COMPARATIVE ANALYSIS OF SOME PHYSICOCHEMICAL PROPERTIES OF BULK CHALCOGENIDES FROM THE $GeTe_4$-Cu, $GeTe_5$-Cu AND $GeTe_6$-Cu SYSTEMS

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ABSTRACT

The article compares several physicochemical properties, such as density, molar volume, compactness, and free volume percentage, of bulk chalcogenides from the systems $(GeTe_4)_{100-x}Cu_x$, $(GeTe_5)_{100-x}Cu_x$, and $(GeTe_6)_{100-x}Cu_x$, where x = 5, 10, 15, and 20 mol %. The influence of the Ge/Te ratio and copper content on the physicochemical performance of the studied compositions is discussed and explained from a structural point of view. The results show that a higher Te content in the Ge/Te ratio leads to an increase in structural flexibility, whereas the incorporation of Cu modifies the configuration of the structure, which in turn causes nonlinear changes in the physicochemical properties.

Keywords: Ge-Te-Cu, chalcogenides, physicochemical properties.

INTRODUCTION

In materials science, the evaluation of basic physicochemical properties like density, compactness, and molar volume is indeed an essential first step in the systematic study of new materials. Usually, their determination requires neither complex experiments nor costly equipment yet provides preliminary assessment of materials suitability for a specific application. Considering, for example, the chalcogenides as an intriguing, intensively developed class of semiconducting materials, knowledge of the density, together with composition and bond-energy data, allows for the prediction of other key characteristics, such as the glass transition temperature (T_g) [1, 2]. Density is also used as a basic input parameter in computational structural simulations [3, 4] and as a baseline for assessing the mechanical stress arising in layered chalcogenides [5].

In the presented work, we perform a comparative analysis of our previously published results [6 - 8] on the physicochemical properties of bulk $GeTe_4$-Cu, $GeTe_5$-Cu and $GeTe_6$-Cu chalcogenides. The selected for this study Ge-Te-Cu system was chosen based on the growing research interest in its potential for practical use in thermoelectric and optical data-storage devices [9 - 18]. The effect of Te amount increase on the density, molar volume, compactness and free volume percentage of the studied compounds has been evaluated and related to structural data obtained from X-ray diffraction (XRD) measurements. We believe that the study may be of fundamental interest and offer valuable insights for compositional engineering and application-oriented research on Ge-Te-Cu chalcogenides.

EXPERIMENTAL

In Table 1 the composition of the samples studied from the three systems - $GeTe_4$-Cu, $GeTe_5$-Cu and $GeTe_6$-Cu is given.

In a previous work Trifonova et al. presents the data obtained from EDS analysis regarding the amount of Ge, Te and Cu in the system $GeTe_6$-Cu [8]. The EDS results confirm the presence of Ge, Te and Cu in the bulk samples in concentrations that correspond to those theoretically determined.

The synthesis of the bulk chalcogenides from the systems $(GeTe_4)_{100-x}Cu_x$, $(GeTe_5)_{100-x}Cu_x$, and $(GeTe_6)_{100-x}Cu_x$, where x = 5, 10, 15, and 20 mol %, carried out by direct single-temperature synthesis in a closed volume from elements Ge, Te with high purity 5N and Cu with purity 4N, and the results from the evaluation of the density, molar volume, compactness and free volume percentage, have been previously reported by us in [6 - 8], as well as results from the XRD analysis carried out on the samples from the systems $(GeTe_4)_{100-x}Cu_x$, $(GeTe_5)_{100-x}Cu_x$, and $(GeTe_6)_{100-x}Cu_x$, where x = 5, 10, 15, and 20 mol %. For the purpose of the presented in the article comparative analysis, the structure of the samples from the system $(GeTe_5)_{100-x}Cu_x$, where x = 5, 10, 15 and 20 mol % has also been studied by X-ray diffraction technique.

The XRD experiment was carried out at "Philips" powder diffractometer working in the Bragg-Brentano (θ - 2θ) geometry, with a CuK_a radiation (λ = 1.54060 Å) and a graphite monochromator for the reflected beams. The XRD patterns were obtained for 75 s at constant scan rate and reflection angle of 2Θ in the scan range from 15° to 70° with a scan step of 0.05°.

The density (ρ) of the bulk samples was estimated by the pycnometer technique, with an accuracy of ± 0.7 %, using water as immersion fluid. The methodology for determining the compactness (δ), the molar volume (V_m) and the free volume percentage (FVP) of the investigated materials has been extensively described in the literature [1, 2, 19, 20] and can also be found in our previous reports [6 - 8].

RESULTS AND DISCUSSION

XRD analysis of the samples from the system $GeTe_5$-Cu

In Fig. 1 the results from the XRD analysis of the samples from the system $(GeTe_5)_{100-x}Cu_x$, where x = 5,

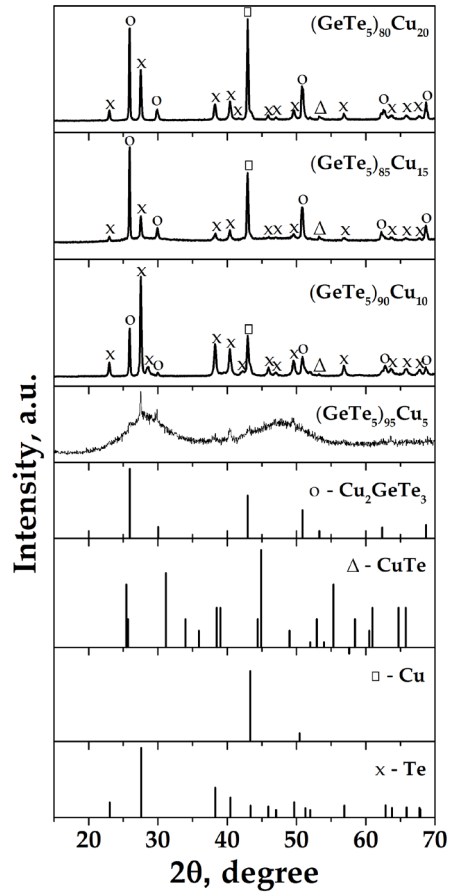


Fig. 1. XRD patterns of the bulk samples from the system $(GeTe_5)_{100-x}Cu_x$, where x = 5, 10, 15 and 20 mol %.

Table 1. Composition of the samples from the three systems studied.

System	Composition, mol %	System	Composition, mol %	System	Composition, mol %
$GeTe_4$-Cu	$Ge_{19}Te_{76}Cu_5$	$GeTe_5$-Cu	$Ge_{16}Te_{79}Cu_5$	$GeTe_6$-Cu	$Ge_{14}Te_{81}Cu_5$
	$Ge_{18}Te_{72}Cu_{10}$		$Ge_{15}Te_{75}Cu_{10}$		$Ge_{13}Te_{77}Cu_{10}$
	$Ge_{17}Te_{68}Cu_{15}$		$Ge_{14}Te_{71}Cu_{15}$		$Ge_{12}Te_{73}Cu_{15}$
	$Ge_{16}Te_{64}Cu_{20}$		$Ge_{13}Te_{67}Cu_{20}$		$Ge_{11}Te_{69}Cu_{20}$

10, 15 and 20 mol % are presented. The X-ray patterns indicate that they are in crystalline form, except sample $Ge_{16}Te_{79}Cu_5$, which shows amorphous nature. The following four crystal phases were identified: hexagonal Te (JCPDS card no. 36-1452), cubic Cu (JCPDS card no. 85-1326), orthorhombic CuTe (JCPDS card no. 07-0110) and orthorhombic Cu_2GeTe_3 [21]. The cooling rate used during the synthesis of sample $Ge_{16}Te_{79}Cu_5$ was of the order of 10^2 °C s^{-1} [7], well below the rate required for amorphization of tellurium-based chalcogenides (≈ 10^4 °C s^{-1}) [22]. We therefore attribute the amorphous state of $Ge_{16}Te_{79}Cu_5$ to the specific ratio of Ge, Te, and Cu atoms within this composition, though this assumption warrants further investigation. Despite the identical cooling rate of the three systems, only the $GeTe_5$-Cu system amorphisms, which may be due to the fact that the critical cooling rate has a compositional maximum around this ratio. It is likely that at this ratio there is a maximum number of broken bonds, leading to a minimum possibility of periodic order.

Comparison of the results from the XRD measurement for the samples from the systems $GeTe_4$-Cu, $GeTe_5$-Cu and $GeTe_6$-Cu

Fig. 2 shows the XRD patterns of the samples from the three systems studied. All samples contain hexagonal Te (JCPDS card no. 36-1452), cubic Cu (JCPDS card no. 85-1326), orthorhombic CuTe (JCPDS card no.

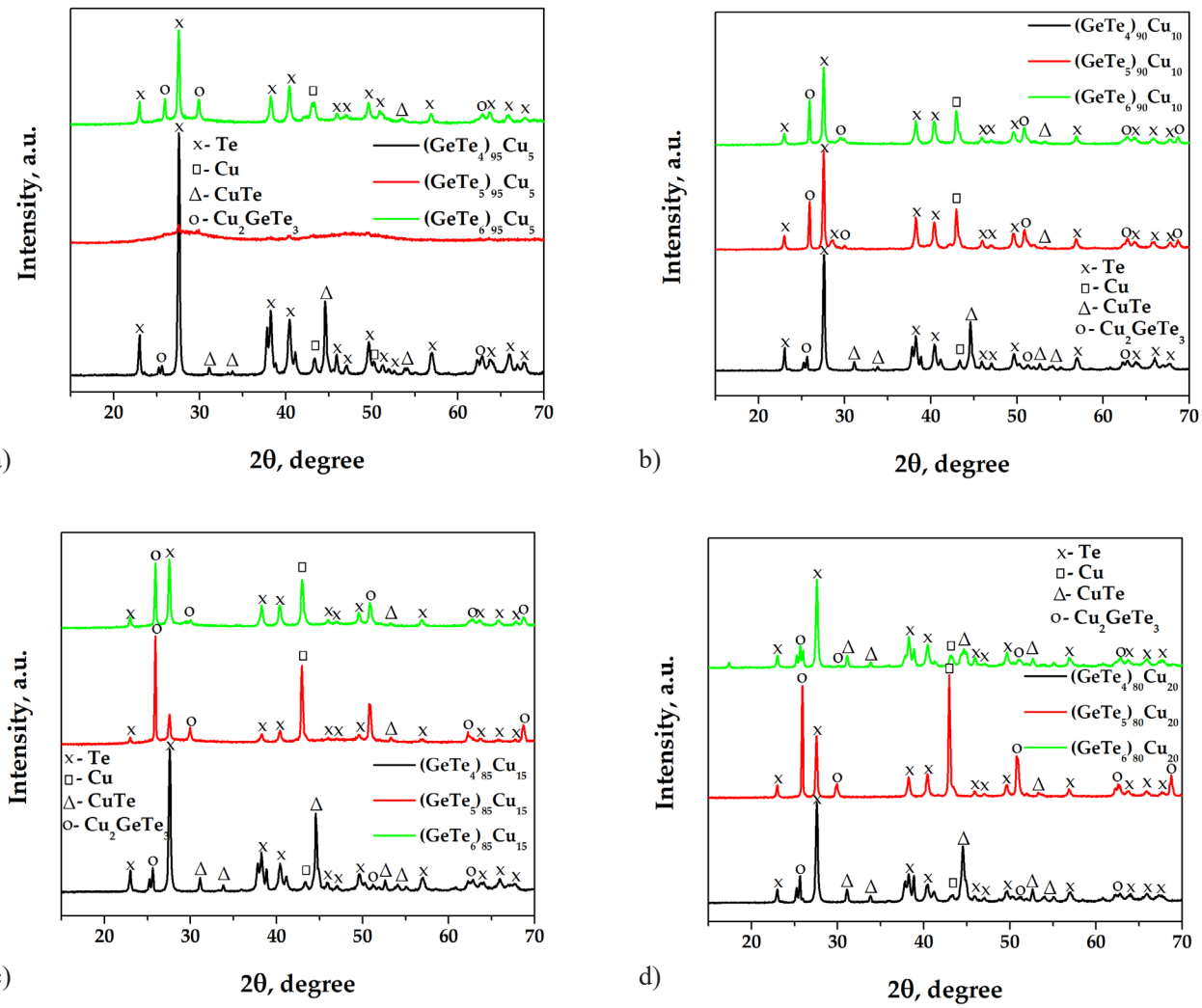


Fig. 2. XRD patterns for the samples from the $GeTe_4$-Cu, $GeTe_5$-Cu and $GeTe_6$-Cu systems containing: (a) 5 mol % copper; (b) 10 mol % copper; (c) 15 mol % copper; (d) 20 mol % copper.

07-0110) and orthorhombic Cu_2GeTe_3. Comparing the results obtained, it is seen that as the tellurium content in the Ge/Te ratio increases, the amount of homopolar-bonded Te decreases in the samples doped with 5 and 10 mol % Cu which promotes the formation of CuTe and Cu_2GeTe_3. For the samples with 15 and 20 mol % Cu, with increasing the Te concentration in the Ge-Te matrix ($GeTe_6$ > $GeTe_5$ > $GeTe_4$), and consequently with decreasing the Ge content, the intensity of the peaks corresponding to the Cu_2GeTe_3 phase decreases. This results in an increase in the amount of homopolar-bonded tellurium. Across all three systems, higher Te content leads to a decrease in the amount of free Cu and of the CuTe phase, while Cu_2GeTe_3 becomes the predominant Cu-containing phase. Furthermore, at a fixed Cu concentration, the increase in the Te content among the Ge/Te ratio, and consequently the reduction in Ge, causes a decrease in the amount of Cu_2GeTe_3.

Physicochemical properties

Fig. 3 presents the dependence of the density (a), compactness (b), molar volume (c) and free volume percentage (d) on the Cu content for all the samples across the three systems compared.

Among the investigated compositions, the value of the density varies within the narrowest range for the samples from the $GeTe_4$-Cu system, namely between 6416 kg m^{-3} and 6549 kg m^{-3}. In contrast, the

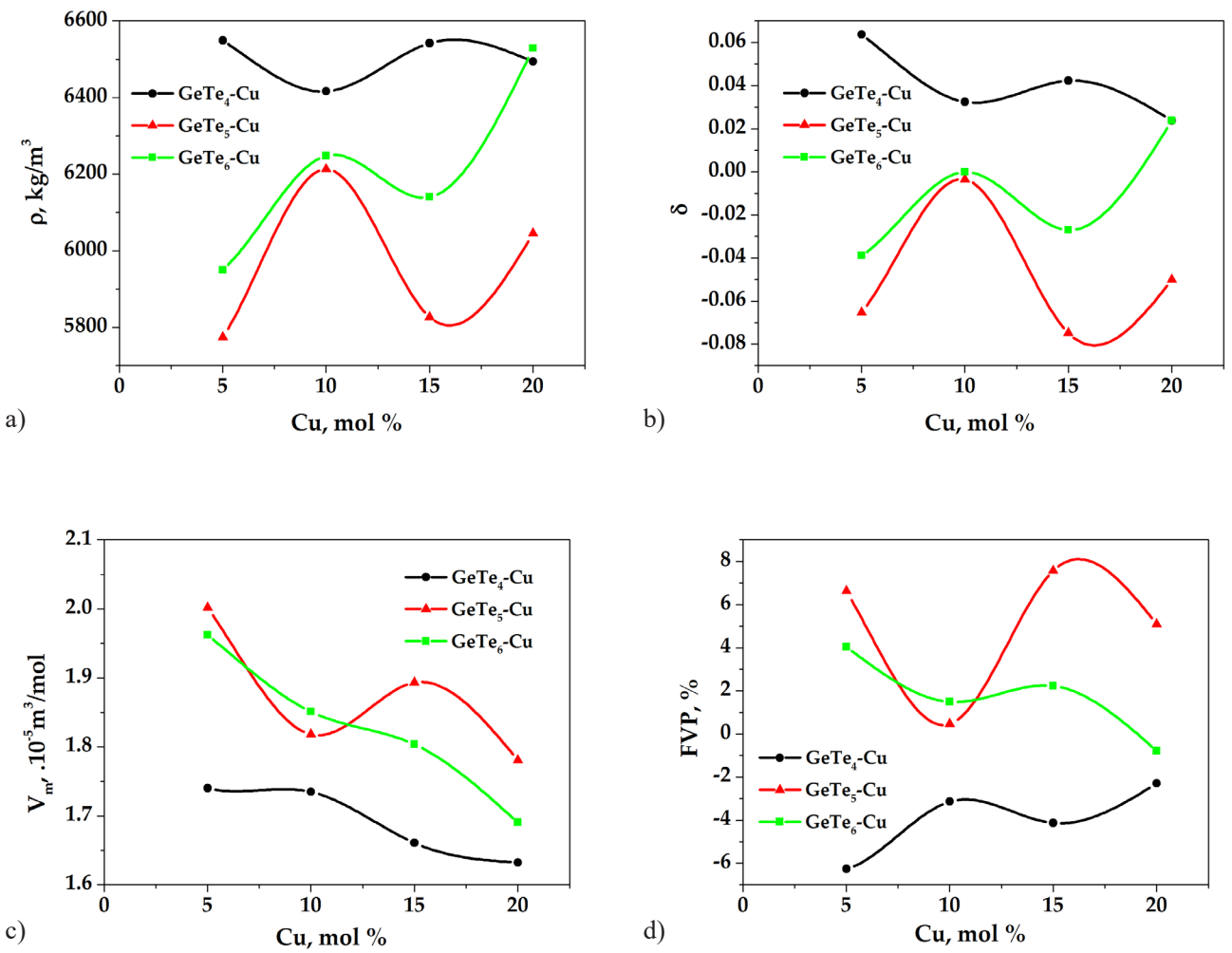


Fig. 3. Physico-chemical properties of the bulk samples studied as a function of the Cu content: (a) density; (b) compactness; (c) molar volume; (d) free volume percentage.

compositions within the $GeTe_6$-Cu system show the widest spread in density, with values in the range from 5950 kg m^{-3} up to 6529 kg m^{-3}. The density of the $GeTe_5$-Cu samples varies from 5550 to 6213 kg m^{-3}. For the samples from the $GeTe_5$-Cu and $GeTe_6$-Cu systems, the dependence of density on Cu content exhibits a similar trend (Fig. 3a). The density initially increases, reaching a maximum at 10 mol % Cu, followed by a decrease to a minimum at 15 mol % Cu, and then rises again with increasing Cu concentration. In contrast, the $GeTe_4$-Cu system exhibits an opposite behaviour: the density first decreases, reaching a local minimum at 10 mol % Cu, then increases up to 15 mol % Cu, and then decreases again at 20 mol % Cu. The results indicate that a higher Te content in the Ge/Te ratio tends to increase structural flexibility, leading to broader density fluctuations, while Cu incorporation modifies packing arrangements in a non-linear, system-dependent manner. The $GeTe_5$-Cu and $GeTe_6$-Cu samples exhibit a less compact structure (Fig. 3b) than the samples from the $GeTe_4$-Cu system. The most compact structure is observed for the sample $Ge_{19}Te_{76}Cu_5$ (from the system $GeTe_4$-Cu), and the lowest compactness is observed for the sample $Ge_{14}Te_{71}Cu_{15}$ (from the system $GeTe_5$-Cu). The molar volume (Fig. 3c) shows similar trends across all three systems. It decreases with increasing Cu content in the Ge-Te matrix. This behaviour can be attributed to the substitution of Te (atomic mass 127.6 g mol^{-1}) by Cu (atomic mass 63.5 g mol^{-1}), which reduces the overall molecular mass of the samples and consequently the molar volume of the materials. The free volume percentage (Fig. 3d) exhibits a pronounced minimum at 10 mol % Cu for the samples from the $GeTe_5$-Cu and $GeTe_6$-Cu systems. In contrast, the $GeTe_4$-Cu shows a maximum in FVP at 10 mol % Cu.

The X-ray diffraction (XRD) analysis of the bulk samples reveals the presence of four crystalline phases, common to all studied compositions (Te, Cu, CuTe, and Cu_2GeTe_3) suggesting that the structural units remain the same across the $GeTe_4$-Cu, $GeTe_5$-Cu and $GeTe_6$-Cu systems. Therefore, we attribute the variation in the physicochemical performance of the investigated samples to the different amount of these structural units within the material and their rearrangement influenced by the thermal history of the samples and subsequent storage at room temperature. Based on the crystallographic data obtained, it could be assumed that the structural units forming the crystal lattice of the samples studied consist of $GeTe_4$ and $CuTe_4$ tetrahedra bonded with Te atoms forming zigzag tellurium chains. Fig. 4 presents a model of these structural units, which has been generated based on experimentally obtained data using the Materials Project Program.

The Cu_2GeTe_3 phase crystallizes in the orthorhombic Imm2 space group featuring a three-dimensional structure consisting of corner-sharing $CuTe_4$ and $GeTe_4$ tetrahedra, with two inequivalent Te^{2-} sites forming $TeCu_2Ge_2$ and $TeCu_3Ge$ tetrahedra [23]. Tellurium crystallizes in the trigonal P3_121 space group. The structure is one-dimensional and consists of one Te ribbon oriented in the (0, 0, 1) direction. Te is bonded in a distorted water-like geometry to two equivalent Te atoms. Both Te-Te bonds have the same length [24]. CuTe crystallizes in the orthorhombic Pmmn space group. The structure is two-dimensional and consists of one CuTe sheet oriented in the (0, 0, 1) direction. Cu^{2+} is bonded to four equivalent Te^{2-} atoms forming a mixture of distorted corner and edge-sharing $CuTe_4$ tetrahedra. There are two shorter (2.61 Å) and two longer (2.75 Å) Cu-Te bond lengths. Te^{2-} is bonded in a 6-coordinate geometry to four equivalent Cu^{2+} atoms [25]. Cu crystallizes in the cubic Fm-3m space group. The structure is three-dimensional. Cu is bonded to twelve equivalent Cu atoms to form a mixture of corner, edge and face-sharing $CuCu_{12}$ cuboctahedra. All Cu-Cu bonds lengths are equal [26].

Considering the Te content in the Ge/Te ratio, it is evident that increasing the amount of tellurium ($GeTe_6$ > $GeTe_5$ > $GeTe_4$) does not lead to a corresponding increase in density. The samples from the $GeTe_4$-Cu system exhibit the highest density, followed by those from the $GeTe_6$-Cu system. The lowest density is observed for the samples from the $GeTe_5$-Cu system. The most compact structure, and since the lowest V_m and FVP, is shown by the compositions within the $GeTe_4$-Cu system. The samples from the system $GeTe_5$-Cu exhibit a less compact structure than those from the $GeTe_4$-Cu and $GeTe_6$-Cu, and since the highest V_m and FVP. Thus, the Te content in the Ge/Te ratio cannot alone explain the observed trends in the physico-chemical properties. Investigations on chalcogenides reveal that in compositions containing an equal number of tetrahedral structural units and chalcogen chains the atomic arrangement exhibits the densest packing [27]. Therefore, it could be assumed that for the $GeTe_4$-Cu

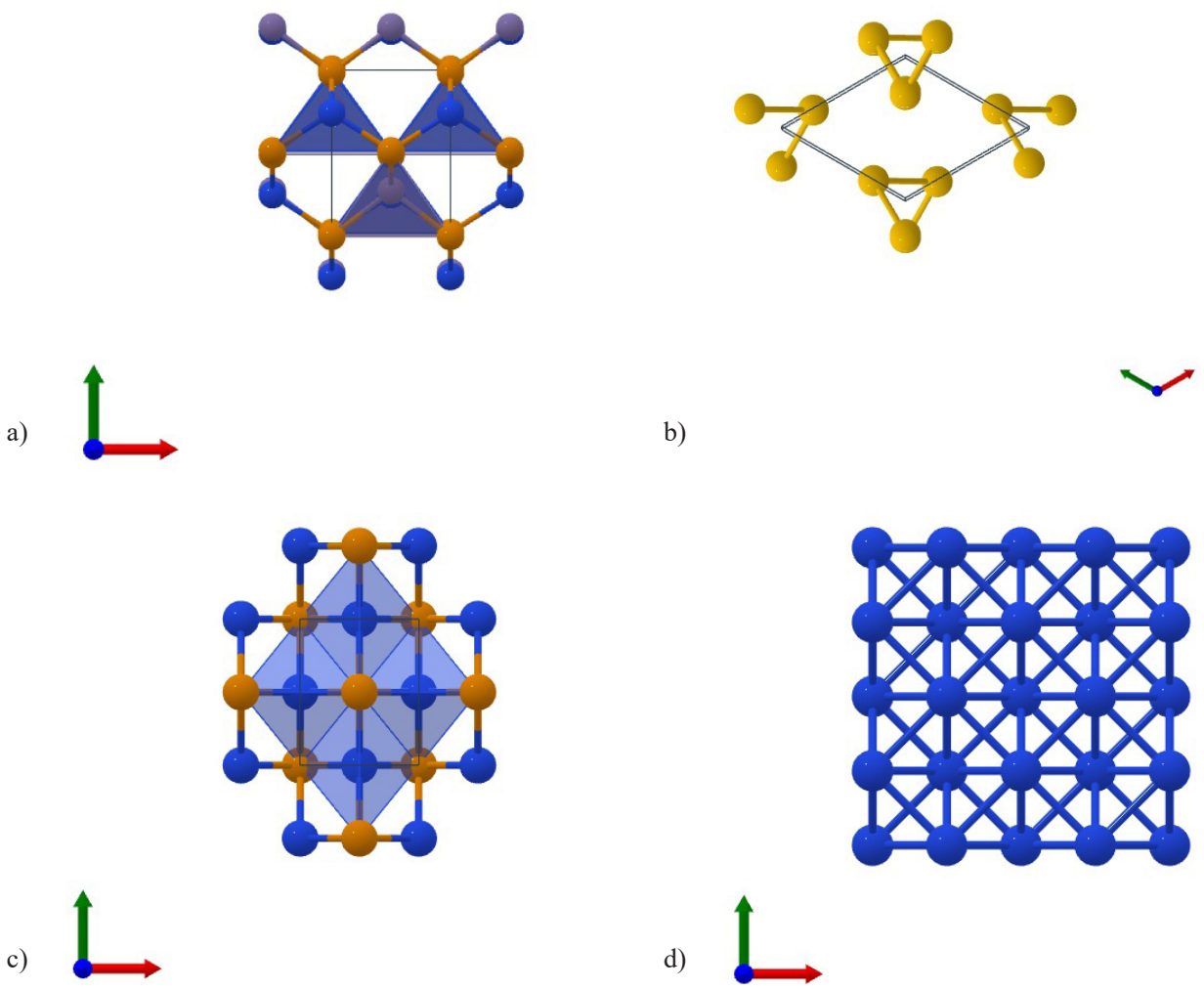


Fig. 4. Structural units in the crystal samples from the $GeTe_4$-Cu, $GeTe_5$-Cu, and $GeTe_6$-Cu systems. The identified four phases: (a) Cu_2GeTe_3; (b) Te; (c) CuTe; (d) Cu form $GeTe_4$ and $CuTe_4$ tetrahedra bonded with tellurium chains.

system an optimum balance between heteropolar bonds (Cu-Te, Ge-Te) forming tightly linked structural units and homopolar Te-Te bonds forming flexible chains, is reached across the Ge/Te ratios compared in this study. Considering the copper content, its effect on the density is non-linear and system dependent. The addition of 10 mol % Cu to the $GeTe_4$-Cu system causes a decrease in ρ. The effect of doping $GeTe_5$-Cu and $GeTe_6$-Cu with 10 mol % Cu is opposite. The results could be assigned to the different role that the replacement of Te atoms by atoms having smaller atomic radii (Cu atomic radii - 1.28 Å; tellurium atomic radii - 1.40 Å) plays by increasing Te content among the Ge/Te ratio. The $GeTe_4$-Cu system initially has the most tightly packed structure (higher δ) and the introduction of 10 mol % copper might create minor interstitial voids within the crystal lattice reducing ρ. The $GeTe_5$-Cu and $GeTe_6$-Cu systems have initially less compact structure. The Cu atoms, being smaller than Te, may fill existing free volume, increasing density at 10 mol % Cu. Further addition of Cu leads to decrease in ρ (at 15 mol % Cu). We can speculate that this behaviour is due to interactions between Te atoms of adjacent chains, which may give rise to formation of loosely packed layered-like arrangements [28, 29]. By doping the $GeTe_5$ and $GeTe_6$ matrices with 20 mol % copper, Cu atoms partially replace these weak Te-Te bonds with stronger Cu-Te bonds, bringing chains closer and as a result causing more compact atomic arrangement.

CONCLUSIONS

In this work, a comparative analysis of some physicochemical properties, including density, molar volume, compactness, and free volume percentage, of bulk chalcogenides from the $GeTe_4$-Cu, $GeTe_5$-Cu and $GeTe_6$-Cu systems has been carried out with respect to variations in the Ge/Te ratio and Cu content.

- The samples from the $GeTe_4$-Cu system exhibit the highest density and the most compact structure, followed by those from the $GeTe_6$-Cu system.
- The samples from the $GeTe_5$-Cu system show the lowest density and the least compact structure.
- The results demonstrate that, although all compositions contain the same crystalline phases (Te, Cu, CuTe, and Cu_2GeTe_3), a delicate balance between Te-Te chains and heteropolar Cu-Te and Ge-Te interactions, governs their physico-chemical properties.

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Authors' contributions

Y.T.: Conceptualization, Y.T., V.L., V.I.: Methodology, Y.T., V.L.: Validation, Y.T., V.L., Y.S.: Investigation, A.S.: Writing - original draft preparation, Y.T.: Writing - review and editing.

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