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Tellurium based phase change materials

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Phase change materials are the most promising materials for innovation in the computer memory industry. Of great importance is the understanding of the processes that take place during the switching from the high resistivity state to the low resistivity state. In this paper we have tried to find out the correlations between the crystallo-chemical parameters and the switching properties of these materials. The crystallo-chemical parameters, average electronegativity, and glass forming ability $\frac{\overline{n}\overline{k}}{\overline{Z}}$ have been calculated for a large number of tellurium chalcogenides. The switching parameters have been correlated with the physical properties of these materials: resistivity, activation energy, and average electronegativity. Change of the chemical bonding during switching would be responsible for the outstanding properties of the phase change materials.

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1. Introduction

The phase change materials (PCM) are the most important materials in the class of chalcogenides (combination of chalcogens (S, Se and Te) with metalloids or metals). The outstanding property of these materials is the reversible switching from a high electrical resistivity state (amorphous state) to a low electrical resistivity state (crystalline state) under a moderate voltage. These materials are also characterized by a strong contrast of optical and electronic properties between the amorphous and crystalline state. Thin film phase change materials are largely used in computer memories, CD's and DVD's devices with high speed and large storage capacity.

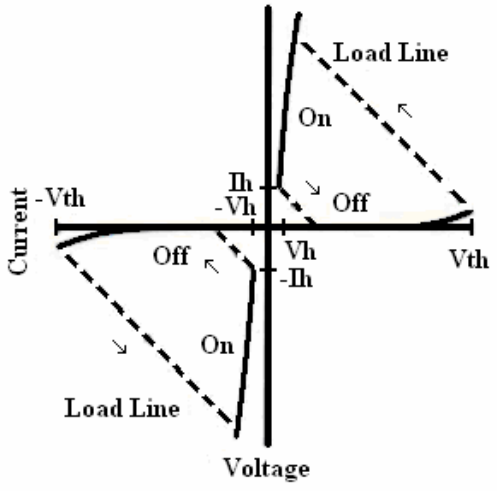


Fig. 1. The switching effect.

The switching effect in amorphous materials has been discovered by Ovshinsky in 1968 [1]. The effect consists in the reversible modification of the resistance of a thin film under the influence of a short electrical pulse applied to the material. Figure 1 illustrates the effect. Initially the material is in the OFF state. When the voltage is applied and a threshold voltage, V_{th} is reached the material turns to ON state. The material remains in this state as long as a holding voltage is maintained, V_h. When the holding voltage is dropped off the material goes back to OFF state.

2. Crystallo-chemical parameters and switching properties

In order to systemize the whole class of chalcogenide phase change materials we have investigated the correlation between different crystallo-chemical parameters and the switching properties of these materials. One of the parameters used is the glass formation ability [2]. This parameter is defined as the product of the average principal quantum number, $\overline{n}$ and the mean number of bonds per atom in the structural unit, $\overline{k}$, normalized by the average atomic number, $\overline{Z}$ of the given material.

$$GFA = \frac{\overline{n} \cdot \overline{k}}{\overline{Z}} \quad (1)$$

The second parameter is average electronegativity (e_{ave}). Electronegativity is the ability of atoms to attract electrons. Electronegativity increases in every group of the Periodical Table of elements with the increase of the

atomic number *Z* and decreases in every group from up to bottom.

L. Pauling [3] was the first who proposed the electronegativity for the characterization of elements. After that many scientists proposed different scales for the electronegativity of an element. Until now, nobody knows which is the correct one. In [4] we have gathered together nine scales of electronegativity and defined a new scale which is the average of all scales. We used this new scale in order to calculate the average electronegativity of the compounds investigated in this article.

In the materials consisting of several structural units, the glass formation ability and average electronegativity are calculated considering the concentration of elements which form the structural unit. For example, for a ternary compound $A_xB_yC_z$, where $x+y+z=1$:

$$\begin{cases} \dfrac{\bar{n}\cdot\bar{k}}{\bar{Z}} = \dfrac{(xn_A+yn_B+zn_C)(xk_A+yk_B+zk_C)}{xZ_A+yZ_B+zZ_C} \\ e_{ave} = xe_{ave}(A)+ye_{ave}(B)+ze_{ave}(C) \end{cases} \quad (2)$$

3. Results

As well known phase change materials are layer type compounds. An example is given in Figure 2.

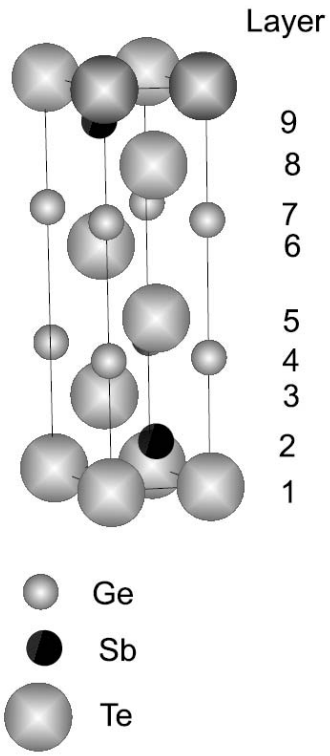
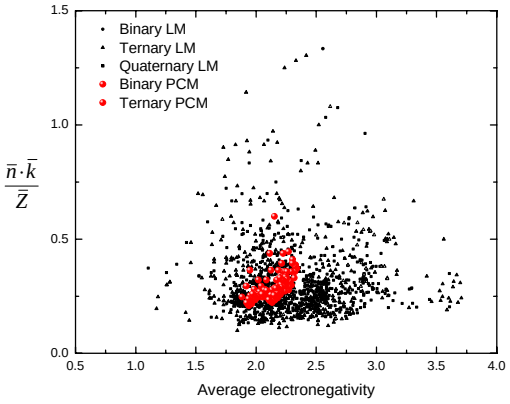
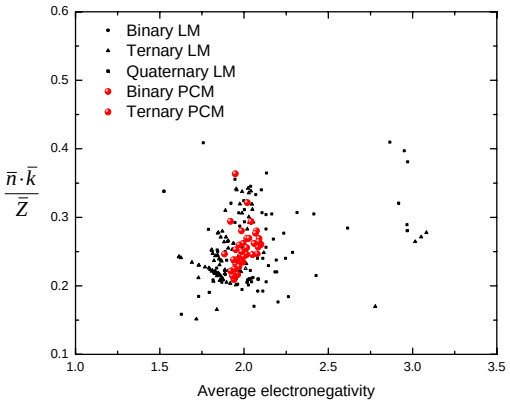


Fig. 2. Layered structure of $Ge_2Sb_2Te_5$ phase change material.

We used a list of layer type compounds (LM) [5] and calculated the two crystallo-chemical parameters. Figure 3 a) shows the glass formation ability versus the average electronegativity for the layered materials. We also included all the phase change compounds from [6] with red dots. Binary, ternary and quaternary compounds were investigated. One can see that phase change materials are situated in a tight area around the value 2.0 for average electronegativity and between 0.2-0.5 for glass formation ability. From all these composition we separated the Te based materials as we can see in Figure 3 b).



a)



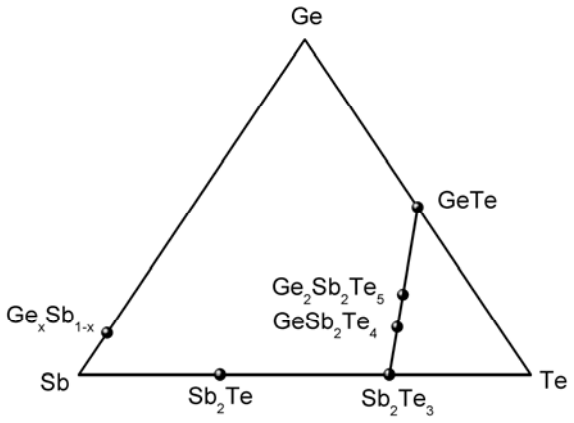
b)

Fig. 3. a) GFA as a function of average electronegativity for layer type materials. b) GFA as a function of average electronegativity for Te based layer type materials.

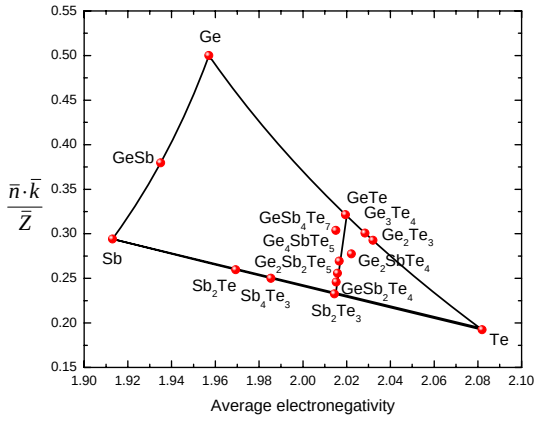
3.1 Ge – Sb – Te system

Data from recent literature show that the Ge – Sb – Te system is the most promising material for new generation storage media and computers memories. In Figure 4 a) it is presented the ternary diagram of Ge – Sb – Te. The most stable phase change materials are those situated on the

pseudo-binary line between GeTe and Sb_2Te_3, around Sb_2Te and in the vicinity of Sb. This diagram transposed in the new defined parameters is shown in Fig. 4 b).



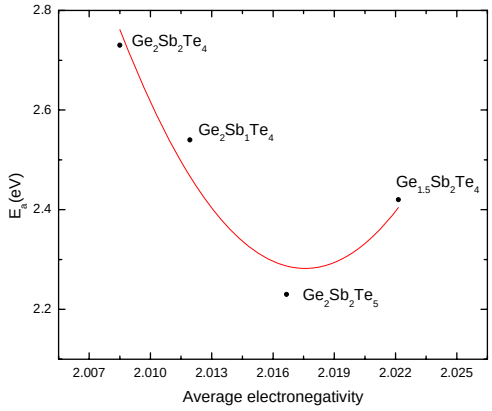
a)



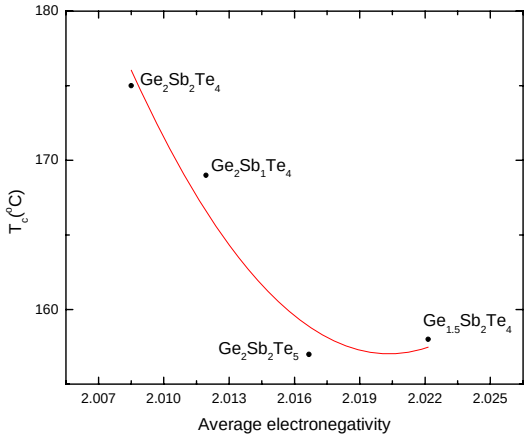
b)

Fig. 4. a) Ternary diagram of Ge – Sb – Te with the phase change materials in the gray area. b) GFA vs. average electronegativity of the ternary diagram of Ge –Sb – Te and the most known phase change materials.

Welnic et al. [7] studied a series of phase change materials from the pseudo-binary line GeTe-Sb_2Te_3. The values obtained by them for the activation energy, E_a and crystallization temperature, T_c were plotted against average electronegativity (Fig. 5 a), b)). In both cases it was obtained a curve with a minimum on $Ge_2Sb_2Te_5$.



a)



b)

Fig. 5. a) Activation energy as a function of average electronegativity for materials from the pseudo-binary line GeTe-Sb_2Te_3. b) Crystallization temperature as a function of average electronegativity for materials from the pseudo-binary line GeTe-Sb_2Te_3.

3.2 Si – Te – As – Ge system

Due to the optical contrast between amorphous and crystalline state, phase change materials are also highly used in optical discs for information storage. A series of switching parameters as threshold voltage, recording voltage, recording current, recording time, erasing voltage, erasing current and erasing time for $Si_{12}Te_{48}As_{30}Ge_{10}$ with electrodes doped by different materials (Cd, Ga, Bi, Sb and Te) are shown in Figure 6. In Figure 6 a), b), c), and d) are plotted the parameters for the recording pulse and in Fig 6 e), f) and g) are plotted the parameters for the erasing pulse versus average electronegativity. Data were taken from [8]. In all the graphs it is obtained a minimum for Gallium doped electrodes.

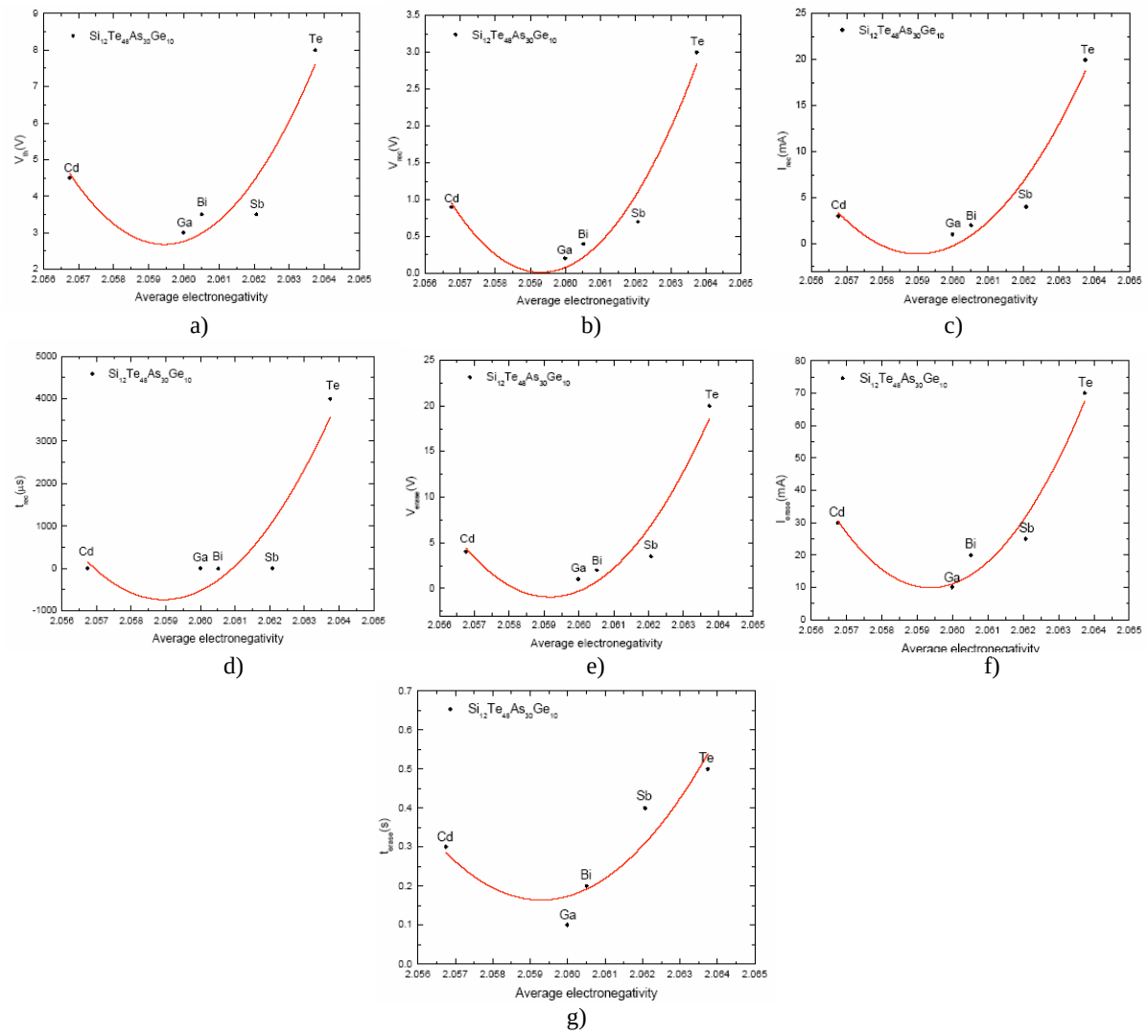
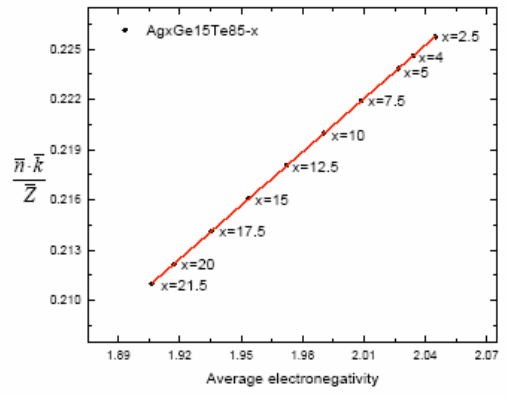


Fig. 6. a) Threshold voltage vs. average elecronegativity. b) Recording voltage vs. average electronegativity. c) Recording current vs. average elecronegativity. d) Recording time vs. average elecronegativity. e) Erasing voltage vs. average elecronegativity. f) Erasing current vs. average elecronegativity. g) Erasing time vs. average elecronegativity .

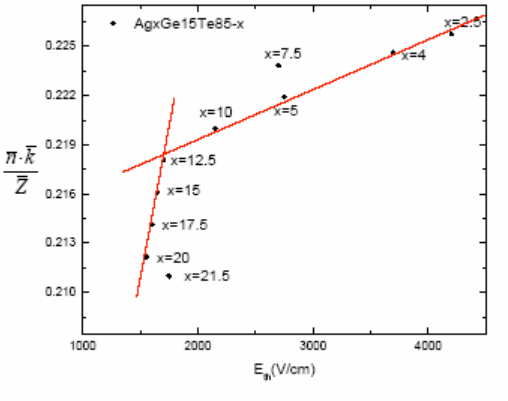
3.3 Ag – Ge – Te system

Ramesh et al [9] studied the system $Ag_xGe_{15}Te_{85-x}$ where x varies between 2.5 and 21.5. Fig. 7 a) shows that glass formation ability is a linear function of average electronegativity.

Fig. 7 b) shows the behaviour of the switching field against the glass formation ability. One can see that in the point x=12.5 the graph breaks. The cause is not known but we suggest that the way Ag enters into chalcogenide network is important. For low Ag concentration, silver occupy the interstitial positions (voids). For high concentration the substitutional occupancy occurs.



a)



b)

Fig. 7 a) GFA vs. average electronegativity for $Ag_xGe_{15}Te_{85-x}$.b) GFA vs. threshold field for $Ag_xGe_{15}Te_{85-x}$.

3.4 As – Se – Te system

We have analyzed the switching in the system As_2Se_3-As_2Te_3 [10] as a function of the parameters: GFA and average electronegativity. Figure 8 shows the results. The correlation between the two parameters is linear. One can observe that the number of reversible cycles is somehow correlated with those parameters. The maximum number of cycles sustained in the material increases with the decrease of the glass formation ability and with the decrease of average electronegativity.

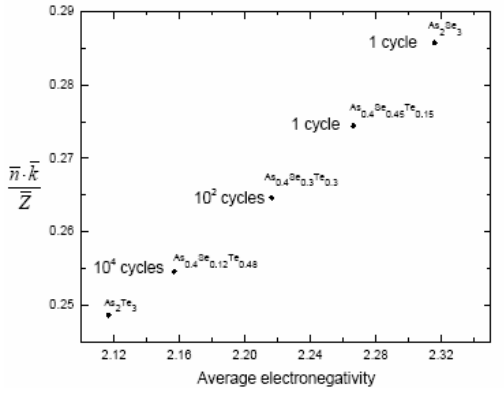


Fig. 8. GFA vs. average electronegativity for As_2Se_3-As_2Te_3 system.

4. Conclusions

The results show that glass formation ability and the average electronegativity are two main parameters for the characterization of the phase change materials.

The best phase change materials are situated in a specific range of glass formation ability and average electronegativity. The results give the possibility to design new compositions with better switching properties.

Acknowledgement

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