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journal homepage: [www.elsevier.com/locate/ssnmr](http://www.elsevier.com/locate/ssnmr) $^{125}\text{Te}$  NMR chemical-shift trends in PbTe–GeTe and PbTe–SnTe alloysB. Njagic<sup>a,b</sup>, E.M. Levin<sup>a,c</sup>, K. Schmidt-Rohr<sup>a,b,\*</sup><sup>a</sup> Division of Materials Sciences and Engineering, Ames Laboratory U.S. DOE, Ames, IA 50011, USA<sup>b</sup> Department of Chemistry, Iowa State University, Ames, IA 50011, USA<sup>c</sup> Department of Physics and Astronomy, Iowa State University, Ames, IA 50011, USA

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## ABSTRACT

Complex tellurides, such as doped PbTe, GeTe, and their alloys, are among the best thermoelectric materials. Knowledge of the change in  $^{125}\text{Te}$  NMR chemical shift due to bonding to dopant or “solute” atoms is useful for determination of phase composition, peak assignment, and analysis of local bonding. We have measured the  $^{125}\text{Te}$  NMR chemical shifts in PbTe-based alloys,  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$  and  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ , which have a rocksalt-like structure, and analyzed their trends. For low  $x$ , several peaks are resolved in the 22-kHz MAS  $^{125}\text{Te}$  NMR spectra. A simple linear trend in chemical shifts with the number of Pb neighbors is observed. No evidence of a proposed ferroelectric displacement of Ge atoms in a cubic PbTe matrix is detected at low Ge concentrations. The observed chemical shift trends are compared with the results of DFT calculations, which confirm the linear dependence on the composition of the first-neighbor shell. The data enable determination of the composition of various phases in multiphase telluride materials. They also provide estimates of the  $^{125}\text{Te}$  chemical shifts of GeTe and SnTe (+970 and  $+400 \pm 150$  ppm, respectively, from PbTe), which are otherwise difficult to access due to Knight shifts of many hundreds of ppm in neat GeTe and SnTe.

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## 1. Introduction

Complex tellurides, such as doped PbTe, GeTe, SnTe, AgSbTe<sub>2</sub>, and their alloys, are among the best-performing thermoelectric materials [1]. In studies of the chemical and electronic structure of these cubic or nearly cubic materials by magic-angle spinning (MAS)  $^{125}\text{Te}$  nuclear magnetic resonance (NMR) [2–4], knowledge of the effects of dopant or “solute” atoms on the  $^{125}\text{Te}$  chemical shift is useful for determination of phase composition, peak assignment, analysis of local bonding, and quantification of Knight shifts. Here we report isotropic  $^{125}\text{Te}$  NMR chemical shifts in series of  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$  and  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  samples. The peak intensities are analyzed in terms of a binomial distribution [5] on the  $N=6$  neighbor sites of Te in the rocksalt-like structure.

The observed chemical shift trends are compared with the results of density functional theory (DFT) calculations. While calculating NMR parameters in solids has become routine for nuclei such as  $^1\text{H}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}$ ,  $^{14}\text{N}$ ,  $^{15}\text{N}$ ,  $^{17}\text{O}$ ,  $^{23}\text{Na}$ ,  $^{27}\text{Al}$ ,  $^{29}\text{Si}$  and  $^{31}\text{P}$ , only a limited number of studies have been conducted on heavier nuclei [6]. Among p-row heavy elements, NMR parameters have been calculated for  $^{69/71}\text{Ga}$  [7],  $^{73}\text{Ge}$  [8–10],  $^{77}\text{Se}$  [10–13],  $^{119}\text{Sn}$  [14],  $^{207}\text{Pb}$  [15], and  $^{209}\text{Bi}$  [16]. Some  $^{125}\text{Te}$  NMR computational

studies of molecules in the gas phase [17,18] and of  $[\text{TePb}_6\text{F}_{18}]^{-8}$  clusters [19] have also been published, but to the best of our knowledge the present work is the first computational study of  $^{125}\text{Te}$  NMR chemical shifts in solids with periodic boundary conditions.

Extrapolation to Te surrounded by six Ge or Sn neighbors is used to estimate the  $^{125}\text{Te}$  chemical shifts in GeTe and SnTe, respectively, which are difficult to determine directly due to Knight shifts of many hundreds of ppm in these materials [20]. The chemical shift of GeTe is also of interest in the analysis of the local structure of GeTe-based phase-change materials for data storage [21,22] by  $^{125}\text{Te}$  NMR [23,24].

## 2. Experimental

## 2.1. Sample synthesis

$\text{Pb}_{1-x}\text{Ge}_x\text{Te}$  alloys with  $x=0.1, 0.2, 0.3$  and  $0.5$ , and  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  alloys with  $x=0.05$  and  $0.3$  were prepared by direct reaction of elemental Pb, Te, Ge or Sn in 12-mm diameter fused silica ampoules. For  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$  alloys, the ampoules were heated up to 1223 K for 4 h to melt the constituents, and periodically shaken to form a homogeneous ingot upon solidification. Then, the materials were cooled to 923 K, held at this temperature for 281 h, and finally quenched in ice water. For the  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  alloys, the ampoules were heated up to 1273 K for 4 h, periodically

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shaken, then cooled to 973 K and held for 168 h, and finally quenched in ice water.

## 2.2. NMR

$^{125}\text{Te}$  NMR experiments were performed at 126 MHz using a Bruker Biospin (Billerica, MA) DSX-400 spectrometer (magnetic field of 9.39 T). The coarsely powdered samples were packed into 2.5-mm zirconia rotors and spun at 22 kHz in a magic-angle-spinning probe head (Bruker). The  $\pi/2$  pulse length was 2.5  $\mu\text{s}$ . Signals were detected after a Hahn echo generated by a  $\pi/2 - t_r - \pi - t_r$  two-pulse sequence, where  $t_r$  denotes a rotation period. Measuring times generally ranged between 15 and 24 h per spectrum. To minimize distortion of relative peak intensities by the pulse excitation bandwidth, the carrier radio frequency was placed near the maximum of the spectrum.  $^{125}\text{Te}$  NMR chemical shifts were referenced to  $\text{Te}(\text{OH})_6$  in solution, using solid  $\text{TeO}_2$  at +750 ppm as a secondary reference [25]. Chemical shifts relative to  $(\text{CH}_3)_2\text{Te}$ , another common reference [24,26], are obtained by adding +712 ppm to the values given here [26]. The spectra of  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$  were recorded with recycle delays of 30 s for  $x=0.1$ , 10 s for  $x=0.2$ , and 1 s for  $x=0.3$  and 0.5. The recycle delays for the spectra of  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  exceeded 12 s. The effect of the recycle delay on the spectral line shape was minimal.

Dephasing by the recoupled chemical-shift anisotropy was measured at 22 kHz MAS with a simple three-pulse sequence  $\pi/2 - t_{\text{CSA}} - \pi - t_{\text{CSA}} - \pi/2 - t_z$ , with  $\gamma$ -averaging by incrementing  $t_z$  in four steps by  $t_r/4$  [27]. The dephasing time  $t_{\text{CSA}}$  was varied from 0 to 20  $\mu\text{s}$ . The effective dephasing time was taken to be  $t_{\text{CSA,eff}} = t_{\text{CSA}} + 4 \mu\text{s}$ , to take into account the finite pulse lengths during the recoupling sequence.

## 2.3. Energy dispersive spectroscopy

To quantify the Sn concentration in the  $\text{PbTe-SnTe}$  alloys, energy dispersive X-ray spectroscopy (EDS) was applied. The polished surfaces of disks cut from the ingots were examined in a JEOL JXA-8200 electron microprobe.

## 2.4. Computational details

A series of *ab-initio* calculations were performed on the  $\text{PbTe}$  system where the amount of Pb was systematically replaced by Sn or Ge in increments of 25%, with each computation being performed in the smallest possible unit cell. That is, 8-atom unit cells were used in calculations on structures containing 25% and 75% Ge/Sn on the Pb sublattice, while 50% Ge/Sn replacing Pb was analyzed in 4-atom unit cells. In addition, the following systems with low doping content were studied in a 64-atom unit cell:  $\text{Pb}_{0.97}\text{Ge}_{0.03}\text{Te}$ ,  $\text{Pb}_{0.88}\text{Ge}_{0.12}\text{Te}$ ,  $\text{Pb}_{0.97}\text{Sn}_{0.03}\text{Te}$ , and  $\text{Pb}_{0.94}\text{Sn}_{0.06}\text{Te}$ . All geometry optimizations and NMR chemical shift calculations were performed using plane wave density functional theory (DFT) employing the Perdew–Burke–Ernzerhof (PBE) functional and on-the-fly generated pseudopotentials [28]. An energy cutoff of 550 eV was used along with the exact representation of the electron density and a Monkhorst-Pack grid of  $0.01 \text{ \AA}^{-1}$  or denser spacing of  $k$ -points. Geometry optimizations were conducted with the following criteria: energy convergence of  $5 \times 10^{-6} \text{ eV/atom}$ , maximum force of  $0.01 \text{ eV/\AA}$ , maximum stress of 0.02 GPa and maximum displacement of  $5 \times 10^{-4} \text{ \AA}$ . The calculated lattice parameters are well converged within less than  $10^{-3} \text{ \AA}$ , and  $^{125}\text{Te}$  NMR chemical shifts within 10 ppm. The calculations were performed using CASTEP and CASTEP NMR programs, and the results were visualized using Materials Studio (Accelrys Software Inc.) [28].

## 3. Results and discussion

### 3.1. Spectra of $\text{PbTe-GeTe}$ alloys

Fig. 1 shows a series of  $^{125}\text{Te}$  MAS NMR spectra of quenched  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$  materials for  $x=0.1, 0.2, 0.3$ , and 0.5 (nominal). At the lowest Ge concentrations, see Fig. 1(a), the largest peak is observed near  $-1860 \text{ ppm}$ , close to the resonance position of  $\text{PbTe}$  with low charge carrier concentration and therefore negligible Knight shift [2]; the long  $T_1$  relaxation time ( $> 5 \text{ s}$ ) confirms the low carrier concentration [2]. The signal near  $-1860 \text{ ppm}$  is from Te bonded to six Pb atoms, as in  $\text{PbTe}$ . The peaks to the left of the  $\text{PbTe}$  signal successively grow in intensity with increasing  $x$ . We attribute these to Ge on the Pb sublattice producing a chemical shift at a  $^{125}\text{Te}$  atom to which it is bonded, with an increment of approximately  $+162 \text{ ppm}$  per Ge atom. An explanation in terms of different Knight shifts (resulting from different charge carrier concentrations) can be ruled out, since the  $T_1$  relaxation times of all the peaks are similar for each material. If the shift by  $+162 \text{ ppm}$  were caused by Knight shift, the  $T_1$  relaxation time of the shifted signal would be shorter by orders of magnitude [2,20,29]. Note that in  $^{207}\text{Pb}$  NMR of  $\text{PbTe}$ -based materials, the Knight shifts are more than an order of magnitude larger than in  $^{125}\text{Te}$  NMR [2,29], making  $^{207}\text{Pb}$  NMR less suitable for detecting chemical-shift effects. X-ray diffraction of the  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$  samples shows peak patterns similar as in cubic  $\text{PbTe}$ , with slight shifts to larger scattering angles indicating incorporation of Ge, which has a smaller radius than Pb, but without indications of a significant distortion of the cubic symmetry.

As in the rocksalt structure of  $\text{PbTe}$ , in  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$  each tellurium atom is bonded to  $N=6$  neighbors on the Pb/Ge sublattice. This holds even in the presence of the small ( $\sim 2^\circ$ ) rhombohedral distortion in the low-temperature phase of  $\text{GeTe}$

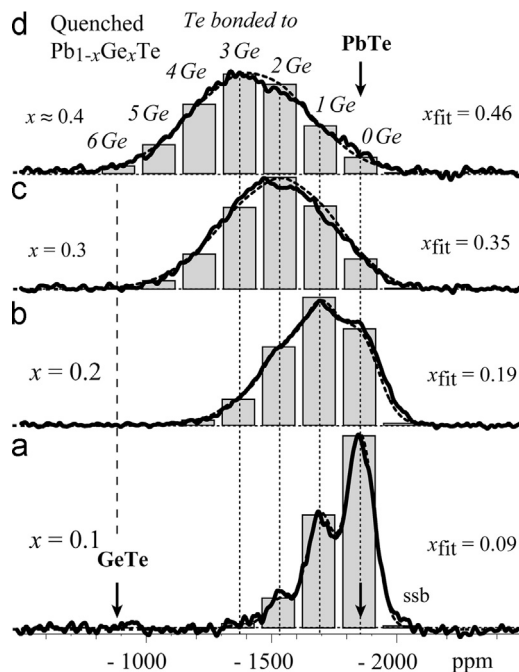


Fig. 1. Series of  $^{125}\text{Te}$  MAS NMR spectra of quenched  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$ , with binomial fits (including small spinning sidebands, see text) superimposed as bar graphs and dashed lines. (a) Nominal  $x=0.1$ , fit with  $x=0.09$  (Gaussian broadening of the simulated spectra with  $\sigma=54 \text{ ppm}$ ). (b) Nominal  $x=0.2$ , fit with  $x=0.19$  (broadening  $\sigma=74 \text{ ppm}$ ). (c) Nominal  $x=0.3$ , fit with  $x=0.35$  (broadening  $\sigma=92 \text{ ppm}$ ). (d) Nominal  $x=0.5$ , with  $x \approx 0.4$  in the  $\text{PbTe}$ -rich phase observed here, and fit for  $x=0.46$  (broadening  $\sigma=92 \text{ ppm}$ ). The predicted chemical-shift position of  $\text{GeTe}$ , assumed to correspond to that of  $\text{Te}$  bonded to six Ge neighbors, is indicated. Spinning frequency: 22 kHz.

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