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Phonon transport in imperfect $G_3H_2SO_4$ crystal

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Abstract : Effect of defects (X-ray irradiation, *L*-alanine admixture and iron sulphate doping) on the phonon thermal conductivity λ_{ph} of triglycine sulphate $G_3H_2SO_4$ along the principal axes were studied, in the temperature range between 300 K and 350 K The measurements exhibit that the effect of irradiation leads to slow increase, followed by rapid decrease of λ_{ph} around a threshold dose of irradiation ($D_0 = 4\ 10^3$ rad) in addition to Curie temperature T_c-shift towards lower temperatures. On the other hand, it is found that *L*-alanine admixture shifts T_c towards higher temperatures but Fe^{3+}-doping shifts it towards lower temperatures, associated with decrease of λ_{ph} in both the cases.

All of these defects produce broadening in the phase transition region which may be attributed to the compositional fluctuations and structural disorder in the solid solutions

Keywords : Phonon transport, phase transition, imperfect triglycine sulphate

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Despite the complex chemical and crystallographic form of triglycine sulphate $G_3H_2SO_4$, it has become the object of active experimental research because of its basically simple ferroelectric character [1]. The previous work [2] dealt with phonon transport in pure $G_3H_2SO_4$ crystals, hence measurments on the imperfect crystals is of current interest. Defects generated due to irradiation and doping in any crystalline lattice, generally cause deformation of the surrounding volume and modification of the local fields. The extent of the crystal deformation depends on the nature of the defect, its site in the crystal and the host-defect interaction. Detailed studies of the X-ray irradiated triglycine sulphate [3] showed that even very small doses can give large changes of its ferroelectric properties. It seems that there are slow relaxation processes associated with the defect motion which affect irradiated crystals [3].

On the other hand, the *L*-alanine molecule is sufficiently similar structurally and chemically to glycine molecule [4]. The effect of this organic admixture, as a symmetric organic molecule of glycine on $G_3H_2SO_4$ compound, is lowering the permittivity and shifting the Curie temperature $T_c = 322$ K of this compound towards higher temperatures [5,6]. Influence of dilute concentration of iron ions has been studied to show decrease of the thermal diffusivity of this compound [7].

The aim of this article is to outline the principal effects of inhomogenities of X-ray irradiation, *L*-alanine admixture and Fe^{3+}-ion doping on the phonon transport in triglycine sulphate.

Steady state method was used to measure the total thermal conductivity of $G_3H_2SO_4$ and then the phonon part of the thermal conductivity λ_{ph} was deduced [2]. The pure samples [2] were irradiated at room temperature using X-ray source at 3 cm distance from the sample. Voltage of 30 KV and current of 15 mA were used for tube's operation. *L*-alanine admixed crystals were grown from aqueous solution of the compound with 0.2, 0.4, 0.6 weight % of *L*-alanine ($C_2H_4NH_2COOH$). Fe^{3+}-doped crystals were grown from aqueous solution of the compound with the same weight % of iron sulphate $Fe_2(SO_4)_3.nH_2O$. The concentration of *L*-alanine in the admixtured crystals are $n.10^{-4}$ (n = 3, 6, 8) weight % and of iron sulphate in the doped crystals are $m.10^{-4}$ (m = 3, 5, 7) weight %.

Figure 1 shows the effect of X-ray irradiation with enhanced doses on λ_{ph} of the compound in *b*-direction at room temperature. It is clear that as the dose increases, λ_{ph} increases till the dose reaches its threshold value (D_0), then it decreases rapidly (part AB and BC of the curve respectively). The slow increase of λ_{ph} for small doses ($D < D_0$) is due to annealing effect of irradiation, which introduces structure relaxation and generates strain induced regions [3]. For doses larger than the threshold value ($D > D_0$), λ_{ph} starts to change markedly and decreases rapidly due to predominance of defect formation and release of such induced stress [8] which are effective for scattering. For demonstration of such induced stress, it has been suggested that the radiation damage effects might be

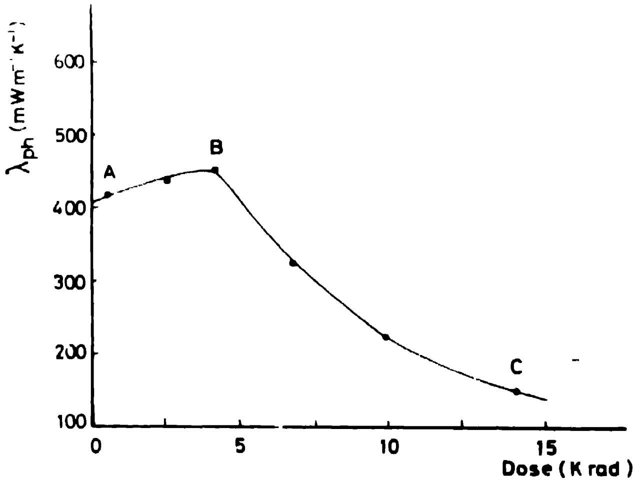

Figure 1. Variation of λ_{ph} of $G_3H_2SO_4$ with X-ray doses at room temperature

ascribed to a migration of the imperfections produced by the X-ray irradiation into the domain walls. This process is quite feasible as there is probably a strong mechanical stress field within or near a domain wall [8], which will provide favourable sites for some crystal imperfections.

Figure 2 shows that the X-ray irradiation introduced marked shift of the Curie temperature T_c towards lower temperatures and also increase of the transition region width (ΔT) with enhanced doses associated with decrease of peak's height.

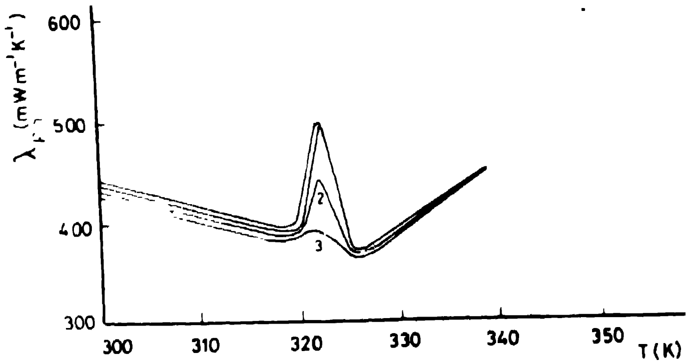

Figure 2. Temperature dependence of λ_{ph} of $G_3H_2SO_4$ for various X-ray doses 5 10^3, 10 10^3, 15 10^3 rad corresponding to curves 1, 2, 3 respectively

Figure 3 exhibits the effect of *L*-alanine admixture on λ_{ph} behaviour. The peak's height decreases and shifts to higher temperatures. Broadening of the phase transition region is also observed presumably and the spontaneous polarization due to the aligned defects at all temperatures above T_c, implies that a true paraelectric state does not exist in *L*-alanine admixed $G_3H_2SO_4$ crystal [5].

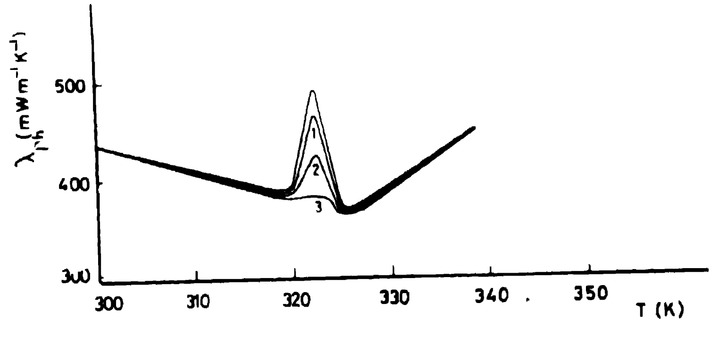

Figure 3. Temperature dependence λ_{ph} of $G_3H_2SO_4$ for various *L*-alanine concentrations 3.10^{-4}, 6 10^{-4}, 8 10^{-4} weight % corresponding to curves 1, 2, 3 respectively.

Figure 4 shows the effect of Fe^{3+}-ions on decreasing λ_{ph}. This decrease depends on the admixture of the doped Fe^{3+}-ions in the crystal and thus their effect on the domain structure [7]. On the other hand, increase of Fe^{3+}-ions concentration decreases λ_{ph} (with about 10% → 20% Fe^{3+}) shifts T_c towards lower temperatures and increases the phase transition region.

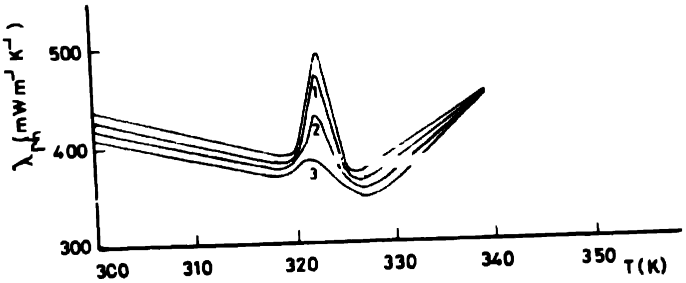

Figure 4. Temperature dependence λ_{ph} of $G_3H_2SO_4$ for various iron sulphate concentration 3 10^{-4}, 5.10^{-4}, 7.10^{-4} per cent weight corresponding to curves 1, 2, 3 respectively.

In all cases of irradiation, admixture and doping, broadening of phase transition region is observed, and can be attributed to the compositional fluctuations and structural disorder in the solid solutions. However, when translational invariance (for perfect structural order) is destroyed as a result of structural disorder [9], broadening of the phase transition region occurs depending on the microscopic detial of this situation. Disordered systems cannot be described by a set of normal modes with well defined wavectors q. In systems with major structural disorder, it is likely that the coupling with hopping defects is so strong that the lattice mode softening is essentially prevented altogether. Generally speaking, the effect of ionization radiation is similar to the effects of admixture and doping and can be accounted for in a similar manner.

In conclusion, X-ray irradiation of $G_3H_2SO_4$ frozen in different phonon scattering mechanisms around the threshold dose, shifts T_c towards lower temperatures as Fe^{3+} ion doping does. *L*-alanine admixture shifts T_c towards higher temperatures. Broadening of phase transition region in all these cases of different defects, is attributed to creation of structural disorder in the solid solutions.

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