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Ultrasonic Attenuation in Doped Bismuth Germanium Oxide

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We have measured the ultrasonic attenuation in single crystals of bismuth germanium oxide, Bi_{12} Ge O_{20} (BGO) at frequencies ($\omega/2\pi$) from 10 to 190 MHz at temperatures (T) from 4.2 to 260K. We have studied both undoped crystals and crystals doped with Aℓ, Ga, Pb, Zn, Cr, P + Ga and Cr + Ga. The doped crystals were very kindly provided by Frau Dr. Grabmeier and R. Oberschmid of Siemens, München.

BGO is one of a group of isomorphous crystals whose formula is approximately Bi_{12} MO_{20} where M represents a metal (usually, but not necessarily, quadrivalent). These are cubic crystals, space group I23, and have interesting piezoelectric, photoconductive and optical properties which have found applications in surface acoustic wave and electro-optic devices.

Some of our measurements in undoped BGO are shown in Figures 1 and 2 and confirm previous results by Rehwald and his co-workers[1,2]. The most striking feature is a very strong attenuation peak at low temperatures only for those modes which involve the elastic constant C_{44} such as the transverse modes, T(100,001) and T_1(110,001) but not for the longitudinal mode L(100,100). This attenuation peak is typical of an anelastic relaxation due to point defects[3] with the attenuation (α) given by

$$\alpha = \frac{A}{T} \frac{\omega^2\tau}{(1 + \omega^2\tau^2)} \qquad (1)$$

where A is a constant proportional to the defect concentration and the relaxation strength. τ is a relaxation time which is well described by the Arrhenius relation

$$\tau(T) = \tau_\infty \exp(\theta/T) \qquad (2)$$

where $k_B\theta$ is an activation energy and the attempt frequency, $1/\tau_\infty$, is of the order of that for a lattice optical phonon. Our data has been fitted to equation (1), as shown in Figure 2, for the T_1(100,001) mode, to obtain values of A, θ and $1/\tau_\infty$.

The magnitude of this attenuation peak in BGO is strongly affected by the presence of dopants, as shown in Figure 3. Doping with the Group II element Zn (dopant fraction per formula unit ≤ 0.009[4] reduced the peak to 0.77 of its undoped value while doping with Aℓ(0.033), Ga (0.004) and Pb (~0.5) removed the attenuation peak completely. However, doping with Cr (0.009) increased the attenuation by a factor of 2.3. The crystals with two dopants, Ga (0.006) + Cr (5×10^{-5}), P (0.029) + Ga (0.004), also showed no large attenuation peak although some very small relaxation peaks may be discernible in the data. These measurements complement the work by Rehwald et al[2] on crystals of the isomorphous crystal, bismuth silicon oxide (BSO), doped with Group III elements. They found that Ga (0.002) and B (0.003) reduced the corresponding peak in BSO while Aℓ (0.008) removed it completely.

We have also investigated the effects of annealing on the ultrasonic attenuation by measuring the low temperature relaxation peak before and after

annealing at 425°C either in a vacuum or in a pure O_2 atmosphere. For an undoped crystal no change in the attenuation peak was found. However, for the Cr doped sample the attenuation was reduced by vacuum annealing to 0.57 of its original value and was restored by oxygen annealing as shown in Figure 4.

There seems to be a strong correlation between the ultrasonic attenuation, α, and the optical absorption, σ, in these crystals. BGO is an insulator with a direct band gap of 3.25 eV but the undoped crystals are a pale yellow colour and have considerable optical absorption in the visible region below the band edge. This absorption is not present [4] in those doped crystals which show no ultrasonic attenuation peak and these crystals are nearly transparent. Similar results in BSO were found by Rehwald et al [2]. Hence it seems probable that the same defect centre may be responsible for both the optical absorption and the ultrasonic attenuation in these crystals. Tanguay [5] found that the optical absorption in undoped BSO was unaffected by vacuum or O_2 annealing and, by inference, this correlates with our results on the annealing of undoped BGO crystals. However, for Cr doped BSO Tanguay found strong photochromic behaviour with very strong optical absorption bands which could be bleached by oxygen annealing and restored by vacuum annealing. This is exactly the opposite to the behaviour of the ultrasonic attenuation in our Cr doped BGO crystal (which is almost black).

The defects responsible for these effects are not yet known. If we assume a point defect is responsible for the ultrasonic attenuation then we can obtain its symmetry from selection rules [3]. Since the relaxation affects C_{44} but not $(C_{11}-C_{12})$ then the defect must have trigonal symmetry. It must therefore be associated with the oxygen atoms in the GeO_4 tetrahedra which lie at the cubic (23) sites in the crystal. Several possible defects have been suggested for the optical absorption, a recent proposal [4] being a Bi^{3+} ion on a Ge site with a hole on one of the surrounding O^{2-} sites. Such a defect would have the correct symmetry to produce the ultrasonic attenuation observed. Several mechanisms for the dopant-bleaching of the optical and ultrasonic absorptions can be envisaged but more work is needed to elucidate the exact mechanism.

For the photochromic effects Tanguay [5] has suggested that a charge transfer mechanism between neighbouring substitutional Cr and Bi ions on tetrahedral sites could produce two metastable states (absorbing and non-absorbing). Our data on Cr doped BGO suggests that one of these states may be the centre responsible for the ultrasonic attenuation.

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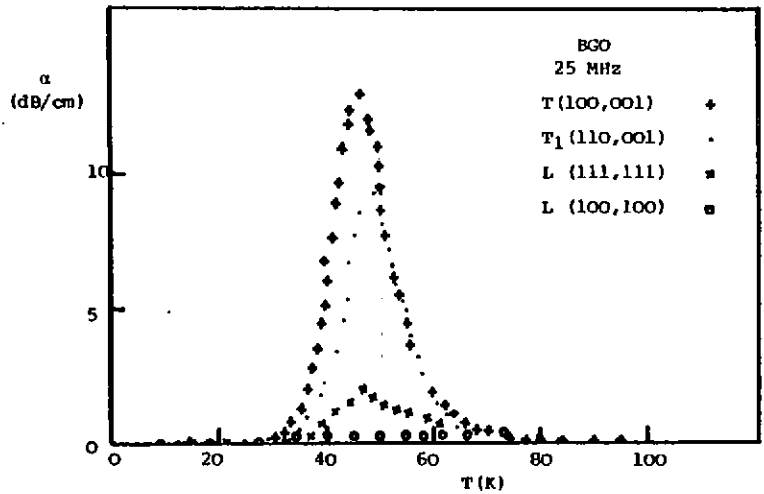

Fig. 1 Ultrasonic attenuation in undoped BGO for several acoustic modes

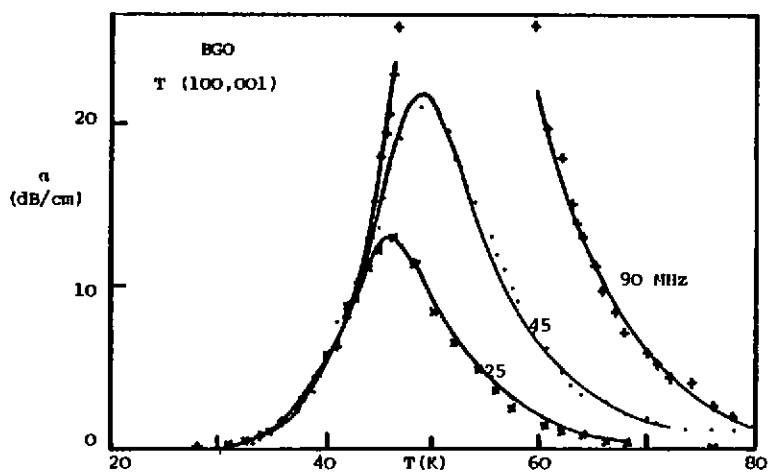

Fig.2 Attenuation of T (100,001) mode in undoped BGO fitted to eq.(1) with A = 34.8 dBK/cm MHz, θ = 460K, $1/\tau_\infty = 4.6 \times 10^{12}$Hz

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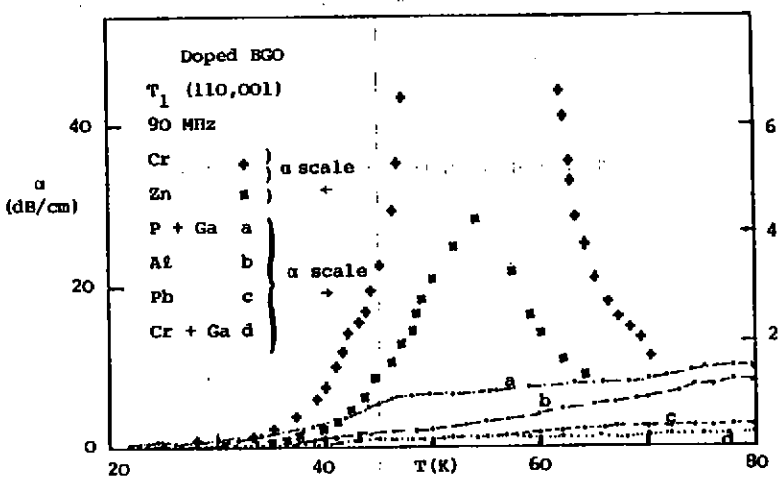

Fig. 3 Attenuation of T_1 (110,001) mode in doped BGO

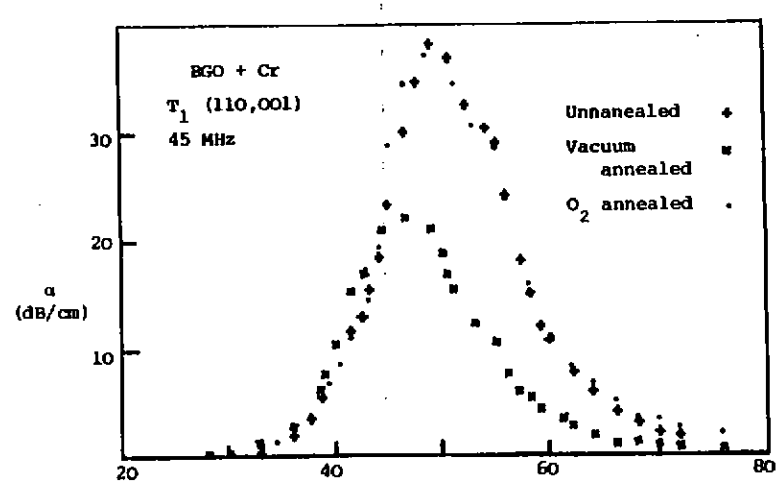

Fig. 4 Attenuation of T_1 (110,001) mode in Cr coped BGO, after annealing in vacuum and in oxygen