Study of Kinetic Coeficients of (GeTe)$_{1-x}$ = $(Ga_2Te_3)_x$ Solid Solutions

Mir Hasan AKPEROV*, **Turgay ATALAY, Halit TAŞKIN,**
A. Mustafa ERER
Department of Physics, Devrek Science And Art Faculty.,
Zonguldak Karaelmas University,
Zonguldak-TURKEY

Abstract

In this study, such kinetic cparametres as thermoelectro motor force (thermo e.m.f), electrical coductivity, heat conductivity, Hall and Nernst-Ettingshausen coeficients are investigated, as a function of chemical composition of $(GeTe)_{1-x}$ − $(Ga_2Te_3)_x$ and temperature, by physicochemical methods and x-rays analysis. The kinetic parameters $(GeTe)_{1-x} - (Ga_2Te_3)_x$ solid solutions are investigated between x=0 and 0,015 and between 77 and 900 K.

Adding of Ga_2Te_3 to GeTe reduces the phase transition temperature of β-GeTe to α-GeTe. It is observed that in the region of solid solution the rhombohedral modification of GeTe are protected.

Doping of GeTe with Ga_2Te_3 does not affect the kinetic parameters of GeTe. Anomalies in the rhombohedral phase of solid solutions are related with splitting of cubic phase extremums due to deformation of the rhombohedral lattice. Decreasing of Hall coefficient while increasing thermo e.m.f near phase transition point, in the cubic phase were explained with changing of Hall factor A.

Introduction

GeTe and similar solid solutions which works 500-900 K temperature intervals have brilliant future.

As known, GeTe has three polymorhphic modifications and is a high temperature modification. Polymorphic phase transitions of GeTe alloys where $\beta \rightarrow \alpha$ and $\alpha \rightarrow \gamma$ happen near the 630-700 K critical temperature [1,5]. This effect can be observed from characteristics of kinetic parameters changing with composition and temperature. There

is a series of anomalies which accompany the composition and temperature dependence of kinetic coefficients. According to Gruzinov et al [6] and Korshuev [7], the reason of this type of behaviour in the lower phase transition is the splitting of γ rhombohedral extremums which are equivalent to the cubic phase. But this model is not completed yet, and not uniqe for quantitative analysis.

GeTe-GaTe system has been widely investigated [8-15]. According to [8,10,12,13,15], dissolution limits of GaTe and Ga_2Te_3 compounds in the GeTe are 5% and 2% molar fraction, respectively. Kinetic parameters of the $(GeTe)_{1-x}-(Ga_2Te_3)_x$ has not yet been investigated for large temperature intervals. This work was realized for the investigation of kinetic parameters of the $(GeTe)_{1-x}-(Ga_2Te_3)_x$ solid solutions between 77 and 900 K.

Experimental Details

Thermal, microstructure and x-ray experiments show that, the solid alloy of β-GeTe, which is high temperature modification, contains 2% Ga_2Te_3 at 873 K. Ga_2Te_3 reduces the phase transition temperature of β-GeTe$\rightarrow$ α-GeTe from 638 to 593 K. Dissolution of Ga_2Te_3 decreases with temperature and disssolution reaches to 1% mole at 523 K.

Rhombohedric α-modification of GeTe are protected at the border of solid solution. In this situation, adding Ga_2Te_3 to GeTe causes augmentation of volume of primitive cell and rhombohedral lattice angle increases very little.

Kinetic coefficient of $(GeTe)_{1-x}-(Ga_2Te_3)_x$ has been investigated on polycrystal samples. Samples were annealed at 723 K for 250 hours and slowly cooled down to room temperature. Thermo e.m.f. (α), electrical conductivity (σ), thermal conductivity (H_T), Hall coefficient (R_H), and Nernst-Ettingshausen cofficient (Q_{N-E}) were researched as a function of compounds, concentration of current carriers and temperature between 77 and 900 K. The change of α, σ and H_T with concentration of Ga_2Te_3 at 300 K is shown in Fig. 1. As shown, thermo e.m.f. weakly depends on composition and σ changes like α. However, H_T decreases with the composition. Temperature dependence of thermo e.m.f. electrical conductivitiy and Hall coefficient are shown in Fig.2 and Fig. 3.

Because of the impossibility of the exact calculation of electronic (H_{el}) and lattice (H_{la}) parts from the total conductivity (H_C), for solid solution alloys we used Wiedemann-Franz law for the simple single zone of H_{el}. The temperature dependence of α has a knee at 600 K and approximately, σ has a knee at the same temperature though in reverse direction. This temperature is related to the phase transition temperature. Temperature dependence of σ is proportional with T^{-S} and the S exponent changes between 0,2 and 0,5 for T<200 K; and between 0,6 and 1,1 for T>300 K for 1,5 % mole Ga_2Te_3. On the other hand, S exponent increases with the rise of Ga_2Te_3 concentration in GeTe.
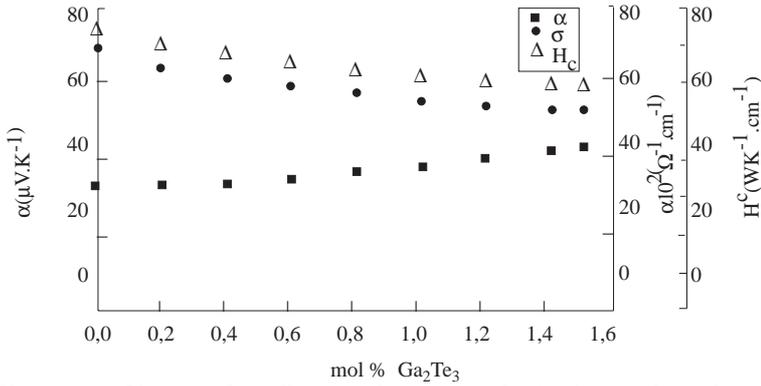
Figure 1. Change of coefficients thermo-e.m.f.(α), electrical conductivity (σ) and heat conductivity (H_c) with Ga_2Te_3 composition at 300 K.
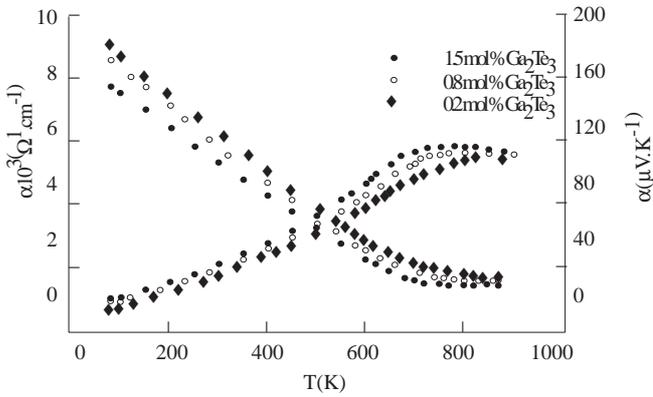

Figure 2. Temperature dependences of coefficients of thermo-e.m.f.(α) and electrical conductivity(σ).

The temperature dependence of Hall coefficient R_H (and also Nerns-Ettingshausen coefficient Q_{N-E}) in solid solutions is similar to GeTe and these parameters have the same bending point at phase transition temperature, Fig.3.

Discussion

As mentioned above, electrophysical properties of GeTe alloys are related to the splitting of L-extramums which are common for α-, β-phases of this compound [6,7]. In the rhombohedral phase of the GeTe, to interperation of the results we assumed that Fermi level of the GeTe is lower than three peaks of the sub zone and the degenerates. This assumption gives us the calculation possibility of the hole concentration from Eq.(1):
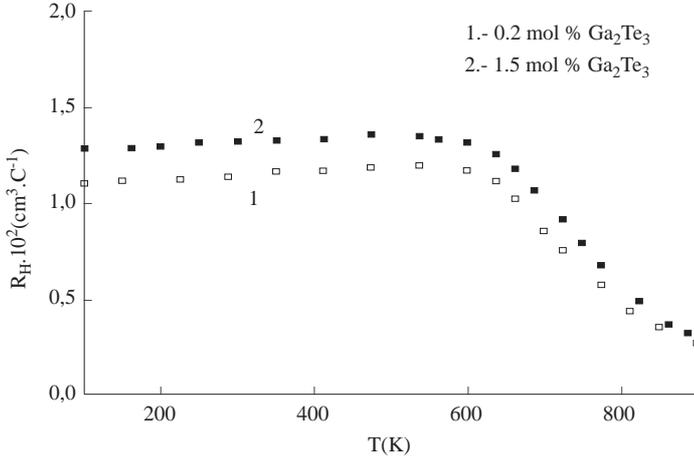
Figure 3. Temperature dependences of Hall coefficient

$$R_H = \frac{A}{e.p} \qquad (1)$$

Here, A is the Hall factor and depends on the temperature and composition. Hole concentration has been calculated as $5,5.10^{20} cm^{-3}$ in GeTe with this method.

On the other hand, Fermi level position is calculated aproximately as 0,27 eV at 300 K for arbitrary degeneration level and assume r=0 (acostic scattering of phonons), from Eq.(2).

$$\alpha = \frac{k}{e} \left[\frac{r + 2 F_{r+1}(\mu^\star)}{r + 1 F_r(\mu^\star)} - \mu^\star \right] \qquad (2)$$

Here, $F_r(\mu^\star)$ and $F_{r+1}(\mu^\star)$ are Fermi integrals and μ is chemical potential energy which is defined as

$$\mu^\star = \frac{\mu}{kT}$$

According to [6,7], energy depth of the three peaks in the zone are calculated as 0,3 eV approximately. With the known value of $\mu^\star$ and p effective mass of electrons in the GeTe are calculated as $m^\star = 1,2 m_0$, at 300 K from Eq. (3).

$$p = \frac{4\pi}{h^3} (2m^\star kT)^{\frac{3}{2}} F_{1/2}(\mu^\star) \qquad (3)$$

So, these calculations show and support that the single zone model is suitable for these hole concentrations.

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The results of x-ray analysis and the rise in the lattice component of heat conductivity and mobility with the composition show that Ga atoms settle in Ge vacancies and the Fermi level goes down. Therefore, electrons and phonos are scattered less than by Ga atoms and the influence of GeTe lattice angle by Ga atoms reduces. Thus, the deformation degree of GeTe lattice by Ga atoms can be neglected because the ionic radius of Ga^{3+} (r_{Ga}=0,62 A°) is not much smaller than ionic radius of Ga^{3+} (r_{Ga}=0,62 A°). In fact, on some occasions the valence state of Ge may change form 2+to 4+.

The analysis of the difference between the scattering of electrons and the phonos from defects and Ga atoms show that scattering radius of defect are approximately equal to the radius of Ge atoms. A qualitative analysis to understand phonon scattering from GeTe lattice defects can be realized with Eq. 4. This equation defines heat conductivity of crystal lattice [16-20].

$$H_{La} = \frac{1}{3} C_H \bar{V}_f \bar{V}_f \bar{l}_f = \frac{1}{3} C_H \bar{V}_f^2 \bar{\tau}_f = \frac{1}{3} \frac{C_H \bar{V}_f}{\bar{\nu}_f} \tag{4}$$

where C_H is the lattice oscillation component of specific heat conductivity C, $\bar{V}_f$ is average velocity, $\bar{l}_f$ is mean free path, $\bar{\tau}_f$ is average relaxation time and $\bar{\nu}_f$ is the average number of collisions. For an accurate calcultion of lattice vibration component of heat conductivity by using Eq. 4., it is necessary to know phono spectrum of GeTe, relatation time as a function of frequency (ω), and the number of phonos in a given frequency and polarization. At present, it's theoretically and experimentally imposibble to calculate the above parameters accurately. For this reason we assumed that $C_H = C/4$ and $\bar{V}_f = V_0/2$ where V_0 is sound velocity. If H_{La} is known, with this approximation we can calculate $\bar{\nu}_f$. Therefore, we can extract scattering amount of defects by comparing $\bar{\nu}_f$ for GeTe defect structure and for occuppied defects. Aproximate computation shows that the scattering radius of phonons from defects is smaller than the radius of Ge ions. This result is suitable for a collision theory of defects [16-20] which gives that the relaxation time of defects is proportional with ω^4. In most crystals heat is conducted by long wavelenght phonons. Obviously, for these phonons λ is large and v_f is small.

Weak increase in α, with the rise of Ga_2Te_3 in GeTe, reduces the degre of covering of the extremums and Fermi level increase, while state density decreases as a result. During transition from rhombohedral phase to cubic phase, redistribution of the current carriers on the extremums are more than before the transition. It brings disappearance of concentration anomaly on the thermo e.m.f. and explains rapid increase in the α with temperature nearby transition temperature. Single zone model is supported by increase of effective mass in the Fermi level; this effective mass is computed from α, $Q_{NE}/R_H.\sigma$ and p at the phase transition point. Increase in σ during phase transition may be explained by the increase of hole mobility. If the scattering is related to the acoustic phonos, relaxation time decreases with increasing of energy and plunge in Fermi level cause mobility increase. The rise of σ partly compansated by the decrease in mobility, affected by soft phonon branch of scattering near by phase transition point.

We can write, for temperatures are smaller than the T_C, namely for the separated zone temperatures

$$R_h = \frac{1}{H_{La}} = A' + BT \qquad (5)$$

where A$'$ is the heat resistance of phonons scattering from defects and BT is the heat resistance of phonon-phonon scattering. It is understood that R_h is proportional with temperature between 77 and 650 K for 1,5% moles of Ga_2Te_3. Deflection from law of $1/H_{La} \sim T$ is related with the separated zone of electronic component of heat conduction. This deflection moves to lower temperature with the increase of Ga_2Te_3 amount in the GeTe.

Temperature dependence of R_H, in the rhombohedral phase, can be explained by the change in Hall factor. If te temperature rises, A increases, but A and R_H decreases when the temperature is past the transition point and this decrease continues at high temperatures in the cubic phase. Therefore, the value of Nernst-Ettingshausen coefficient remains negative for all temperature intervals.

In conclusion, we notice that a detailed quantitative analysis is impossible in this stage. Kinetic coefficients are affected by the change of zone's structures but there is no theoretical explanation for this effect.

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