UNEC Journal of Engineering and Applied Sciences
Vol. 3, No. 1, 2023, pp. 28-32
https://doi.org/10.61640/ujeas.2023.0505

SECTION: PHYSICS

Mechanism and kinetics of thermal processes in $Ge_{0.99}Nd_{0.01}S$ compound

A.O. Dashdamirov*, A.S. Alekbarov, Y.I. Aliyev

Azerbaijan State Pedagogical University, 68 Uzeir Hajibaili, Baku AZ1000, Azerbaijan
email: *dashdamirovarzu@gmail.com*

Abstract

The mechanism and kinetics of thermal processes in the $Ge_{0.99}Nd_{0.01}S$ compound were studied. The thermal parameters were studied by the Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) in the temperature range 25 ^{0}C ≤ T ≤ 800 ^{0}C. Several thermal transitions were observed in the specified temperature range and the nature of these transitions is explained. It was determined that in the temperature range of 494 ^{0}C ≤ T ≤ 601 ^{0}C, a thermoeffect observed with energy absorption in the $Ge_{0.99}Nd_{0.01}S$ compound. Mass loss of 38.84% was observed during this effect with phase transition from solid to liquid.

***Keywords**:* thermal properties, chalcogenides, thermal analysis, thermogravimetry.
PACS numbers: 61.05.cp, 61.50.Nw, 61.66.Fn

Received: 6 march 2023 *Accepted: 30 april 2023* *Published: 29 may 2023*

1. Introduction

Chalcogenide semiconductors are widely used in electronics for various purposes. Depending on the energy band gap, it is possible to make different converters from them. Therefore, various studies are being conducted to study the physical and chemical properties of these materials. It was determined that the structural features and defects of chalcogenide semiconductors affect the formation of their physical properties. Therefore, the structural properties of these materials (crystal and electronic structure) are widely studied [1-5].

The GeS compound occupies a special place among chalcogenide semiconductors. It was determined that interesting optical properties can be observed when replacements are made with rare earth elements in this compound [6, 7]. It is known that during substitutions, certain changes occur in the crystal structure depending on the ionic radii of metal atoms. These changes also affect the electronic structures of crystals. Therefore, changes in many physical properties of samples occur during partial substitutions. Especially it has a strong effect on magnetic and electrical properties. That is why, partial substitutions are made for obtaining new functional materials on the basis of known compounds. However, during these substitutions, the ionic radii and valences of atoms should be taken into account [8-10].

Physical properties of semiconductors are depends on the temperature. As the temperature increases, electrical conductivity increases due to the increase of additional charge carriers [11]. Therefore, it is important to study the thermal properties of the materials. It was determined that the method of Differential Thermal Analysis allows to study the thermal processes occurring in semiconductors with high accuracy. Through these methods, it is possible to determine thermodynamic parameters: Wigner potential, Gibbs potential, free energy, enthalpy [12]. Although many physical properties of solid solutions of GeS compound have been studied, thermal processes in $Ge_{0.99}Nd_{0.01}S$ compound have not been sufficiently studied. In this work, the thermal properties of the $Ge_{0.99}Nd_{0.01}S$ compound were studied in detail.

2. Experiments

Germanium with a resistance of 50 Ohm·cm, sulfur (B5) and neodymium (Nd-2) were taken as starting materials. A stoichiometric mixture of these elements is placed in a quartz tube. A 10^{-3} mm Hg vacuum was obtained in a quartz tube. To prevent the explosion of the ampoule, the germanium was powdered and the amount of the substance was limited to about 10-15 g. The synthesis process was carried out in two stages. In the first stage, the ampoule was kept in the furnace and heated. The temperature was raised to 300 ^{0}C at a rate of 3-5 ^{0}C/min and maintained for 10-12 hours. At the next stage, the furnace temperature was raised to 1000 ^{0}C at a rate of 2-3 ^{0}C/min and this temperature was maintained for 18-20 hours. After that, the furnace was cooled down to room temperature with the sample. The structure of the polycrystal of the synthesized $Ge_{0.99}Nd_{0.01}S$ compound was studied on a D8 ADVANCE X-ray diffractometer and it was found that a single-phase sample was obtained.

The thermophysical properties of the $Ge_{0.99}Nd_{0.01}S$ compound with a purity of 99.99% and a density of 2.56 g/cm^3 were studied by the DSC method in the temperature range of T = 25-800 ^{0}C. DSC measurements were performed on a TGA/DSC3+ instrument manufactured by METTLER TOLEDO and temperature control was performed using MULTISTAR sensors. A standard adiabatic calorimeter was performed in the temperature range from 25 ^{0}C to 800 ^{0}C in an argon (Ar) atmosphere at a heating rate of 20 ml/min, 5 ^{0}/min. The cooling process was achieved with the NITROGEN UN 1977 SOFRIGERATED LIQUID analyzer cooling system and "digital temperature controller".

3. Results and discussion

Figure 1 shows the differential heat flux and heat flux spectra of the alloy in the $Ge_{0.99}Nd_{0.01}S$ compound temperature range 25 ^{0}C ≤ T ≤ 800 ^{0}C. Data measured at 3654 points for heat flux are given in the spectra. Despite the separation of the heat flux into two parts depending on the temperature, the differentiated spectrum of the heat flux clearly includes structural transformations, phase transitions and decomposition processes.

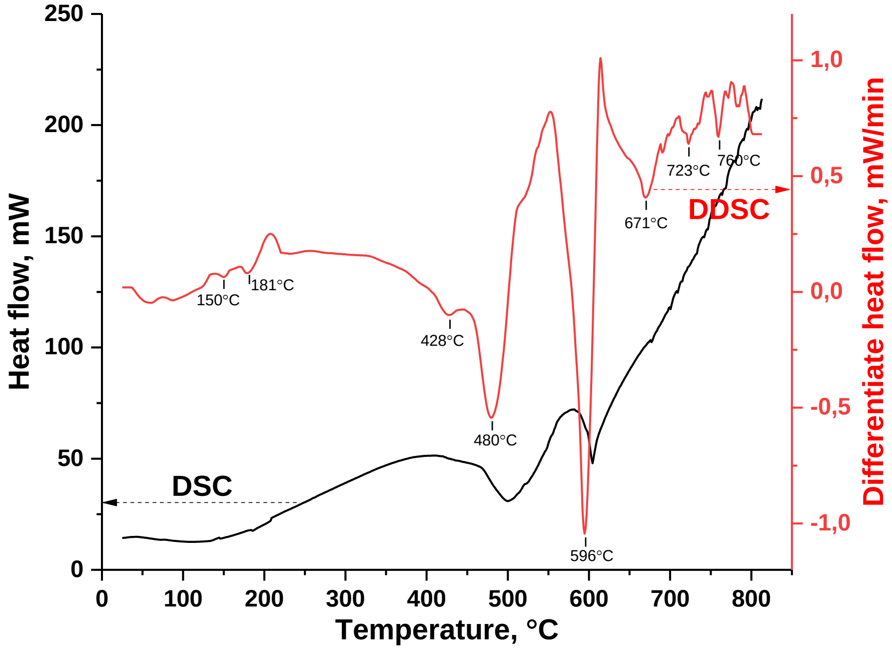

Figure 1. Heat flux and differential heat flux spectrum of $Ge_{0.99}Nd_{0.01}S$ compound in the temperature range 25 ^{0}C ≤ T ≤ 750 ^{0}C.

In the differentiated spectrum, endo effects observed in the temperature range 25 ^{0}C ≤

T ≤ 170 ^{0}C are observed at temperatures of 150 ^{0}C, 181 ^{0}C, 428 ^{0}C, 480 ^{0}C, 596 ^{0}C, 671 ^{0}C, 723 ^{0}C and 760 ^{0}C has been done. The effects mentioned at the values of central temperature 150 ^{0}C and 181 ^{0}C are characterized by the decomposition of water molecules and hydroxide groups adsorbed from the atmosphere with weak chemical interaction by the active surface of the $Ge_{0.99}Nd_{0.01}S$ compound. The decomposition of the hydroxide layer in the DSC spectrum was observed in experiments at high temperatures. As a mechanism, it is possible to describe the decomposition schematically as follows.

$$2Me(OH)_x \xrightarrow{200-600\ ^\circ C} Me(OH)_{x-y}(OH)_{2x} + 2(3-x)HOH$$

Figure 2 shows the areas of effects characterizing the structural transformations, phase transitions and decomposition processes occurring in the $Ge_{0.99}Nd_{0.01}S$ compound in the temperature interval 25 ^{0}C ≤ T ≤ 800 ^{0}C.

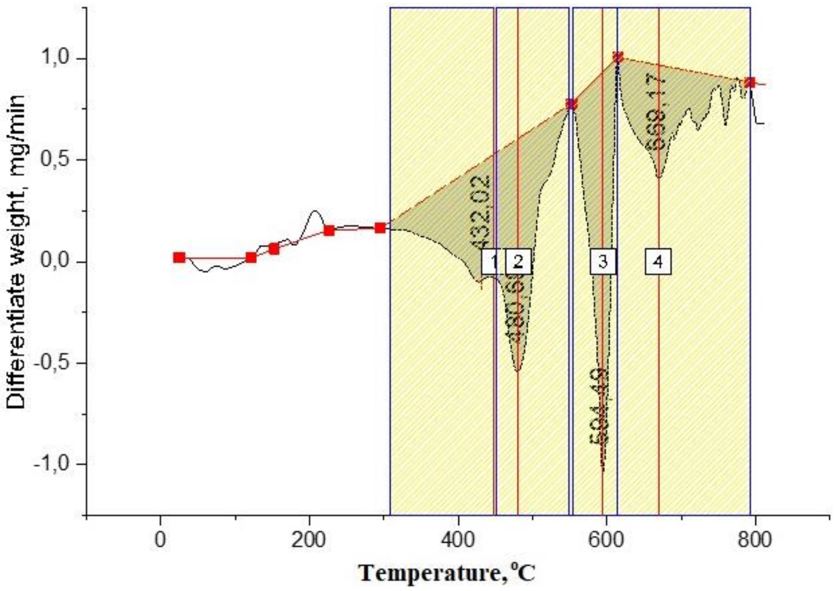

Figure 2. Areas of transitions occurring in the $Ge_{0.99}Nd_{0.01}S$ compound in the temperature range 25 ^{0}C ≤ T ≤ 800 ^{0}C.

Depending on the temperature in the $Ge_{0.99}Nd_{0.01}S$ compound, the energy of the effect areas due to heat flux inside the crystal decreases from 186 mC to 154 mC. The value of the heat flux was calculated according to the central peak shown in the spectrum at 432 ^{0}C, 480 ^{0}C, 584 ^{0}C and 669 ^{0}C. Also, small anomalous effects are observed at high temperatures in the differential value of heat flux. It is possible to observe these effects more clearly around the temperature T > 669 ^{0}C. Figure 3 shows the mass and differential spectrum of the $Ge_{0.99}Nd_{0.01}S$ compound in the temperature range 25 ≤ T ≤ 750 ^{0}C. The mass of the compound at a temperature of 25 ^{0}C was 16.45 mg, at 494 ^{0}C it was 15.74 mg. In the temperature range of 25 ^{0}C ≤ T ≤ 494 ^{0}C, the mass loss is equal to 4.31%. Starting from 494 ^{0}C and completed at 601 ^{0}C temperature, it was expressed as a sharp decomposition in the mass spectrum and a loss area characterizing this decomposition in the differential spectrum. The mass loss in the temperature interval 494 ^{0}C ≤ T ≤ 601 ^{0}C during the jump decomposition was 38.84 %. The interval 601 ^{0}C ≤ T ≤ 800 ^{0}C can be considered as the thermally stable region for the crystal. In the mass of the $Ge_{0.99}Nd_{0.01}S$ compound there is no phase decomposition in the temperature range of 25 ^{0}C ≤ T ≤ 800 ^{0}C. The total mass loss varies around 43.0 %. At this time, all physical processes, including the decomposition of adsorbed water with weak chemical interaction on the surface, decomposition of free and structural hydroxide groups, and phase transitionare taken into account.

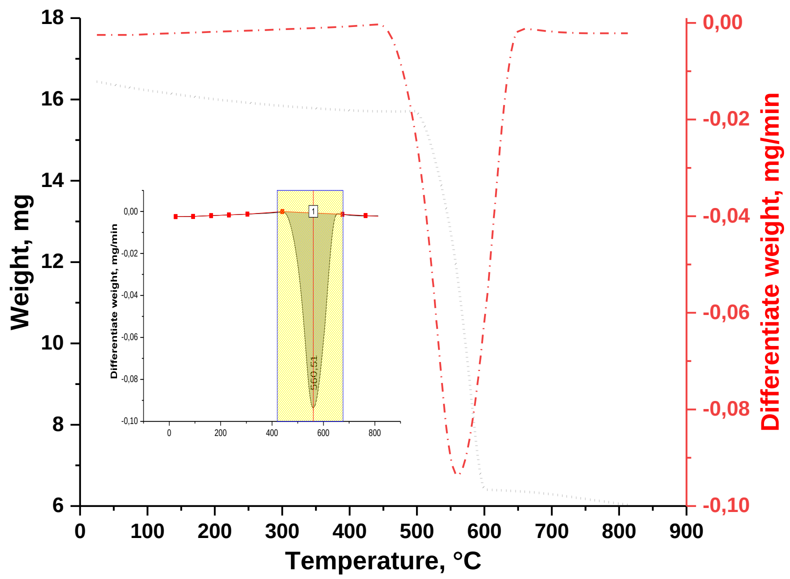

Figure 3. Mass change in $Ge_{0.99}Nd_{0.01}S$ compound in the temperature range 25 ^{0}C ≤ T ≤ 800 ^{0}C.

4. Conclusion

The $Ge_{0.99}Nd_{0.01}S$ compound was synthesized with partial replacements of Ge atoms with Nd atoms in the GeS compound. The thermophysical properties of polycrystals of this compound were studied at high temperatures. It was determined that this compound contains water in a suspended state in the form of free and hydroxide groups. As the temperature rises, the hydroxide groups decomposited and the water molecules leave the sample. For these thermal effects, the temperature value and the area of the effect were evaluated. At higher temperatures, melting occurred in the sample and transition to liquid state occurred at 596 ^{0}C. As a result of thermogravimetric analysis, it was determined that during melting, the mass of the sample significantly decreases. This process is explained by the fact that high-energy atoms on the surface leave the sample.

References.

1. R.F. Hashimov, N.A. Ismayilova, F.A. Mikailzade, A.O. Dashdemirov, A.V. Trukhanov, S.V. Trukhanov, Y.I. Aliyev, E.B. Asgerov, S.H. Jabarov, N.T. Dang, Modern Physics Letters B **32** (2018) 1850186.
2. Y.I. Aliyev, Y.G. Asadov, R.D. Aliyeva, T.G. Naghiyev, S.H. Jabarov, Modern Physics Letters B **33**(11) (2019) 1850128.
3. E.M. Huseynov, T.G. Naghiyev, U.S. Aliyeva, Physica B: Condensed Matter **577** (2020) 411788.
4. E.M. Huseynov, T.G. Naghiyev, Vaccum **212** (2023) 111990.
5. T.G. Naghiyev, Modern Physics Letters B **37**(12) (2023) 2350021.
6. T.G. Naghiyev, U.R. Rzayev, E.M. Huseynov, I.T. Huseynov, S.H. Jabarov, UNEC J. Eng. Appl. Sci **2**(1) (2022) 85.
7. A.O. Dashdemirov, A.S. Alekperov, N.A. Ismayilova, A.A. Hadieva, A.N. Jafarova, A.S. Abiyev, Advanced Physical Research **5** (2023) 12.
8. G.Sh. Ayyubova, S.H. Jabarov, UNEC J. Eng. Appl. Sci. **1**(1) (2021) 49.
9. M.N. Mirzayev, Kh.F. Mammadov, V.A. Skuratov, E. Demir, S.H. Jabarov, N.A. Ismayil ova, S. Biira, B. Abdurakhimov, E. Popov, Journal of Alloys and Compounds **801** (2019) 15.
10. F.G. Agayev, S.H. Jabarov, G.Sh. Ayyubova, M.N. Mirzayev, S.V. Trukhanov, E.L.

Trukhanova, M.A. Darwish, S.V. Podgornaya, D.A. Vinnik, T.P. Hoang, N.T. Dang, A.V. Trukhanov, Physica B: Condensed Matter **580** (2020) 411772.

11. S.H. Jabarov, T.G. Mammadov, A.I. Mammadov et al., J. Surf. Investig. **9** (2015) 35.
12. T.G. Naghiyev, R.M. Rzayev, Modern Physics Letters B **35**(31) (2021) 2150469.
13. S.H. Jabarov, S.I. Ibrahimova, F.V. Hajiyeva, E.M. Huseynov, Y.I. Aliyev, Arabian Journal for Science and Engineering **47** (2022) 7817.
14. Y.I. Aliyev, Y.G. Asadov, T.M. Ilyasli, F.M. Mammadov, T.G. Naghiyev, Z.A. Ismayilova, M.N. Mirzayev, S.H. Jabarov, Modern Physics Letters B **34** (2020) 2050066.