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Crystal structure, magnetization, ^{125}Te NMR, and Seebeck coefficient of $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ (R = La, Pr, Gd, Dy, and Yb)

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Abstract

GeTe, a self-doping semiconductor, is a well-known base compound for thermoelectric and phase-change materials. It is known, that replacement of Ge in $\text{Ag}_{6.5}\text{Sb}_{6.5}\text{Ge}_{37}\text{Te}_{50}$ (TAGS-85) material by rare earth Dy significantly enhances both the power factor and thermoelectric figure of merit. Here we demonstrate how replacement of Ge in GeTe by rare earths with different atomic size and localized magnetic moments affect XRD patterns, magnetization, ^{125}Te NMR spectra and spin-lattice relaxation, and the Seebeck coefficient of the alloys with a nominal composition of $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ (R = La, Pr, Gd, Dy, and Yb). SEM, EDS and WDS data show that rare earth atoms in the matrix are present at smaller extent compared to a nominal composition, whereas rare earth also is present in the inclusions. Rare earths affect the Seebeck coefficient, which is a result of interplay between the reduction due to higher carrier concentration and enhancement due to magnetic contribution. The effect of replacement of Ge in GeTe by Dy on the Seebeck coefficient is smaller than that observed in $\text{Ag}_{6.5}\text{Sb}_{6.5}\text{Ge}_{36}\text{Te}_{50}\text{Dy}_1$. This can be explained by larger amount of rare earth, which can be embedded into the lattice of materials containing [Ag+Sb] atomic pairs and possible effect from these pairs.

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Keywords: GeTe alloyed with rare earth; lattice parameters; ^{125}Te NMR spectra and spin-lattice relaxation; magnetization; Seebeck coefficient.

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1. Introduction

GeTe is a self-doping narrow-band semiconductor where a high concentration of free charge carriers is generated by Ge vacancies [1-3]. At 300 K, GeTe possesses a rhombohedral, i. e., slightly distorted cubic, crystal structure; when temperature increases, rhombohedral distortion decreases and the lattice becomes cubic above ~640 K [4,5]. Due to specific crystal structure and electronic transport properties, GeTe serves as the base compound for high efficiency thermoelectric [6-9] and phase-change materials [10,11].

It was reported in Ref. 5 and then confirmed in Ref. 12 that the power factor, $PF = S^2/\rho$, of GeTe at 720 K, $42 \mu\text{Wcm}^{-1}\text{K}^{-2}$, is one of the highest among thermoelectric materials due to a relatively high Seebeck coefficient, S , and low electrical resistivity, ρ . Replacement of Ge in GeTe by [Ag+Sb] atoms forms well-known high efficiency $\text{Ag}_x\text{Sb}_x\text{Ge}_{50-2x}\text{Te}_{50}$ materials, which typically are shown as $(\text{GeTe})_{100-m}(\text{AgSbTe}_2)_m$ (TAGS series) [6-8]. This replacement significantly increases the Seebeck coefficient and electrical resistivity, resulting in a smaller power factor, whereas a reduction in thermal conductivity increases the thermoelectric figure of merit [6-8]. It was also shown that an additional replacement of Ge by 1 at.% rare earth Dy, forming $\text{Ag}_{6.5}\text{Sb}_{6.5}\text{Ge}_{36}\text{Te}_{50}\text{Dy}_1$ alloy (using well-known thermoelectric material TAGS-85 as a base), enhances the Seebeck coefficient and thermoelectric efficiency by ~20% [9]. Hence, chemical substitution is an effective way to better understand the Seebeck effect and other important parameters of GeTe-based thermoelectric materials.

The Seebeck coefficient in GeTe depends on free (mobile) charge carrier concentration, which can be tuned by the replacement of Ge with various elements, e.g. by Ag, Sb, Pb, or Bi [13-15]. Based on our findings for $\text{Ag}_{6.5}\text{Sb}_{6.5}\text{Ge}_{36}\text{Te}_{50}\text{Dy}_1$ [9] we have suggested that the replacement of Ge in GeTe by rare earths with different atomic sizes [16] and localized magnetic

moments [17] can affect electronic and thermal transport and enables better understanding of the possible effects from lanthanide substitution. The Seebeck coefficient is sensitive not only to carrier concentration, but also to charge carrier scattering, which in the case of rare earth atoms can be enhanced by magnetic contribution due to large localized magnetic moments of Gd and Dy compared to a smaller one in Pr and Yb, and zero in La. It is also important to understand the effects of rare earths on the lattice parameters, rhombohedral distortion, and the temperature-induced rhombohedral-to-cubic structural transformation.

Here we report on the effects of rare earth atoms on the crystal structure (300-750 K), magnetization (1.8-350 K), ^{125}Te NMR spectra and spin-lattice relaxation (300 K), Seebeck coefficient, electrical resistivity, and thermal conductivity (all in the temperature range 300-800 K) of materials with the nominal composition of $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ ($\text{R} = \text{La, Pr, Gd, Dy, and Yb}$). Our data provides a better understanding the effect of rare earths on the Seebeck coefficient of GeTe-based materials.

2. Experimental details

Material synthesis and sample preparation. Five ingots with a nominal composition of $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ where $\text{R} = \text{La, Pr, Gd, Dy, and Yb}$ were prepared by the direct reaction of the constituent elements in fused silica ampoules. Quartz ampoules were cleaned with methanol and pre-fired at 1173 K. For synthesis we used Ge (Materion G-1038, 99.999% purity), and Te (Alfa Aesar, 99.9999% purity, product #12607) [18]. An identical procedure of synthesis was used for all samples: appropriate quantities of the constituent elements were placed in a quartz tube with a diameter of 10 mm and sealed in Ar environment with a pressure of ~ 17 kPa and then placed in an outer quartz tube of a larger diameter and sealed under the same conditions.

Ampoules with the constituent elements were heated up to 1325 K to melt the constituents and periodically shaken to form a homogeneous melt. After ~4 hours, the melt was cooled down within the furnace at a rate of 100 °C/hour. All ingots had a mass of 20 g, diameter of 10 mm, and length of ~40 mm. The melt did not react with the ampoule and the ingots were easily removed from the ampoule after cooling.

Disc samples with a diameter of 10 mm and thickness of 2 mm were prepared by cutting the ingots with a diamond saw perpendicular to the ingot axis. For Seebeck coefficient and electrical resistivity measurements, two flat parallel surfaces $\sim 2 \times 3 \text{ mm}^2$ on opposite, initially curved, sides of each disc sample were prepared.

X-ray diffraction (XRD). Room temperature XRD patterns were obtained from ground powders prepared from each of the alloys studied using a Pananalytical X'Pert Pro MPD system fitted with an Anton Paar HTK1200N furnace and an X'Celerator detector. Diffraction measurements with Co-K $_{\alpha}$ radiation ($\lambda = 1.79 \text{ \AA}$) were taken at temperature steps from 300 K to 800 K. The crystal structure of each sample was determined by conducting Rietveld refinements in the program X'Pert HighScore Plus; more details can be found in Refs. 5,19.

Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), and Wavelength Dispersive Spectroscopy (WDS). Samples were examined in an FEI Quanta 250 field-emission scanning electron microscopy (SEM) equipped with an Oxford Instrument Aztec energy-dispersive spectrometer (EDS) similar to that reported for GeTe-based samples in Ref. 6. *In addition, samples were examined by Electron Probe MicroAnalyser (EPMA) with Wavelength Dispersive Spectrometer (WDS), which has better resolution than that does EDS.*

Backscattered electron (BSE) imaging was used to differentiate the phases. The signal brightness is dependent of the average atomic number of the components in a phase. An electron

beam of 15 kV led to an excitation volume of about 600 nm in diameter. Samples were embedded in epoxy resin and polished using 1200-grit SiC paper and 1- μ m diamond slurry to prepare cross-section, and then coated with 10 nm of carbon for better conductivity in high vacuum mode.

Bulk magnetization. The bulk magnetization of samples was measured at 1.8 and 300 K in a Quantum Design superconducting quantum interference device magnetometer in a magnetic field, H , varying from 0 to 55 kOe. The temperature dependence of the magnetic susceptibility was measured in the temperature range of 1.8-350 K in a 10-kOe magnetic field. For measurements, the samples were placed in a gel capsule of low diamagnetic susceptibility, $\chi_{\text{dia}} = -1.3 \times 10^{-8} \text{ emu} \cdot \text{g}^{-1} \cdot \text{Oe}^{-1}$, which is more than an order of magnitude smaller than the diamagnetic susceptibility of GeTe. The uncertainties of the magnetic measurements were less than 2% [9].

Nuclear Magnetic Resonance (NMR). ^{125}Te NMR experiments were performed at 126 MHz using a Bruker 400 spectrometer with TopSpin software from Bruker in a magnetic field of 9.4 T at 300 K without sample spinning (static regime) [15]. To reduce the absorption of radiofrequency power, coarse powder of each material studied was mixed with the powder of a diamagnetic electrical insulator, synthetic laponite clay; sample masses were ~ 80 mg. Signals were detected after a Hahn echo generated by a 2 μ s and 4 μ s two-pulse sequence. Recycle delay time varies from 0.1 ms to 150 ms and measuring times for each samples were about 22 h. ^{125}Te NMR chemical shifts were referenced to $\text{Te}(\text{OH})_6$ in solution and chemical shifts relative to $(\text{CH}_3)_2\text{Te}$ in benzene were larger by +712 ppm [20]. ^{125}Te NMR spin-lattice relaxation measurements were conducted in order to obtain the values of spin-lattice relaxation time, T_1 , and estimate free (mobile) charge carrier concentration in tellurides using the approach reported for ^{207}Pb NMR [21] and for ^{125}Te NMR [19,20]. The spin-lattice relaxation time was determined

by fitting the dependence of the signal intensity vs. time delay; the uncertainty of T_1 determination was ± 0.2 ms [20].

Seebeck coefficient (thermopower) and electrical resistivity. Measurements of the Seebeck coefficient, S , and electrical resistivity, ρ , were performed using an LSR-3 measuring system (Linseis Inc.) in a helium environment in the temperature range from 300 to 780 K. The Seebeck coefficient and electrical resistivity were measured simultaneously on the same sample using the four-probe method; the temperature difference for thermopower measurements was between 8 and 9 K in the entire temperature range with uncertainty ≤ 0.1 K. The Seebeck coefficient was measured relative to the Pt legs of a Pt-(Pt+Rh) thermocouple from which the absolute Seebeck coefficient was calculated. The uncertainties in the thermopower and electrical resistivity measurements are $\leq 5\%$ and 3% , respectively [9].

Thermal diffusivity measurements. The same disc samples were used for thermal diffusivity measurements by flash method. The samples were coated with a layer of graphite to minimize the error of measurements. The thermal diffusivity, λ , was measured with an XFA-500 measuring system (Linseis Inc.) in helium environment; the uncertainty of these measurements is $\sim 6\%$ [9]. The thermal conductivity, κ_{tot} , was calculated as $\kappa_{\text{tot}} = \lambda c_p d$, where c_p is specific heat capacity of GeTe measured by XFA-500 and the mass density, d , of GeTe measured by the Archimedes method using AT261 Delta Range, Mettler Toledo, is $d = 6.18 \text{ g cm}^{-3}$ [5].

3. Results and discussion

3.1. X-ray diffraction, SEM, EDS, and WDS

XRD patterns for $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ alloys with $\text{R} = \text{La, Pr, Gd, Dy, and Yb}$ obtained at 300 K are shown on Figure 1(a); data for GeTe [5] are shown for comparison. All $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ samples at

300 K have rhombohedral crystal lattice similar to that of GeTe. Additional peaks were found for all $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ alloys with $\text{R} = \text{La}, \text{Pr}, \text{Gd}, \text{Dy}, \text{and Yb}$, showing that small amounts of second phase are present in these alloys; no additional peaks were found for $\text{Ge}_{49}\text{Te}_{50}\text{Gd}_1$. The inset in Fig. 1(a) presents an expanded view for the same samples for $34^\circ \leq 2\Theta \leq 36^\circ$ showing (202) peak, which is shifted to the direction of larger angles on average by $\sim 0.07^\circ$ when Ge is replaced by rare earth. Figure 1(b) presents the expanded view for $48^\circ \leq 2\Theta \leq 52^\circ$, showing two (024) and (220) peaks, which are a signature of rhombohedral lattice distortion [4,5]; both peaks also shift to the direction of larger angles on average by $\sim 0.07^\circ$.

Table 1 shows lattice parameters and rhombohedral lattice distortion obtained by Rietveld refinement. In spite of the large atomic size of rare earth atoms, both lattice parameters and rhombohedral distortion of $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ alloys studied are similar to those of GeTe. The shifts in XRD peaks observed for all samples [shown on the inset in Fig. 1(a) and Fig. 1(b)] gives evidence that at least some rare earth atoms are incorporated into the lattice.

Figure 2 presents XRD patterns of two samples, $\text{Ge}_{49}\text{Te}_{50}\text{La}_1$ and $\text{Ge}_{49}\text{Te}_{50}\text{Gd}_1$ in the vicinity of (024) and (220) peaks obtained at temperatures varying from 300 K to 750 K. These peaks move toward each other when temperature increases, showing that the low-temperature rhombohedral structure gradually transforms into the high-temperature cubic structure. At some temperature, T_{cubic} , it becomes mostly cubic; for our GeTe sample $T_{\text{cubic}} \approx 640$ K [5]. The most interesting feature for $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ samples is that although the lattice parameters and rhombohedral distortions are similar to that of GeTe, T_{cubic} changes: as can be seen in Figs. 2(a)(b), T_{cubic} is 700 ± 10 K for $\text{Ge}_{49}\text{Te}_{50}\text{La}_1$ and 650 ± 10 K for $\text{Ge}_{49}\text{Te}_{50}\text{Gd}_1$. The values of T_{cubic} for other $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ samples are shown in Table 1.

Our data demonstrates that La and Pr increase T_{cubic} while Gd, Dy, and Yb decrease it compared to that of GeTe (Fig. 2); this also is evidence that rare earth atoms are incorporated into the lattice. Because the lattice parameters and rhombohedral distortion of all samples studied are similar (Table 1), a change in T_{cubic} cannot be attributed to the atomic size of rare earth atoms, but rather some effect from well-known lanthanide contraction such as when the number of 4f-electrons increases cannot be excluded. Nevertheless, rare earths atoms with larger atomic size, La and Pr, increase the stability of rhombohedral phase while atoms with smaller atomic size, Gd, Dy, and Yb, decrease it.

BSE images (Fig. 3) show that all samples contain inclusions embedded in the matrix. Inclusions can be attributed to nearly pure Ge (dark areas) and rare earth-based phases (light areas). EDS and WDS data show that in all samples rare earth are present in the matrix at lower level than the nominal composition. In contrast, rare earth content in light inclusions is much higher compared to the matrix, and depends on rare earth. As an example, Figure 3(a) shows BSE image of $\text{Ge}_{49}\text{Te}_{50}\text{La}_1$ and demonstrates the presence of both dark and light inclusions. EDS and WDS data shows that La content in the matrix is less than 0.2 at.%, whereas Ge and Te contents are close to ~50 at.%. Electron beam scan along the sample [Figure 3(b)] demonstrates that in light inclusions, Ge content is lower, ~1 at.%, whereas La content is higher, ~30 at.%, compared to the matrix; Te content also increases, up to ~60 at.%. Similar picture is observed in the other $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ alloys, showing that rare earth atoms, about 0.2 at.%, are incorporated into the crystal lattice, i.e., less than the nominal composition. This indicates that solubility of rare earth in the GeTe matrix is low, which is consistent with ternary phase diagram known only for Ge-Te-La and Ge-Te-Yb [22]. Rare earths also are present in the inclusions and form phases, which produce additional low-intensity XRD patterns.

3.2. Magnetic field and temperature dependencies of the magnetization

It is obvious that rare earth addition to diamagnetic GeTe can result in an appearance of paramagnetic contribution due to localized magnetic moments and affect different magnetic field and temperature dependencies of the magnetization. Figure 4(a) shows magnetization of $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ alloys with $\text{R} = \text{La, Pr, Gd, Dy, and Yb}$ at temperature 300 K; data for GeTe are shown for comparison. $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ with $\text{R} = \text{La}$ and Yb similar to GeTe demonstrates diamagnetic properties while those with $\text{R} = \text{Pr, Gd, and Dy}$ show paramagnetic properties. The inset in Fig. 4(a) shows magnetization of the same samples at 1.8 K; note that samples with $\text{R} = \text{Pr}$ and Yb demonstrate paramagnetic properties, which can be explained by interplay between the contributions from diamagnetic GeTe matrix, M_{dia} , and from localized magnetic moments of rare earths atoms, M_{para} , so the total magnetization can be shown as $M_{\text{total}} = M_{\text{para}} - M_{\text{dia}}$ (note that diamagnetic contribution is negative). The magnetization of alloys with $\text{R} = \text{Gd}$ and Dy is mostly determined by M_{para} , particularly at 1.8 K, whereas that of alloys with $\text{R} = \text{Pr}$ and Yb is low due to small M_{para} and reduction due to M_{dia} (Table 2). Magnetization of the samples with $\text{R} = \text{Gd}$ and Dy demonstrates saturated behavior, which for paramagnetic systems can be described by the Brillouin function [17,23].

Figure 4(b) shows temperature dependencies of the M/H ratio (where M is the measured mass magnetization and H is the magnetic field, and $M/H = \chi$, i.e. the magnetic susceptibility) of $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ samples measured in a 10-kOe magnetic field. The inset in Fig. 4(b) demonstrates temperature dependencies of the H/M ratio $= 1/\chi$, for GeTe and $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ with $\text{R} = \text{La, Pr, and Dy}$. Both GeTe and $\text{Ge}_{49}\text{Te}_{50}\text{La}_1$ are diamagnetic in the temperature range of 1.8-350 K, which agree well with the fact that La atom does not carry localized magnetic moment. In contrast, $1/\chi \sim T$ dependencies for $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ with $\text{R} = \text{Gd}$ and Dy can be described by Curie law, which is

typical for materials with not interacting localized magnetic moments. Unfortunately, measurements of the magnetization do not allow us to separate the effects from rare earth atoms present in the GeTe matrix from that due to inclusions, but they demonstrate that these atoms are present in all alloys studied here.

3.3. ^{125}Te NMR spectra and spin-lattice relaxation time

In contrast to magnetization, which is a bulk property, NMR is a local probe, i.e., it is a microscopic method. ^{125}Te NMR collects signal from all Te nuclei and can distinguish Te atoms in different environments. Figure 5 shows ^{125}Te NMR spectra of $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ alloys with $\text{R} = \text{La}, \text{Pr}, \text{Gd}, \text{Dy}, \text{and Yb}$ at temperature 300 K. Only one peak is observed, which demonstrate that Te in these alloys has, in general, similar chemical environment, but the peak position depends on the rare earth element used. This is evidence that La, Pr, Gd, Dy, and Yb are incorporated in the GeTe lattice. Only for $\text{Ge}_{49}\text{Te}_{50}\text{Gd}_1$ the resonance shifts to the lower frequency, to the right, +130 ppm, of that for GeTe, +160 ppm [5], while for the rest of the alloys it shifts to the higher frequency, to the left; the maximal shift is found for $\text{Ge}_{49}\text{Te}_{50}\text{Dy}_1$, +220 ppm. Note that if NMR atoms in the same material have quite different environments, two resonances can be observed, as it was shown for ^{29}Si NMR in $\text{Mg}_2\text{Si-Si}$ eutectic alloys [24].

The resonance position, the total shift, δ_{total} , relative to reference material (see Experimental Details), depends on two contributions, $\delta_{\text{total}} = \delta_{\text{chem}} + K$, where δ_{chem} is the chemical shift due to chemical environment of Te atoms, and K is the Knight shift due to hyperfine interaction between Te nuclei and free charge carriers [25,26].

In materials containing paramagnetic ions or a magnetically ordered separate phase, NMR spectra can be affected by paramagnetic effect [27], which can produce paramagnetic shift

(change in resonance frequency), δ_{tot} , and paramagnetic broadening (the width of NMR signal becomes larger). Paramagnetic shift, δ_{par} , contains two contributions: (i) due to Fermi contact interaction, δ_{cont} , and (ii) due to magnetic dipole-dipole interaction, δ_{dip} , and $\delta_{par} = \delta_{cont} + \delta_{dip}$. Fermi contact interaction results in a magnetic field on nuclei due to hyperfine interaction between these nuclei and atoms with unpaired electrons, i.e., rare earths in our samples. It is observed in materials where each paramagnetic ion is a regular element of the lattice and affects nuclei through bonds. If no bonds occur between atoms used in NMR experiment and paramagnetic atoms, no contact shift would be observed.

Magnetic dipole-dipole interaction is analogous of the classical interactions between two magnetic dipoles, nucleus and paramagnetic ions. It can be observed in all types of materials containing paramagnetic centers or magnetic particles as the second phase [28]. In general, Fermi contact interaction is a local effect, while the magnetic dipole-dipole interaction can be observed even if a magnetic ion is located far from NMR nucleus, e. g., ~ 0.4 nm. In $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$, a paramagnetic effect can be expected for $\text{R} = \text{Gd}$ and Dy with large magnetic moments, and a lesser extent for $\text{R} = \text{Pr}$ and Yb with smaller magnetic moments (Table 2). However, similar ^{125}Te NMR resonance frequencies, 210 ± 10 ppm, for $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ with $\text{R} = \text{La}$, Pr , Dy , and Yb shows that its shift compared to that of GeTe is mostly due chemical environment, i.e. due to presence of rare earth atoms close to Te and affecting δ_{chem} .

Our data show that Gd and Dy in $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ produce a shift in opposite directions. Because ^{125}Te NMR spin-lattice relaxation time is similar in $\text{Ge}_{49}\text{Te}_{50}\text{Gd}_1$ and $\text{Ge}_{49}\text{Te}_{50}\text{Dy}_1$, ~ 4 ms (Table 3), and the effective magnetic moments of Gd^{3+} and Dy^{3+} are, in general, similar, the carrier concentration (see discussion of the Seebeck coefficient below) and the Knight shift are also expected to be similar. The shift of ^{125}Te NMR signal due to only magnetic dipole-dipole

interactions between magnetic moments of Te nuclei and Gd or Dy should be in the same direction. However, our observation of an opposite shift should be explained mostly by the Fermi contact interaction; note that the opposite effect from Gd compared to other rare earth elements was discussed in Ref. 29. This is additional evidence that rare earth atoms are incorporated into the lattice and form chemical bonds. Also, both Gd and Dy located in the inclusions cannot produce strong effect on the majority of Te atoms which are located in the GeTe matrix, i.e., far from these inclusions.

Dependencies of the normalized integral (and/or intensity) vs. delay time [19,20] allow us to obtain spin-lattice relaxation time. Our data shows that replacement of Ge in GeTe by rare earth atoms result in shorter nuclear spin relaxation times compared to that in GeTe. Note that very short spin-lattice relaxation in GeTe, $T_1 = 5.3$ ms, is due to hyperfine interaction between Te nuclei spins and free charge carriers of high concentration, $8 \times 10^{20} \text{ cm}^{-3}$ [2,5]. Spin-lattice relaxation time in $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ alloys with R = La, Pr, Gd, Dy, and Yb is, in general, slightly shorter than that of GeTe. Figure 6 shows ^{125}Te NMR spectra for $\text{Ge}_{49}\text{Te}_{50}\text{La}_1$ and $\text{Ge}_{49}\text{Te}_{50}\text{Gd}_1$ measured at various saturation recovery times demonstrating a very short spin-lattice relaxation time in both samples. More data for ^{125}Te NMR of $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ can be found in Table 3).

Shorter spin-lattice relaxation time estimated for all $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ alloys can be attributed to (i) higher carrier concentration in addition to (ii) faster relaxation due to dipole-dipole interactions between the magnetic moments of Te nuclei and $4f$ -electrons of rare earth atoms. Taking into the consideration larger width of ^{125}Te NMR signal observed for $\text{Ge}_{49}\text{Te}_{50}\text{Gd}_1$ and $\text{Ge}_{49}\text{Te}_{50}\text{Dy}_1$, and their magnetization, contribution (ii) can be relatively significant in $\text{Ge}_{49}\text{Te}_{50}\text{Gd}_1$ ($T_1 = 3.9$ ms) and $\text{Ge}_{49}\text{Te}_{50}\text{Dy}_1$ ($T_1 = 4.0$ ms), which can explain why their T_1 is shorter than that in both $\text{Ge}_{49}\text{Te}_{50}\text{La}_1$ and $\text{Ge}_{49}\text{Te}_{50}\text{Pr}_1$, $T_1 = 4.8$ ms. A short time found for

$\text{Ge}_{49}\text{Te}_{50}\text{Yb}_1$ ($T_1 = 3.7$ ms) can be explained by a higher carrier concentration, but small reduction due to paramagnetic effect also cannot be ignored.

The values of ^{125}Te NMR spin-lattice relaxation time agree well with the shift of resonance for all alloys studied: the shorter the spin-lattice relaxation, the larger the shift of the resonance to the left. The exception is the data for $\text{Ge}_{49}\text{Te}_{50}\text{Gd}_1$ where the resonance is observed at +130 ppm, which can be explained by paramagnetic effect produced by Gd [29]. Hence, replacement of Ge in GeTe by rare earth results in a change in the ^{125}Te NMR signal frequency and spin-lattice relaxation, which is evidence that rare earth atoms are located in the lattice and form chemical bonds with Te atoms. Our data demonstrates that Dy and Gd with large magnetic moments produce strong paramagnetic effect in ^{125}Te NMR due to both Fermi contact and dipole-dipole interactions.

3.4. Seebeck coefficient, electrical resistivity, and thermal conductivity

Figure 7 shows temperature dependencies of the Seebeck coefficient of $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ with R = Dy and Yb; data for GeTe are shown for comparison. For R = Gd the Seebeck coefficient is similar to that of Dy and for R = La and Pr (not shown here) the Seebeck coefficients are similar to that with R = Yb.

In general, replacement of Ge in GeTe by rare earth elements decreases the Seebeck coefficient, particularly at temperatures above ~550 K and when R = La, Pr, and Yb. Such a decrease can be attributed mostly to a higher carrier (holes) concentration, which was deduced from ^{125}Te NMR signal position and spin-lattice relaxation measurements. Hence, rare earths in GeTe act as an acceptor producing more free holes and affecting properties even if their concentration in the GeTe matrix is small. Samples with R = Dy and Gd have shorter spin-lattice

relaxation times which can be explained by paramagnetic effect while the hole concentration in these samples can be similar to that in samples with $R = \text{La, Pr, and Yb}$. In principle, if the value of the localized magnetic moment is ignored, rare earth atoms can affect the Seebeck coefficient nearly in the same way. Taking into consideration the difference between the Seebeck coefficients of $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ with $R = \text{Dy, and Gd}$, compared to that of alloys with $R = \text{La, Pr, and Yb}$, which reflects the magnetic contribution from $4f$ -localized magnetic moments.

Kasuya [30] has developed theory of the s - d -exchange contribution to the thermoelectric effects and showed that the Seebeck coefficient in ferromagnets and spin-diluted magnetic alloys depends on the spin-dependent carrier scattering. The Seebeck coefficient in this case is $S = S_{\text{dif}} + S_{\text{mag}}$ where S_{dif} and S_{mag} are the diffusion and magnetic components, respectively. Comparison of the Seebeck coefficient of $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ shows that the value of $S_{\text{mag}} = S_{R=\text{Dy}} - S_{R=\text{Yb}}$ is $\sim 14 \mu\text{V/K}$ at 750 K for (see the lower inset in Fig. 7); similar value, $\sim 12 \mu\text{V/K}$ at 750 K, is observed for $S_{\text{mag}} = S_{R=\text{Dy}} - S_{R=\text{La}}$, whereas the value of $S_{\text{mag}} = S_{R=\text{Dy}} - S_{R=\text{Gd}}$ is small, $\sim 3 \mu\text{V/K}$ at 750 K. Hence, the Seebeck coefficient of $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ samples is determined by the diffusion component, but the magnetic component due to large magnetic moment of rare earth ions can be significant.

Similar enhancement was reported by Radchenko *et al.* [31] for $\text{Pb}_{1-x-y}\text{Sn}_y\text{Mn}_x\text{Te}$ ($x = 0.12$ and $y = 0.72$, the composition in atomic % can be shown as $\text{Pb}_8\text{Sn}_{36}\text{Mn}_6\text{Te}_{50}$). The magnetic contribution in $\text{Pb}_8\text{Sn}_{36}\text{Mn}_6\text{Te}_{50}$ with the hole concentration of $p = 3.0 \times 10^{21} \text{ cm}^{-3}$ increases up to $\sim 4 \mu\text{V/K}$ at 35 K and then reduces when temperature rises; this was explained by the effect from a ferromagnetically ordered Mn sublattice with the Curie temperature of 32.7 K [31]. Our $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ containing 1 at.% of Gd and Dy show paramagnetic properties with non-interacting localized magnetic moments. However, the magnetic contribution is much larger than that in $\text{Pb}_8\text{Sn}_{36}\text{Mn}_6\text{Te}_{50}$. Our data demonstrates that Gd and Dy with their large magnetic moments

result in a much larger magnetic contribution to the Seebeck coefficient compared to the maximum due to S_{mag} observed for $\text{Pb}_8\text{Sn}_{36}\text{Mn}_6\text{Te}_{50}$ [31].

Tsujii and Mori [32] and Ang *et al.* [33] also show that the strong interaction between the charge carriers and the magnetic moment of Fe ions in magnetic semiconductor $\text{Cu}_{1+x}\text{Fe}_{1-x}\text{S}_2$ results in enhancement of the Seebeck coefficient.

Temperature dependencies of the electrical resistivity of $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ samples show metal-like behavior, indicating a highly degenerate state (see the data for R = Dy and Yb in comparison with GeTe on the inset in Fig. 7). Rare earth ions in GeTe matrix can reduce carrier mobility via magnetic scattering, but the electrical resistivity of $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ alloys in this case should be larger. The lower electrical resistivity of rare earth containing samples compared to that of GeTe can be explained by higher carrier concentration, which agrees well with shorter ^{125}Te NMR T_1 (Table 3).

Hence, based on the data for $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ with R = La, Pr, and Yb, i.e., rare earth with zero or small localized magnetic moments, we suggest that replacement of Ge in GeTe by rare earths, in general, slightly increases the carrier concentration. This can explain the smaller Seebeck coefficients observed, for example, for $\text{Ge}_{49}\text{Te}_{50}\text{Yb}_1$, $S_{750\text{K}} = +140 \mu\text{V/K}$, whereas that of GeTe is $S_{750\text{K}} = +160 \mu\text{V/K}$ (Fig. 7). In contrast, if R = Gd or Dy, i.e., rare earth with large localized magnetic moments, the Seebeck coefficient is not reduced so significantly; for example, $\text{Ge}_{49}\text{Te}_{50}\text{Dy}_1$ shows $S_{750\text{K}} = 154 \mu\text{V/K}$ (Fig. 7), which is a result of interplay between the reduction due to higher carrier concentration and enhancement due to magnetic contribution from Dy.

Similar enhancement of the Seebeck coefficient due to 1 at.% Dy was observed for $\text{Ag}_{6.5}\text{Sb}_{6.5}\text{Ge}_{36}\text{Te}_{50}\text{Dy}_1$ [9]. However, the Seebeck coefficient of $\text{Ag}_{6.5}\text{Sb}_{6.5}\text{Ge}_{36}\text{Te}_{50}\text{Dy}_1$ is

enhanced compared to that of the same materials without Dy, while in $\text{Ge}_{49}\text{Te}_{50}\text{Dy}_1$ it is reduced compared to that of GeTe. This fact shows that the enhancement of the Seebeck coefficient in GeTe-based materials is larger when rare earths are present in the GeTe matrix simultaneously with [Ag+Sb] atoms.

Finally, we would like to compare the effects from rare earths on thermal transport. The largest difference between the values of the thermal diffusivity compared to that of GeTe is observed for $\text{Ge}_{49}\text{Te}_{50}\text{Dy}_1$ (Figure 8). The inset in Fig. 8 demonstrates the temperature dependence of the thermal conductivity of GeTe [5] and $\text{Ge}_{49}\text{Te}_{50}\text{Dy}_1$ calculated within the assumption that the values of specific heat capacity and mass density of the alloy containing 1 at.% Dy are similar to that in GeTe [5]. At 300 K, thermal diffusivity (and conductivity) of $\text{Ge}_{49}\text{Te}_{50}\text{Dy}_1$ is smaller than that of GeTe by ~20%, whereas at 720 K the difference between them is about twice smaller.

The total thermal conductivity contains two contributions, $\kappa_{\text{total}} = \kappa_{\text{lat}} + \kappa_{\text{car}}$ where κ_{lat} and κ_{car} are contributions from lattice and free charge carriers. At 300 K and 720 K, κ_{car} of GeTe is significant, ~64 % of κ_{total} , due to high carrier concentration [5]. ^{125}Te NMR and Seebeck coefficient data show that the carrier concentration in $\text{Ge}_{49}\text{Te}_{50}\text{Dy}_1$ is higher than that in GeTe, which, in principle, should result in larger κ_{car} . However, smaller values of the thermal diffusivity (conductivity) of $\text{Ge}_{49}\text{Te}_{50}\text{Dy}_1$ shows that a reduction on κ_{lat} due to the presence of rare earth atoms in the lattice prevail an increase of κ_{car} . The thermoelectric figures of merit, ZT , of GeTe at 300 K and 720 K are 0.03 and 0.8 [5]. ZT values of $\text{Ge}_{49}\text{Te}_{50}\text{Dy}_1$ are slightly larger, 0.04 and 1.0, which can be attributed to lower electrical resistivity and reduction in lattice thermal conductivity due to the presence rare earth atoms in the lattice.

4. Summary

XRD patterns for $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ alloys with $\text{R} = \text{La, Pr, Gd, Dy, and Yb}$ obtained in the temperature range of 300 - 800 K demonstrate that rhombohedral distortion gradually decreases with temperature and at T_{cubic} all samples transform to cubic structure. La and Pr additions increase the transition temperature, T_{cubic} , whereas additions of Gd, Dy, and Yb decrease T_{cubic} . SEM, EDS and WDS shows that $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ alloys contain rare-earth enriched inclusions; rare earth atoms in the matrix are present at a lower level than the nominal composition, but they affect properties of the materials. The inclusions contain rare earth and tellurium and also are detected by XRD. $\text{Ge}_{49}\text{Te}_{50}\text{La}_1$ and GeTe show diamagnetic properties; $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ with $\text{R} = \text{Pr, Gd, and Dy}$ demonstrate paramagnetic properties due to localized magnetic moments of 4f-electrons. Due to interplay between diamagnetic matrix of GeTe and small effective magnetic moment of Yb, $\text{Ge}_{49}\text{Te}_{50}\text{Yb}_1$ shows paramagnetic properties below ~78 K and diamagnetic above. Response to a magnetic field of $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ materials is determined by the magnetism of the rare earth present in both the matrix and inclusions.

The position of ^{125}Te NMR signal is shifted compared to that of GeTe. Shorter spin-lattice relaxation time allows us to suggest that the shift can be mostly attributed to the Knight shift, indicating that rare earths reduce the carrier (hole) concentration. Both Gd and Dy produce strong paramagnetic effect in NMR mostly due to Fermi contact interaction, which is additional evidence that at least some rare earth atoms are incorporated into the lattice and form chemical bonds.

Replacement of Ge in GeTe by rare earths affects the Seebeck coefficient, which is a result of interplay between the reduction due to higher carrier concentration and enhancement due to magnetic contribution. The effect due to replacement of Ge in GeTe by Dy on the Seebeck

coefficient is smaller than that observed in $\text{Ag}_{6.5}\text{Sb}_{6.5}\text{Ge}_{36}\text{Te}_{50}\text{Dy}_1$. This can be explained by a larger amount of rare earth, which can be embedded into the lattice of materials containing [Ag+Sb] atomic pairs and possible effect from these pairs.

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Fig. 1. (a) XRD patterns ($\text{Co-}K_\alpha$ radiation, $\lambda = 0.179$ nm) for $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ alloys with $\text{R} = \text{La}$ (#1), Pr (#2), Gd (#3), Dy (#4), and Yb (#5) at 300 K (data for GeTe are shown for comparison), and (b) an expanded view for the same samples for $48^\circ \leq 2\theta \leq 52^\circ$ showing (024) and (220) peaks. Additional peaks attributed to the second phases are shown by arrows. The inset in (a) presents an expanded view for the same samples for $34^\circ \leq 2\theta \leq 36^\circ$ showing (202) peak.

Fig. 2. X-ray diffraction patterns obtained for (a) $\text{Ge}_{49}\text{Te}_{50}\text{La}_1$ and (b) $\text{Ge}_{49}\text{Te}_{50}\text{Gd}_1$ at temperatures varying from 300 to 800 K for $48^\circ \leq 2\theta \leq 52^\circ$ showing (024) and (220) peaks.

Fig. 3. (a) BSE image of $\text{Ge}_{49}\text{Te}_{50}\text{La}_1$ showing electron beam scanning along the matrix (gray) and two La-rich inclusions (light) with a width of 3-4 μm , and (b) the concentration of Ge, Te, and La in the sample matrix with nearly homogeneous distribution of these elements, and in both inclusions with much lower Ge content, higher La content, and slightly higher Te content. Dark area (left upper corner) is Ge inclusion [5,19].

Fig. 4. (a) The magnetization, M , measure at 300 K in varying magnetic field, H , and (b) temperature dependencies of the M/H ratio of $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ alloys with $\text{R} = \text{La}, \text{Pr}, \text{Gd}, \text{Dy}$, and Yb measured in 10 kOe magnetic field. The insets show (a) the magnetization measured at 1.8 K and (b) temperature dependencies of the H/M ratio for GeTe , and $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ with $\text{R} = \text{La}, \text{Pr}$, and Dy .

Fig. 5. ^{125}Te NMR saturated spectra (delay time 50 ms) of $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ with $\text{R} = \text{La}, \text{Pr}, \text{Gd}, \text{Dy},$ and Yb at 300 K. The values of the resonance position (at the right) and full width at half maximum ($FWHM$) (at the left) are shown; the dashed line shows the resonance position for GeTe at +160 ppm [5].

Fig. 6. (a) ^{125}Te NMR spectra of $\text{Ge}_{49}\text{Te}_{50}\text{La}_1$ and (b) $\text{Ge}_{49}\text{Te}_{50}\text{Gd}_1$ measured at various saturation recovery (delay) times showing that spin-lattice relaxation in $\text{Ge}_{49}\text{Te}_{50}\text{Gd}_1$ slightly is faster than that in $\text{Ge}_{49}\text{Te}_{50}\text{La}_1$. All spectra are fully saturated at delay time of 50 ms.

Fig. 7. Temperature dependencies of the absolute Seebeck coefficient of $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ with $\text{R} = \text{Dy}$ and Yb , and GeTe for a comparison. The upper inset shows the electrical resistivity of the same samples, the lower inset shows the magnetic contribution obtained as a difference between the Seebeck coefficients of $\text{Ge}_{49}\text{Te}_{50}\text{Dy}_1$ and $\text{Ge}_{49}\text{Te}_{50}\text{Yb}_1$, $S_{\text{mag}} = S_{\text{R=Dy}} - S_{\text{R=Yb}}$.

Fig. 8. Temperature dependencies of the thermal diffusivity of $\text{Ge}_{49}\text{Te}_{50}\text{Dy}_1$ and GeTe . The inset shows temperature dependencies of the thermal conductivity for the same samples.

Table 1. Lattice parameters and rhombohedral distortion, rare earths atomic radii for R^{3+} [16], the temperature when the crystal lattice becomes mostly cubic, T_{cubic} , for $\text{Ge}_{49}\text{Te}_{50}R_1$ alloys with $R = \text{La, Pr, Gd, Dy, and Yb}$ at 300 K.

Nominal composition	Lattice parameters $a = b = c$ (Å)	Rhombohedral angle $\alpha = \beta = \gamma$ (degree)	Rare earth atomic radius (Å)	T_{cubic} ± 10 K
GeTe	5.980(7)	88.37(1)	-	640
$\text{Ge}_{49}\text{Te}_{50}\text{La}_1$	5.981(5)	88.27(6)	2.740	700
$\text{Ge}_{49}\text{Te}_{50}\text{Pr}_1$	5.982(0)	88.27(7)	2.670	700
$\text{Ge}_{49}\text{Te}_{50}\text{Gd}_1$	5.984(4)	88.31(9)	2.540	650
$\text{Ge}_{49}\text{Te}_{50}\text{Dy}_1$	5.981(3)	88.27(8)	2.490	630
$\text{Ge}_{49}\text{Te}_{50}\text{Yb}_1$	5.981(1)	88.26(8)	2.400	630

Table 2. Nominal composition, theoretical magnetic moments for R^{3+} [17,29], dominant magnetic state, and magnetization of GeTe and $\text{Ge}_{49}\text{Te}_{50}R_1$ alloys with $R = \text{La, Pr, Gd, Dy, and Yb}$ measured in a 10-kOe magnetic field.

Nominal composition	Theoretical effective magnetic moment of R^{+3} (μ_B)	Dominant magnetic state ^(a)		Magnetization (emu/g)	
		1.8 K	300 K	1.8 K	300 K
GeTe	-	DM	DM	-0.0031	-0.0031
$\text{Ge}_{49}\text{Te}_{50}\text{La}_1$	-	DM	DM	-0.0025	-0.0026
$\text{Ge}_{49}\text{Te}_{50}\text{Pr}_1$	3.47	PM	PM	0.0277	0.0018
$\text{Ge}_{49}\text{Te}_{50}\text{Gd}_1$	7.94	PM	PM	0.7836	0.0134
$\text{Ge}_{49}\text{Te}_{50}\text{Dy}_1$	10.64	PM	PM	1.5888	0.0434
$\text{Ge}_{49}\text{Te}_{50}\text{Yb}_1$	4.3	PM	DM	0.0622	-0.0018

(a) DM - diamagnetic state, PM - paramagnetic state.

Table 3. ^{125}Te NMR peak position, full width and half maximum, spin-lattice relaxation time for $\text{Ge}_{49}\text{Te}_{50}\text{R}_1$ alloys with R = La, Pr, Gd, Dy, and Yb at 300 K.

Nominal composition	^{125}Te NMR peak position ± 5 (ppm)	Full width at half maximum (<i>FWHM</i>) ± 5 (ppm)	^{125}Te NMR spin-lattice relaxation time ± 0.2 (ms)
GeTe	+160	460	5.3
$\text{Ge}_{49}\text{Te}_{50}\text{La}_1$	+200	420	4.8
$\text{Ge}_{49}\text{Te}_{50}\text{Pr}_1$	+210	420	4.8
$\text{Ge}_{49}\text{Te}_{50}\text{Gd}_1$	+130	540	3.9
$\text{Ge}_{49}\text{Te}_{50}\text{Dy}_1$	+220	550	4.0
$\text{Ge}_{49}\text{Te}_{50}\text{Yb}_1$	+210	420	3.7