

Structural, Electrical and Mechanical Properties of GaTe for Radiation Detector Applications

P. M. Reshmi, A. G. Kunjomana, K.A. Chandrasekharan, M. Meena, C. K. Mahadevan

Abstract—Single crystals of gallium monotelluride (GaTe) have been grown by the horizontal freezing technique. The lattice parameters, crystallite size and lattice strain were evaluated from the x-ray diffraction (XRD) studies. Energy dispersive analysis by x-rays (EDAX) was performed on these samples to confirm the stoichiometry and chemical homogeneity. The layer-feature of GaTe was examined using a scanning electron microscope (SEM). Dielectric and AC conductivity measurements were carried out in the temperature range 313–423 K. The dielectric constant ϵ_1 and dielectric loss $\tan\delta$ were determined. Microindentation analysis was done on the cleaved planes of GaTe for different applied loads (5–35 g), to understand its mechanical behaviour. The Vickers microhardness has been computed and its correlation with energy gap E_g of the grown crystals was investigated. The energy gap of GaTe crystals was found to be ~ 1.69 eV, suitable for using it as high energy radiation detectors.

Index Terms—AC conductivity, dielectric constant, gallium monotelluride, horizontal freezing, microhardness, SEM.

I. INTRODUCTION

Gallium monotelluride is a potential candidate of III-VI layered semiconducting compounds due to its opto-electronic applications [1-3]. The physical properties of this monoclinic crystal are highly anisotropic, because of covalent bond within the layers and weak Van der Waals bonding between the layers [4]. The electrical and optical properties of GaTe crystals grown from melt have been reported by many authors [2,5-10]. However, not much work is reported on the AC conductivity and dielectric properties of stoichiometric GaTe crystals grown by horizontal freezing. Such studies on layered chalcogenide have been extensively used to understand the types of polarization and conduction mechanism in these materials. The operation of electro-optic devices is based on the Pockel's effect, in which the change in dielectric constant is a linear function of the applied field [11]. Gupta et al. [12], based on the Philip's and Van Vechten's theory have evaluated the polarizability, ionicity and heat of formation of gallium mono telluride. Recently, there has been immense research in the development of radiation detectors for use in atmospheres with high concentration of nuclear radiations. The conventional elemental and p-n junction detectors become unstable in

those hostile situations. In this context, compound semiconductor radiation detectors, which are stable against high doses of radiation are very much in need. III-VI layered semiconductors are of considerable interest because, in spite of their low structural perfection, they offer high sensitivity to IR, UV, x-ray and gamma radiations [13]. There is good prospect for GaTe as an efficient room temperature gamma ray detector due to its high indirect band gap of 1.67 eV [3]. Hence, it could be considered as a model compound among sensors for both experimental and theoretical study. During the fabrication of these devices, it is necessary to have careful mechanical handling techniques since it is extremely easy to introduce work damage into the specimen. This work damage may be deleterious to the performance of devices. In this regard, the analysis of microindentation to explain glide and cracking in single crystals of compound semiconductors has its own importance. The microhardness measurements on the cleavage faces of melt grown gallium telluride crystals are rarely reported. As such, the present work highlights the structural, electrical and mechanical characterization of these crystals, in order to explore their suitability for device applications.

II. EXPERIMENTAL PROCEDURE

Pure GaTe crystals were grown by the horizontal freezing method in a double zone tubular furnace. The temperature was controlled by microprocessor based temperature controllers. For charge synthesis, 5 N pure Ga and Te were used as-received, without any chemical treatment. The stoichiometric mixture was maintained at 1123 K for a period of 48 h in a muffle furnace. The synthesized charge was filled and vacuum sealed (10^{-6} mbar) into a precleaned quartz ampoule of 10 mm diameter. A temperature gradient of 70 K was maintained along the length of the melt and controlled solidification was promoted by appropriately programming the temperature-time profile. Powder XRD has been carried out using a BRUKER D8 ADVANCE diffractometer ($\text{CuK}\alpha$). The chemical composition of the grown crystal was studied by EDAX. SEM investigations were performed by a NOVA NANOSEM 600 microscope operated at 15 kV. The temperature variation of capacitance and dielectric loss ($\tan\delta$) for frequencies ranging from 1 kHz to 1 MHz was recorded by a LCR meter (AGILENT 4284A). The observations were made while cooling the sample from 423 K to 313 K. The dielectric constant and AC conductivity were evaluated using the procedure described elsewhere [14].

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The microindentation was performed using a Vickers microhardness tester (MVH-I) for 5–35 g load and adequate time lapse has been given so as to avoid any influence between the successive indentations. The pyramidal diamond indenter was loaded and unloaded consecutively at a constant rate, maintaining dwell time at 20 s. The Vickers microhardness (H_v in kg/mm^2) was computed for different loads using the QUANTIMET software. The energy gap (E_g in eV) of GaTe is calculated using the relation,

$$E_g = \frac{H_v V_{\text{cell}}}{1.6 \times 10^{-19} \times 10^2}$$

where the unit cell volume, V_{cell} is in mm^3 [15].

III. RESULTS AND DISCUSSION

The grown crystals were cleaved at ice temperature to minimize deformations and used for structural, dielectric and indentation analysis.

A. Structural studies

Fig. 1 depicts the powder XRD spectrum of GaTe crystals. The diffraction peaks ($\bar{4}20$), ($\bar{4}40$) and (650) could be indexed to the monoclinic system (JCPDS No. 75-2220). The lattice parameters of these crystals were found to be $a = 17.45 \text{ \AA}$, $b = 10.47 \text{ \AA}$, $c = 4.09 \text{ \AA}$ and $\gamma = 104.5^\circ$. The average grain size of the samples was calculated using Debye-Scherrer's formula $D = 0.9\lambda / \beta \cos\theta$, where D is the diameter of crystallite, λ is the wavelength of Cu K α line, β is full width at half maximum (FWHM) in radians and θ is Bragg's angle. The results are recorded in Table 1.

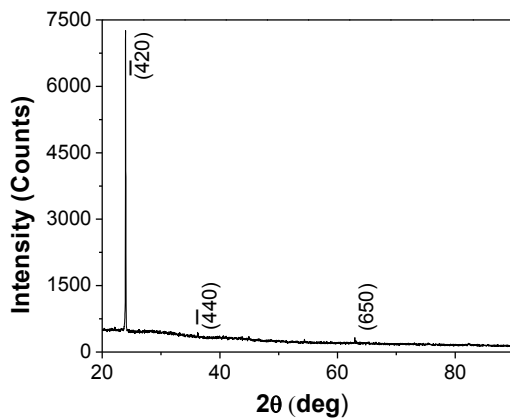


Fig. 1 XRD pattern of GaTe crystals

Table 1 Structural parameters of GaTe crystals grown by horizontal freezing

Pos. [$^{\circ}2\theta$]	d-spacing [\AA]	FWHM [$^{\circ}2\theta$]	Rel. Int. [%]	Crystallite size [\AA]	Lattice strain [%]
23.96	3.71	0.112	10.4	725	0.230
36.23	2.48	0.224	0.08	373	0.299
62.94	1.47	0.136	0.15	680	0.098

The average grain size shows high crystalline nature of the grown samples. The evaluation of lattice strain is important to control the electrical characteristics of semiconductor devices [16]. The computed values of lattice strain (Table 1) using the X $^{\circ}$ PERT HIGHSCORE, indicate the usefulness of the grown samples for device studies.

B. Surface morphology and compositional analysis

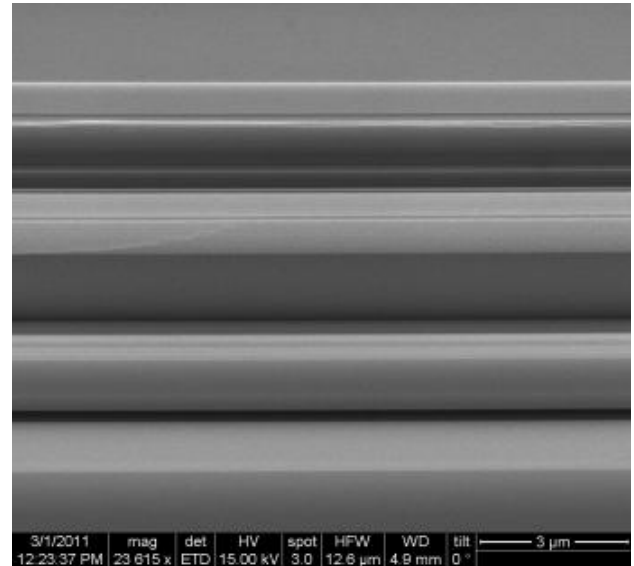


Fig. 2 SEM image of the cleaved GaTe crystal

The SEM micrograph on the cleavage face (Fig. 2) revealed parallel striations characteristic of the layered GaTe crystal, indicative of weak Van der Waals force between the different layers. There was no observable waviness along their length which implied the existence of perfect cleavage planes. Similar type of stair-like structure was described by Balitskii et al. [5].

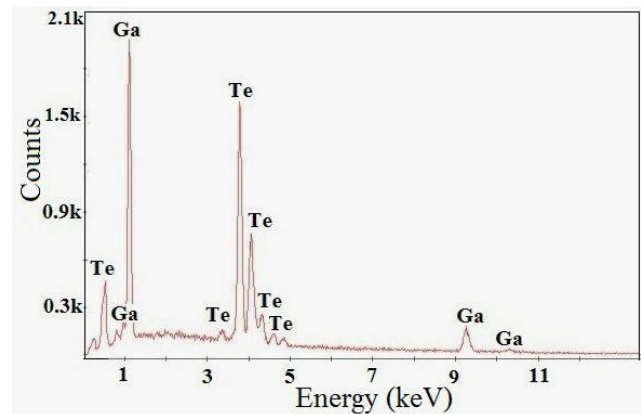


Fig. 3 EDAX profile of gallium monotelluride

The stoichiometry of compound semiconductor crystal is very crucial for the growth behaviour and properties, which depend on the intrinsic defects due to non-uniformity in chemical composition [17]. The EDAX spectrum shown in Fig. 3 indicates the absence of any chemical impurity in the grown crystal. The atomic percentages of Ga and Te are found to be in the ratio 1:0.965, which confirmed the stoichiometry of the grown crystal.

C. Dielectric studies

Fig. 4 shows the frequency dependence of dielectric constant, ϵ_1 at different temperatures. It is evident that ϵ_1 decreases with increasing frequency and increases with increasing temperature.

At high frequencies, the orientational polarization P_o gradually comes to a halt due to the phase lag of voltage behind the current in the capacitor and only ionic and electronic components of polarization are active. At low temperature, dipoles are randomly oriented and as the temperature increases, they align themselves along the field, which increases the value of P_o . This in turn leads to an increase of ϵ_1 with the increase of temperature.

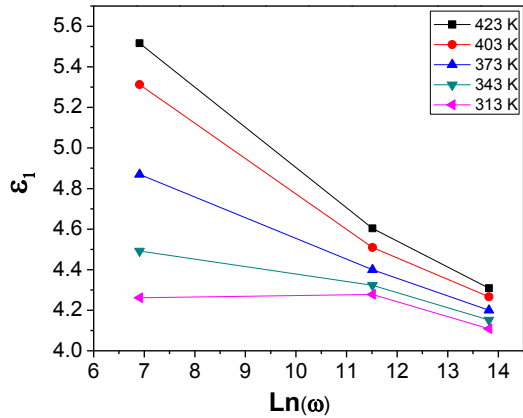


Fig. 4 Variation of dielectric constant with frequency for cleaved GaTe crystal at ■ 423 K, ● 403 K, ▲ 373 K ▼ 343 K and ▼ 313 K

The frequency dependence of dielectric loss was measured at different temperatures for the GaTe sample.

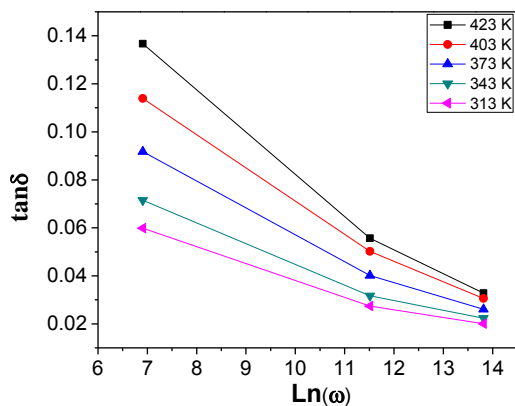


Fig. 5 Frequency dependence of dielectric loss for GaTe at ■ 423 K, ● 403 K, ▲ 373 K, ▼ 343 K and ▼ 313 K

It is found to decrease with increasing frequency and increase with increasing temperature as shown in Fig. 5.

D. AC conductivity studies

The AC conductivity of semiconductors increases with frequency according to the equation $\sigma_{ac}(\omega) = A\omega^s$, where s is the frequency exponent, A is a constant and ω is the angular frequency. Fig. 6 shows the variation of σ_{ac} with frequency at different temperatures in the range 313–423 K. It is clear from the figure that σ_{ac} increases linearly with frequency. The values of slope s and their temperature dependence is shown in Table 2, which appears to be consistent with the hopping process of charge carriers between localized sites separated by a barrier. The frequency exponent decreases slightly with temperature, similar to that reported by Hegab et

al. [18] for the amorphous thin films of Ge-Se. The variation of frequency exponent with temperature gives information on the specific mechanism behind the conductivity [19]. The observed temperature dependence of the frequency exponent follows the Correlated Barrier Hopping (CBH) model between centres forming Intimate Valence Alternate Pairs (IVAP), as suggested by Hegab et al. [18]. Hence, hopping between close pairs of these centres can be proposed as the mechanism involved for conduction.

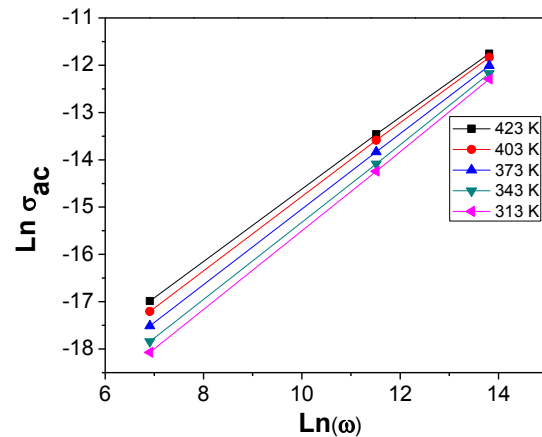


Fig. 6 Logarithmic plots of AC conductivity against frequency of GaTe crystal at ■ 423 K, ● 403 K, ▲ 373 K ▼ 343 K and ▼ 313 K

Table 2 Values of frequency exponent for different temperatures of GaTe

T [K]	s
313	0.8357
343	0.8196
373	0.7966
403	0.7790
423	0.7586

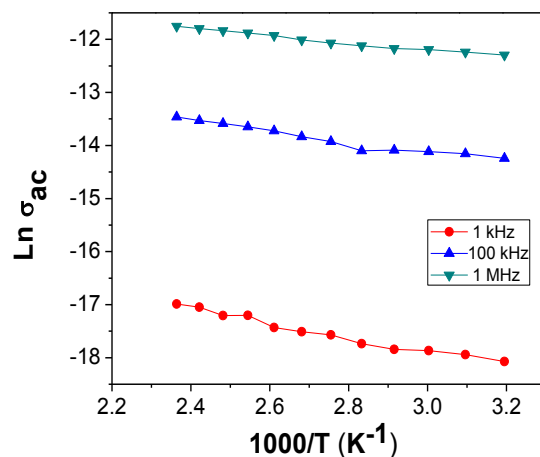


Fig. 7 Temperature dependence of AC conductivity for GaTe at ◆ 1 kHz, ▲ 100 kHz and ▼ 1 MHz

The activation energy E_{ac} can be determined using the expression:

$$\sigma_{ac} = \sigma_0 \exp\left[\frac{-E_{ac}}{kT}\right]$$

where k is the Boltzmann's constant, T is the absolute temperature and σ_0 is a constant depending on the material. The semi-logarithmic relations of this equation for different frequencies are shown in Fig. 7. The variation of AC conductivity with temperature indicates the semiconducting nature of gallium monotelluride with comparatively low activation energy. The values of E_{ac} tend to decrease with increase in frequency (Table 3), confirming the hopping conduction to be the dominant mechanism [20]. As the applied field frequency is increased, the electronic jumps between the localized states enhances, leading to a lowering of energy required for activation (E_{ac}).

Table 3 Thermal activation energies of GaTe samples for different frequencies

ω [kHz]	E_{ac} [eV]
1	1.3279
100	0.9838
1000	0.6718

E. Microhardness studies

The microindentation analysis is an important experimental tool to assess the structural deformation on the cleavage faces of a semiconductor. Microhardness is strongly related to the structure, bonding and chemical composition of solids. So, the grown crystals with smooth cleaved surfaces and free from any defects were selected for the indentation studies [21]. The results of microhardness measurements carried out on the cleavage faces of GaTe crystals for various loads are represented in Fig. 8. Fig. 9(a) depicts a well defined indentation mark for a load of 10 g.

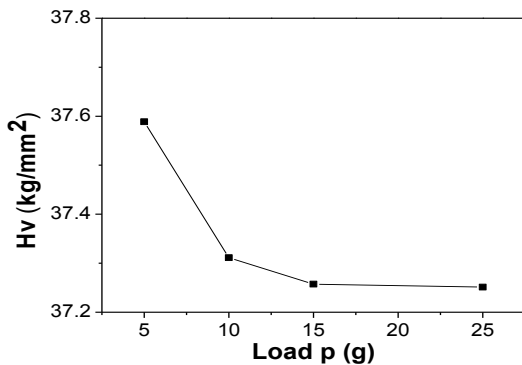


Fig. 8 Plot of microhardness vs applied load

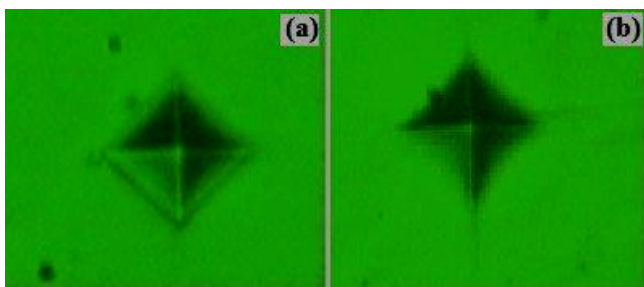


Fig. 9 Square indentation mark for a load of (a) 10 g and (b) 35 g on the cleaved surface of GaTe

Since the cleavage plane is easy to glide, it will slip during the indentation process. Hence, as the load is increased, the amount of plastic strain is also increased, which in turn slightly reduces the value of microhardness. Beyond 25 g, cracks were initiated on the crystal surface. Fig. 9(b) shows the formation of radial cracks at 35 g.

Table 4 Correlation of microhardness (Hv) with energy gap (Eg) of GaTe crystal

Load p [g]	Hv [kg/mm²]	E_g [eV]
5	37.589	1.699
10	37.311	1.687
15	37.257	1.685
25	37.251	1.685

Table 4 presents the calculated values of energy gap for GaTe, which supports the consistent results of hardness and cell volume. The results are in agreement with that reported in literature [8]. The obtained energy gap ~ 1.69 eV indicates that the grown crystal can be used for room temperature gamma ray spectroscopy applications [3].

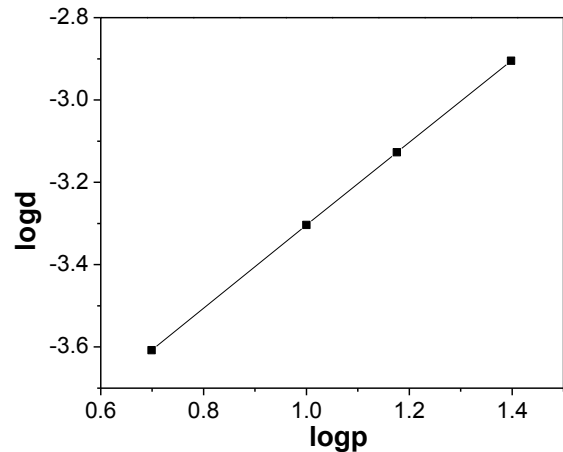


Fig. 10 Meyer's plot between log p and log d

The plot of $\log p$ against $\log d$ (Fig. 10), yields a straight line following the Meyer's relation, $p = Kd^n$, where p is the load applied (g), d is the diagonal length (mm) and K is a constant for a given material. The work hardening index, measured as the slope, n is equal to 1.006. It follows the concept of Onitsch [22] that if the slope is less than two, the hardness number decreases with increasing load.

IV. CONCLUSION

Gallium monotelluride crystals were grown by the horizontal freezing technique and characterized using XRD, EDAX and SEM analysis. The dielectric properties were studied in the temperature range 313–423 K. The thermal activation energy was calculated from the AC conductivity data and the mechanism responsible for conduction has been proposed using the CBH model between IVAP centers. The microhardness was found to decrease slightly with applied load and then became constant.

The energy gap of GaTe crystals was computed to be ~1.69 eV, suitable for using them as high energy radiation detectors.

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