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Synthetic Strategy of Solution Process Precursors for Phase Change Memory

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**ABSTRACT.** In this study, the relationship between the steric hindrance of the alpha carbon substituent group of aminoalkoxy ligand and formation of germanium telluride (GeTe) and

antimony telluride (Sb<sub>2</sub>Te<sub>3</sub>) was elucidated. A series of germanium and antimony precursors was prepared using aminoalkoxide-type bidentate ligands of different sizes such as dmampH, dmapH and dmaeH. These precursor materials were further treated with bis(trimethylsilyl)tellurium in hexadecane through thermal reaction and studied with powder X-ray diffraction (pXRD) to compare the formation of germanium telluride (GeTe) and antimony telluride (Sb<sub>2</sub>Te<sub>3</sub>) alloys which are potential precursor materials for phase change random access memory devices. While the pXRD patterns of the thermal reaction materials of compounds **2** and **3** at 190 °C revealed a rhombohedral phase of GeTe and tellurium, compounds **5** and **6** at 190 °C showed a rhombohedral phase of Sb<sub>2</sub>Te<sub>3</sub> and tellurium at this temperature. These results suggested that the formation of chalcogenide alloys was more favorable when relatively less bulk ligand was used.

Keywords: Aminoalkoxy Ligand; Antimony Telluride; Germanium Telluride; Phase Change Random Access Memory; Precursor Chemistry

# **1. INTRODUCTION**

Materials that exist in two distinct states, either amorphous or crystalline phases, and are capable of switching between them are known as phase change materials. Previous research has revealed that the crystalline and amorphous phases of such materials can be switched repeatedly at a desired operating temperature. Owing to the different electrical properties of the material in its different phases, the materials are able to store information. This feature reflects the

tremendous potential of phase change materials for application in the field of information technology. These materials are have gained widespread recognition owing to their application in rewritable optical phase change storage system such as CDs and DVDs, and current aspiration for these materials include developing phase change random access memory (PCRAM) devices as a next generation data storage technology. Novel phase change materials must demonstrate non-volatile memory and also compete with flash memory drives in terms of high read and write speeds in dynamic random access memory (DRAM) [1-3].

For example, chalcogenides, non-metallic group 16 elements, are known to be suitable for PCRAM devices as they exhibit numerous glass transition and melting temperatures, which gives them different electrical resistivities. This property allows chalcogenides to exist in two different phases, i.e., amorphous and crystalline. Typically, when applied as a binary state device, the amorphous phase can represent the 'OFF' state logic of '0' by having high resistance while the crystalline phase represents the 'ON' state logic of '1' by having a lower resistance [4-6]. Switching of the resistance state from high to low can be achieved by applying voltage that is higher than the threshold voltage. On the other hand, it can be reversed by applying current through the memory device while the material is being heated above its melting point to return to its amorphous status.

Among the various materials reported to date, the alloy of Ge and Sb, Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> (GST225), is a widely known general phase change material for PCRAM devices. It is a pseudo binary compound, GeTe–Sb<sub>2</sub>Te<sub>3</sub>, made up of Ge material that has good data stability and Sb material with fast switching speeds [7-14].

Recently, the synthesis of nanostructured metal chalcogenide materials by solution processing

has been reported. Previous research has mainly focused on the synthesis of crystalline metal chalcogenide nanomaterials by thermal decomposition of single metal precursors [15-17]. However, it is difficult to control the atomic ratio of the desired materials using single source materials. Therefore, studies on dual source materials, i.e., using separate metal and chalcogen sources, have been performed [17-21]. While various organometallic precursors have been studied to obtain these materials, aminoalkoxide-based complexes are garnered interest owing to their good reactivity with the chalcogen source in a solution reaction. These complexes have also been used as precursors for atomic layer deposition and chemical vapor deposition for metal oxide thin film growth [22-25].

In recent years, extensive studies have been conducted on the synthesis of metal chalcogenides by solution processing using aminoalkoxide precursors and its mechanism [26,27]. Schulz et al. reported the synthesis and mechanism of antimony and germanium telluride materials from the reaction of aminoalkoxide complexes of antimony and germanium with Te(SiEt<sub>3</sub>)<sub>2</sub>. Aminoalkoxide-containing precursors were reacted with Te(SiEt<sub>3</sub>)<sub>2</sub> to generate antimony telluride or germanium telluride with silyl ether, Et<sub>3</sub>SiOC<sub>2</sub>H<sub>4</sub>Me<sub>2</sub>, as a byproduct in diisopropylbenzene (DIPB) under inert conditions and studied using temperature dependent in situ <sup>1</sup>H NMR.

Our group recently attempted the synthesis of GeTe using a Ge precursor with an aminoalkoxide ligand, i.e.,  $Ge(dmamp)_2$ , (dmampH = 1-(dimethylamino)-2-methylpropan-2-ol). Interestingly, the reaction of this precursor with *bis*(trimethylsilyl)tellurium was unsuccessful and GeTe was not formed. This was probably attributable to the sterically bulky  $\alpha$ -carbon substituents of the aminoalkoxy ligand that prevented bond formation between silicon and oxygen, as shown in Fig. 1.



Fig 1. Synthetic mechanism of GeTe

To elucidate the phenomena described above, we compared aminoalkoxide-based precursors with different substituents. Since the solution process is a convenient and well-established method, the reactivity of various aminoalkoxide-based precursors with dialkylsilyl tellurium was investigated to compare the electronic and steric effects of the ligands and identify the best organic ligands for alternative precursors. Herein, we report the preparation of germanium precursors,  $Ge(dmap)_2$  (1),  $Ge(dmap)_2$  (2), and  $Ge(dmae)_2$  (3), and antimony precursors,  $Sb(dmap)_3$  (4),  $Sb(dmap)_3$  (5), and  $Sb(dmae)_3$  (6). These precursors were used for thermal reactions with *bis*(trimethylsilyl)tellurium in hexadecane to form chalcogenide alloys for PCRAM devices by varying the sizes of the aminoalkoxide ligands (dmapH = 1-(dimethylamino)propan-2-ol, dmaeH = 2-(dimethylamino)ethan-1-ol). All of the synthesized materials were characterized by powder X-ray diffraction (pXRD) studies to track the relationship between the steric effect and hindrance to the formation of GeTe and Sb<sub>2</sub>Te<sub>3</sub>. Results from pXRD revealed that the reason for the failure of formation GeTe from Ge(dmamp)<sub>2</sub> was due to the hindrance effect of methyl groups when compared with the successful formation of germanium telluride (GeTe) and antimony telluride (Sb<sub>2</sub>Te<sub>3</sub>) using relatively smaller ligands

used during the thermal reaction.



Chart 1. Aminoalkoxide type ligands used in this study

# 2. Experimental

All manipulations were performed under a dry, oxygen-free nitrogen or argon atmosphere using standard Schleck techniques or in a glove box. All solvents were purified by the Innovative Technology PS-MD-4 solvent purification system. All reagents were purchased from Sigma Aldrich and/or Acros. Functionalized bidentate amino alcohols, dmampH, (CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>OH, and Na(dmamp) were prepared according to a literature procedure [24]. Na(dmap) and Na(dmae) were prepared following a similar procedure as for Na(dmamp). Ge(dmamp)<sub>2</sub> was synthesized by modifying a previously reported method[28]. Although  $Ge(dmae)_2$  and  $Sb(dmae)_3$  compounds are known, they were synthesized following the same method as for Ge(dmamp) [29,30]. Ge(dmap)<sub>2</sub> and Ge(dmae)<sub>2</sub> were prepared by a similar procedure as for Ge(dmamp)<sub>2</sub>. Sb(dmamp)<sub>3</sub> was obtained by modifying reported methods [31,32]. Sb(dmap)<sub>3</sub> and Sb(dmae)<sub>3</sub> were prepared in a similar manner as Sb(dmamp)<sub>3</sub>. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker DPX 500 MHz FT-NMR spectrometer. All samples for NMR measurements were contained in sealed NMR tubes and referenced using benzene- $d_6$  as the standard. Powder X-ray diffraction (pXRD) patterns of the materials obtained by thermal reaction of the complexes were measured using a Rigaku D/Max-2200 V X-ray diffractometer operating at 40 kV and 40 nA using Cu Ka as the target.

### 2.1. Preparation of starting materials

**Na(dmamp)**. dmampH (5.1 g, 43.5 mmol) was slowly added to a suspension of sodium (1.0 g, 43.5 mmol) in hexane (50 mL) at 0 °C, and the mixture was allowed to reflux overnight. After cooling to room temperature, the solvent was removed to obtain Na(dmamp) as a white powder (5.3 g, 87%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz):  $\delta$  1.23 (s, 6H, OC(CH<sub>3</sub>)<sub>2</sub>), 2.24 (s, 8H, N(CH<sub>3</sub>)<sub>2</sub> and CH<sub>2</sub>).

**Na(dmap)**. dmapH (8.9 g, 87 mmol) was slowly added to a suspension of sodium (2.0 g, 87 mmol) in hexane (100 mL) at 0 °C, and the mixture was allowed to reflux overnight. After cooling to room temperature, the solvent was removed to obtain Na(dmap) as a white powder (8.9 g, 82%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz):  $\delta$  1.25 (d, 3H, OCCH<sub>3</sub>), 2.03 (d, 1H, NCH<sub>2</sub>), 2.20 (t, 1H, NCH<sub>2</sub>), 2.25 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 4.28 (m, 1H, OCH).

**Na(dmae)**. dmaeH (7.7 g, 87 mmol) was slowly added to a suspension of sodium (2.0 g, 87 mmol) in hexane (100 mL) at 0 °C, and the mixture was allowed to reflux overnight. After cooling to room temperature, the solvent was removed to obtain Na(dmae) as a white powder (7.7 g. 80%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz):  $\delta$  2.30 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 2.50 (t, 2H, NCH<sub>2</sub>), 4.15 (t, 2H, OCH<sub>2</sub>).

### 2.2. Preparation of germanium complexes 1-3)

 $Ge(dmamp)_2$  (1).  $GeCl_2$ ·dioxane (0.80 g, 3.50 mmol) was slowly added to a solution of Na(dmamp) (1.0 g, 7.30 mmol) in hexane. The reaction mixture was allowed to stir overnight at room temperature. After filtering the mixture to remove the salts, the filtrate was concentrated *in* 

*vacuo* to afford the desired product. Pure product was obtained as a colorless liquid by distillation under vacuum (80 °C/0.5 Torr). Yield: 0.9 g (81%); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz):  $\delta$  1.37 (s, 6*H*, OC(CH<sub>3</sub>)<sub>2</sub>), 2.25 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 2.31 (s, 2H, CH<sub>2</sub>N).

**Ge**(**dmap**)<sub>2</sub> (**2**). GeCl<sub>2</sub>·dioxane (1.0 g, 4.30 mmol) was slowly added to a solution of Na(dmap) (1.1 g, 8.8 mmol) in hexane. The reaction mixture was allowed to stir overnight at room temperature. After filtering the resultant solution, the filtrate was concentrated *in vacuo* to afford the product. Pure product was obtained as a colorless liquid by distillation under vacuum (80 °C/0.5 Torr). Yield: 0.77 g (65%); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz): δ 1.09 (d, 3H, OCCH<sub>3</sub>), 1.76 (d, 1H, NCH<sub>2</sub>), 1.92 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 2.00 (t, 1H, NCH<sub>2</sub>), 3.66 (m, 1H, OCH). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 125 MHz): δ 23.4 (N(CH<sub>3</sub>)<sub>2</sub>), 43.7 (NCH<sub>2</sub>), 66.2 (OCH), 68.1 (CHCH<sub>3</sub>). IR (KBr, cm<sup>-1</sup>): 830, 945, 1026, 1145, 1346, 1457, 2568, 2638, 2776, 2818, 2850, 2640. Anal. Calcd. for C<sub>10</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>Ge: C, 43.4; H, 8.73; N, 10.11%. Found: C, 42.5; H, 8.14; N, 9.12%.

**Ge(dmae)**<sub>2</sub> (**3**). GeCl<sub>2</sub>·dioxane (1.0 g, 4.30 mmol) was slowly added to a solution of Na(dmae) (1.0 g, 8.90 mmol) in hexane. The reaction mixture was allowed to stir overnight at room temperature. The mixture was subsequently filtered to remove the salts and the filtrate was concentrated *in vacuo* to afford the product as white solid. Yield: 0.99 g (93%); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz): δ 2.23 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 2.43 (t, 2H, NCH<sub>2</sub>), 3.92 (t, 2H, OCH<sub>2</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 125 MHz): δ 45.9 (N(CH<sub>3</sub>)<sub>2</sub>), 61.8 (NCH<sub>2</sub>), 66.9 (OCH<sub>2</sub>). IR (KBr, cm<sup>-1</sup>): 776, 876, 945, 1035, 1123, 1276, 1370, 1455, 1616, 2517, 2600, 2663, 2773, 2942. Anal. Calcd. for C<sub>8</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>Ge: C, 38.6; H, 8.10; N, 11.3%. Found: C, 39.2; H, 9.03; N, 11.7%.

### 2.3. Preparation of Ge(dmatfp)<sub>2</sub>

Ge(dmatfp)<sub>2</sub> was synthesized by modifying the synthetic method of Ge(dmamp)<sub>2</sub>. GeCl<sub>2</sub>·dioxane (3.2 g, 14 mmol) was slowly added to a solution of Na(dmatfp) (5.0 g, 28 mmol) in tetrahydrofuran (THF). The reaction mixture was allowed to stir overnight at room temperature. Subsequently, the mixture was filtered to remove salts, and the filtrate was concentrated *in vacuo* to afford the desired product. Pure product was obtained as a white solid by sublimation under vacuum (90 °C/0.5 Torr). Yield: 4.0 g (75%); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz):  $\delta$  1.86 (s, 7*H*, N(CH<sub>3</sub>)<sub>2</sub>, CH<sub>2</sub>N), 2.83 (t, 1H, CH<sub>2</sub>N), 4.19 (br, 1H, OCH(CF<sub>3</sub>)). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 125 MHz):  $\delta$  56.8 (N(CH<sub>3</sub>)<sub>2</sub>), 72.7 (NCH<sub>2</sub>), 73.1 (OCH), 124.8 (CHCF<sub>3</sub>).

2.4. Preparation of antimony complexes 4-6

**Sb(dmamp)**<sub>3</sub> (**4**). SbCl<sub>3</sub> (1.0 g, 4.40 mmol) was slowly added to a solution of Na(dmamp) (2.0 g, 14.60 mmol) in hexane. The reaction mixture was allowed to stir overnight at room temperature and then filtered to remove salts. The filtrate was concentrated *in vacuo* to afford the desired product. The pure product was obtained as a colorless liquid by distillation under vacuum condition (120 °C/0.5 Torr). Yield: 1.57 g (76%); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz):  $\delta$  1.50 (s, 6H, C(CH<sub>3</sub>)<sub>2</sub>), 2.25 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 2.45 (s, 2H, CH<sub>2</sub>N).

**Sb(dmap)**<sub>3</sub> (**5**). SbCl<sub>3</sub> (1.2 g, 5.30 mmol) was slowly added to a solution of Na(dmap) (2.0 g, 16.00 mmol) in hexane. The reaction mixture was allowed to stir overnight at room temperature. After filtering the resulting solution, the filtrate was concentrated *in vacuo* to afford the product as a white solid. Yield: 2.07 g (91%); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz):  $\delta$  1.24 (d, 3H, OCCH<sub>3</sub>), 1.96 (d, 1H, NCH<sub>2</sub>), 2.19 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 2.27 (t, 1H, NCH<sub>2</sub>), 4.12 (br, 1H, OCH). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 125 MHz):  $\delta$  23.4 (N(CH<sub>3</sub>)<sub>2</sub>), 43.7 (NCH<sub>2</sub>), 66.2 (OCH), 68.1 (CHCH<sub>3</sub>). Melting point : 71 °C. IR (KBr, cm<sup>-1</sup>): 499, 578, 612, 698, 773, 945, 983, 1037, 1144, 1176, 1206, 1311, 1456, 2780,

2821, 2845, 2946. Anal. Calcd. for C<sub>15</sub>H<sub>36</sub>N<sub>3</sub>O<sub>3</sub>Sb: C, 32.0; H, 8.47; N, 9.81%. Found: C, 33.5; H, 7.26; N, 9.11%.

**Sb(dmae)**<sub>3</sub> (6). SbCl<sub>3</sub> (1.3 g, 5.70 mmol) was slowly added to a solution of Na(dmae) (2.0 g, 18.00 mmol) in hexane. The reaction mixture was allowed to stir overnight at room temperature. After removing the salts by filtration, the filtrate was concentrated *in vacuo* to afford the desired product as a white solid. Yield: 1.23 g (56%); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz):  $\delta$  2.30 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 2.47 (br, 2H, NCH<sub>2</sub>), 4.07 (br, 2H, OCH<sub>2</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 125 MHz):  $\delta$  45.7 (N(CH<sub>3</sub>)<sub>2</sub>), 61.5 (NCH<sub>2</sub>), 66.3 (OCH<sub>2</sub>). IR (KBr, cm<sup>-1</sup>): 574, 776, 876, 946, 1035, 1121, 1277, 1370, 1456, 1614, 2664, 2730, 2774, 2817, 2849, 2944, 2974. Anal. Calcd. for C<sub>12</sub>H<sub>30</sub>N<sub>3</sub>O<sub>3</sub>Sb: C, 37.5; H, 7.83; N, 10.9%. Found: C, 37.5; H, 8.14; N, 9.73%.

### 2.4. Thermal reaction of prepared compounds

The thermal reaction was conducted according to a literature procedure [26]. Germanium complexes (3.5 mmol) and *bis*(trimethylsilyl)tellurium (1 mL, 3.5 mmol) were added to hexadecane (19 mL, 64.6 mmol) at room temperature. The solution was heated overnight at 150 °C or 190 °C under a nitrogen atmosphere. Subsequently, the reaction mixture was cooled to room temperature and centrifuged at 10,000 rpm for 7 min. The obtained black precipitates were washed three times with toluene.

Ge(dmatfp)<sub>2</sub> (3.5 mmol) and *bis*(trimethylsilyl)tellurium (1 mL, 3.5 mmol) were mixed in hexadecane (19 mL, 64.6 mmol) at room temperature. The solution was heated overnight at 150  $^{\circ}$ C or 190  $^{\circ}$ C under nitrogen. The reaction mixture was subsequently cooled to room

temperature and centrifuged at 10,000 rpm for 7 min. The obtained black precipitates were washed thrice with toluene.

Antimony complexes (2.4 mmol) and *bis*(trimethylsilyl)tellurium (1 mL, 3.5 mmol) were added to hexadecane (19 mL, 64.6 mmol) at room temperature. The solution was heated overnight at 190 °C under nitrogen atmosphere. Subsequently, the reaction mixture was cooled to room temperature and centrifuged at 10,000 rpm for 7 min. The obtained black precipitates were washed with toluene three times.

All synthesized materials were characterized by powder X-ray diffraction (pXRD) to study the relationship between the steric effect and formation of GeTe and Sb<sub>2</sub>Te<sub>3</sub> from the thermal reaction.

# **3. RESULTS AND DISCUSSION**



Scheme 1. Synthesis of germanium complexes (1-3) and antimony complexes (4-6)

Scheme 1 summarizes the synthesis of Ge and Sb-containing compounds prepared in this study. Reaction of GeCl<sub>2</sub>·dioxane with 2 equivalents of Na(dmamp) afforded a colorless liquid,

 $Ge(dmamp)_2$  (1), which was purified by vacuum distillation (90 °C/0.5 Torr), in 81% yield [28].  $Ge(dmap)_2$  (2) and  $Ge(dmae)_2$  (3) were synthesized following a similar procedure as for 1. For these complexes, Na(dmap) and Na(dmae) were used instead of Na(dmamp). Complexes 2 and 3 were obtained as a colorless liquid and white solid in 65% and 93% yields, respectively (Scheme 1). Reaction of SbCl<sub>3</sub> with 3 equivalents of Na(dmamp) afforded a colorless liquid, Sb(dmamp)<sub>3</sub> (4), which was purified by vacuum distillation (120 °C/0.5 Torr), in 76% yield [31]. Sb(dmap)<sub>3</sub> (5) and Sb(dmae)<sub>3</sub> (6) were prepared by following a similar procedure as for 4. Complexes 5 and 6 were obtained as white solids in 91% and 56% yields, respectively (Scheme 1). The <sup>1</sup>H NMR spectrum of complex 1 recorded in benzene- $d_6$  showed three singlets at 1.37 ppm (OC(CH<sub>3</sub>)<sub>2</sub>), 2.25 ppm (N(CH<sub>3</sub>)<sub>2</sub>), and 2.31 ppm (CH<sub>2</sub>), which were shifted downfield with respect to Na(dmamp) ( $\delta_{\rm H} = 1.23$  ppm (OC(CH<sub>3</sub>)<sub>2</sub>), 2.24 ppm (N(CH<sub>3</sub>)<sub>2</sub>, CH<sub>2</sub>)). In the case of complex 2, the signals for the OCCH<sub>3</sub>, NCH<sub>2</sub>, N(CH<sub>3</sub>)<sub>2</sub>, and OCH groups of the dmap ligand appeared as a doublet at 1.09 ppm, doublet at 1.76 ppm and triplet at 2.00 ppm, singlet at 1.92 ppm, and a multiplet at 3.66 ppm, respectively. These peaks were shifted upfield as compared to those of Na(dmap) ( $\delta_{\rm H} = 1.25$  ppm (OCCH<sub>3</sub>), 2.03 ppm (NCH<sub>2</sub>), 2.20 ppm (NCH<sub>2</sub>), 2.25 ppm(N(CH<sub>3</sub>)<sub>2</sub>, and 4.28 ppm (OCH)). Further, complex 3 was characterized by a singlet at 2.23 ppm (N(CH<sub>3</sub>)<sub>2</sub>) and two triplets at 2.43 ppm (NCH<sub>2</sub>) and 3.92 ppm (OCH<sub>2</sub>), which were upfield with respect to Na(dmae) ( $\delta_{\rm H} = 2.30$  ppm (N(CH<sub>3</sub>)<sub>2</sub>), 2.50 ppm (NCH<sub>2</sub>), 4.15 (OCH<sub>2</sub>)). The <sup>1</sup>H NMR spectrum of complex 4 showed three singlets at 1.50, 2.25, and 2.45 ppm, which corresponded to  $OC(CH_3)_2$ ,  $N(CH_3)_2$ , and  $CH_2$  groups, respectively, and downfield with respect to Na(dmamp). For complex 5, the OCCH<sub>3</sub> and  $N(CH_3)_2$  peaks of the dmap ligand appeared as a doublet at 1.24 ppm and singlet at 2.19 ppm, respectively. The NCH<sub>2</sub> protons appeared as two distinctive peaks,

one at 1.96 ppm as a doublet and another at 2.27 ppm as a triplet. The OCH proton appeared as a broad peak at 4.12 ppm. These NMR signals were shifted upfield in comparison to Na(dmap). The <sup>1</sup>H NMR spectrum of complex **6** showed a singlet at 2.30 ppm, and two broad peaks at 2.47 ppm and 4.07 ppm, which corresponded to N( $CH_3$ )<sub>2</sub>, NCH<sub>2</sub>, and OCH<sub>2</sub> groups, respectively. These signals were upfield with respect to the proton peaks of Na(dmae).

# 3.1. Thermal decomposition reaction of preparing germanium telluride complexes (GeTe)



Scheme 2. Synthesis of germanium telluride and antimony telluride using complexes (1-3) and antimony complexes (4-6).

The preparation of germanium telluride (GeTe) using the germanium complexes 1-3 and *bis*(tr imethylsilyl)tellurium were investigated in hexadecane at 150 °C and 190 °C (Scheme 2). The p XRD patterns of the materials by thermal reaction of complexes 1-3 in the presence of *bis*(trimet hylsilyl)tellurium are shown in Fig. 2. The pXRD patterns of the thermal reaction products betwe en complexes 1-3 with *bis*(trimethylsilyl)tellurium at 150 °C were confirmed to be only telluriu m (JCPDS Card No: 97-004-0041) (Fig. S9). The pXRD pattern of the reaction products of comp lex **1** at 190 °C displayed only the hexagonal phase of tellurium (JCPDS Card No: 97-004-0041).

It is well known that Te(SiMe<sub>3</sub>)<sub>2</sub> is thermally unstable and decomposes in solution at high temper atures with subsequent formation of tellurium. Te(SiMe<sub>3</sub>)<sub>2</sub> did not react with Ge precursors and si mply decomposed to tellurium [33,34]. In contrast, the pXRD patterns of the materials formed in the thermal reaction of **2** and **3** at 190 °C were confirmed to be the rhombohedral phase of GeTe ( JCPDS Card No: 01-071-4854) and tellurium. Additionally, the EDS results of the materials obta ined by the thermal reaction at 190 °C displayed GeTe (Ge:Te = 28:43) in complex **2** and GeTe ( Ge:Te = 25:47) in complex **3**. GeTe was formed at a temperature at which Te(SiMe<sub>3</sub>)<sub>2</sub> could react with the Ge precursors without pyrolysis.



Fig 2. pXRD pattern of thermal reaction products of germanium complexes (1-3) at 190 °C.

Additional experiments were conducted to clearly define the substituent structural steric hindran ce effect of the  $\alpha$ -carbon of the aminoalkoxy ligand on the resulting GeTe. For this purpose, germ anium compounds containing –CF<sub>3</sub> as the substituent, Ge(dmatfp)<sub>2</sub>, was synthesized using amino alkoxide ligands with same skeleton as dmapH (dmatfpH = 3-(dimethylamino)-1,1,1-trifluoropro pan-2-ol) [35,36]. The thermal generation of GeTe was investigated to identify whether the result

ing compounds were affected by the electronic effects through the thermal reaction of the Ge(dm atfp)<sub>2</sub> with *bis*(trimethylsilyl)tellurium in the same way as in the previous experiment. The pXRD pattern of the materials synthesized by the thermal reaction of Ge(dmatfp)<sub>2</sub> and *bis*(trimethylsilyl) tellurium at 190 °C was confirmed to be the rhombohedral phase of GeTe (JCPDS Card No: 01-0 71-4854) and tellurium (JCPDS Card No: 97-004-0041) (Fig. S10). EDS analysis of the material s formed by the thermal reaction of Ge(dmatfp)<sub>2</sub> and *bis*(trimethylsilyl)tellurium at 190 °C showe d GeTe where Ge:Te was 17:31. Therefore, we concluded that the steric hindrance on the  $\alpha$ -carbo n of the aminoalkoxy ligand was a more important factor than the electronic effects in the therma l synthesis of GeTe.

# 3.2. Thermal decomposition reaction of preparing antimony telluride complexes (Sb<sub>2</sub>Te<sub>3</sub>)

Antimony telluride (Sb<sub>2</sub>Te<sub>3</sub>) was synthesized by reacting the antimony complexes **4**–**6** with *bis*(trimethylsilyl)tellurium via thermal treatment in hexadecane at 190 °C (Fig. 3). The pXRD pattern of the product in the case of complex **4** confirmed it as tellurium (JCPDS Card No: 01-086-2268). Similarly, Te(SiMe<sub>3</sub>)<sub>2</sub> did not react with Sb(dmamp)<sub>3</sub> and simply decomposed to tellurium. In contrast, the pXRD patterns of the materials formed in the thermal reaction of **5** and **6** were confirmed as coexisting rhombohedral phase of Sb<sub>2</sub>Te<sub>3</sub> (JCPDS Card No: 01-071-0393) and hexagonal phase of tellurium. Moreover, EDS of the obtained materials confirmed the formation of Sb<sub>2</sub>Te<sub>3</sub> (Sb:Te = 12:27) and Sb<sub>2</sub>Te<sub>3</sub> (Sb:Te = 21:36) from complexes **5** and **6**, respectively.



Fig 3. pXRD pattern of thermal reaction products of antimony complexes (4-6) at 190 °C.

### **4. CONCLUSIONS**

Germanium and antimony complexes containing aminoalkoxide ligands were synthesized and used for the preparation of germanium telluride (GeTe) and antimony telluride (Sb<sub>2</sub>Te<sub>3</sub>) by thermal reaction in the presence of *bis*(trimethylsilyl)tellurium in solution. The pXRD patterns of the thermal reaction products of germanium and antimony compounds at 190 °C revealed a mixture of rhombohedral GeTe and Sb<sub>2</sub>Te<sub>3</sub>, which had good yields with complexes having the least substituted ligands on the alkoxy carbon of aminoalkoxides. These results showed that the steric hindrance on the alkoxy carbon should be removed while designing organic ligands to obtain better properties of germanium and antimony precursors for PCRAM devices

# ■ ASSOCIATED CONTENT

Supporting information

<sup>1</sup>H and <sup>13</sup>C NMR spectra of complexes 1-6, pXRD patterns of resultants of 1-3 at 150 °C, pXRD patterns of resultants of Ge(dmatfp)<sub>2</sub> are provided in the supporting information.

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### Notes

The authors declare no competing financial interest.

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Series of germanium and antimony precursors with varying  $\alpha$ -carbon substituent group were synthesized. Prepared substances were further converted into GeTe or Sb<sub>2</sub>Te<sub>3</sub> by thermal reaction to elucidate the size and electronic effects of  $\alpha$ -carbon substituent suggesting that less bulky group leads to better conversion of desired complexes.