالشوائب عنها في حالة البلورات النقية، وتتميز بتأثير أكبر في هذا الشأن البلورات المطعمة بأيونات ثلاثية التكافؤ عن البلورات المطعمة بأيونات ثنائية التكافؤ. لوحظ في طور الباراكهربية أن قيم الانتشارية الحرارية ـ في حالة العينات المطعمة بالكوبلت والنحاس على وجه الخصوص ـ أعلى من قيمها في حالة البلورات النقية، وقد يعزى ذلك إلى قوى ربط الأيونات الشائبة بالشبكية البلورية.

يمكن اعتبار الشبكية البلورية في حالة العينات المطعمة بالشوائب وكأنها تتكون من طورين أحدهما مثالي والآخر قد حدثت به بعض التشويهات نتيجة لوجود الأيونات الشائبة. أمكن حساب سمك الطبقة التي حدثت بها تشويهات، ووجد أن لهذا السمك علاقة بنصف قطر الأيون الشائب وتكافؤه.