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Local environment of germanium atoms in $Ge_3Sb_2Te_6$, $Ge_2Sb_2Te_5$, $GeSb_2Te_4$ and $GeSb_4Te_7$ amorphous and crystalline films

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Abstract. The valence state and local environment of germanium atoms in $Ge_3Sb_2Te_6$, $Ge_2Sb_2Te_5$, $GeSb_2Te_4$ and $GeSb_4Te_7$ amorphous and crystalline films were determined by Mössbauer spectroscopy on the ^{119}Sn isotope. In crystalline films, divalent germanium is located in octahedral positions in a rhombohedrally distorted NaCl-type crystal lattice. In amorphous films, tetravalent germanium atoms form a tetrahedral system of chemical bonds. In all the films, the nearest environment of germanium contains mainly tellurium atoms.

Keywords: local structure, Mössbauer spectroscopy, amorphous and crystalline films, valence state, local environment

Introduction

Due to a significant contrast in conductivity and reflectivity between the crystalline and amorphous phases, phase transition materials can be used to store and encode data for non-volatile memory (Lencer et al. 2011). It is believed that the compositions lying on the GeTe–Sb_2Te_3 pseudobinary line ($Ge_3Sb_2Te_6$, $Ge_2Sb_2Te_5$, $GeSb_2Te_4$ and $GeSb_4Te_7$, let us denote them as GeSbTe) are the most promising materials for creating rewritable optical storage devices, since they have a short crystallization time, ideal reversibility between amorphous and crystalline states and high thermal stability (Qiao et al. 2019). To date, the crystal structures of GeSbTe alloys (let us denote them as *c*-GeSbTe) have been studied in detail (Lotnyk et al. 2016; Sun et al. 2007; Urban et al. 2013; Wang et al. 2017; Zhang et al. 2016; Zheng et al. 2019). Many studies have also been carried out in order to determine the short-range structure of GeSbTe amorphous alloys (let us denote them as *a*-GeSbTe) (Baker et al. 2006; Jóvári et al. 2008; Kolobov et al. 2004; Paesler et al. 2007); however, these structures are still being discussed (Qiao et al. 2019; Stellhorn et al. 2020).

Mössbauer spectroscopy (MS) can be an effective tool for changes detecting in the local environment of atoms and their electronic structure during GeSbTe compounds amorphization. However, apart from the works (Bordovskii et al. 2021; Marchenko et al. 2021) and the work (Ledda et al. 1988), which presents the ^{121}Sb Mössbauer spectra of $GeSb_2Te_4$, $Ge_2Sb_2Te_5$ and $GeSb_4Te_7$ crystalline compounds, there are no Mössbauer studies of GeSbTe ternary compounds.

This work is devoted to studying the nature of the local environment of germanium atoms in $Ge_3Sb_2Te_6$, $Ge_2Sb_2Te_5$, $GeSb_2Te_4$ and $GeSb_4Te_7$ crystalline and amorphous films by absorption MS on ^{119}Sn isotope.

Experimental technique

Undoped and tin-doped X-ray $Ge_3Sb_2Te_6$, $Ge_2Sb_2Te_5$, $GeSb_2Te_4$, $GeSb_4Te_7$, $Ge_{2.95}Sn_{0.05}Sb_2Te_6$, $Ge_{1.95}Sn_{0.05}Sb_2Te_5$, $Ge_{0.95}Sn_{0.05}Sb_2Te_4$ and $Ge_{1.95}Sn_{0.05}GeSb_4Te_4$ amorphous films (let us denote them as *a*-Ge(Sn)SbTe) were obtained by magnetron sputtering of polycrystalline targets. The films were annealed at 150 °C to obtain GeSbTe and Ge(Sn)SbTe crystalline films. The films composition was monitored by the X-ray fluorescence analysis.

The Mössbauer spectra were measured with a SM 4201 TerLab spectrometer at 80 K using a $Ca^{119mm}SnO$ source. Isomer shifts (δ) of the ^{119}Sn spectra are given relative to the $CaSnO_3$ absorber.

Experimental results and their discussion

The Mössbauer spectra of ^{119}Sn impurity atoms in Ge(Sn)SbTe amorphous and crystalline films are shown in Figs. 1 and 2. All spectra are single lines with a FWHM $G \sim 1.30–1.36$ mm/s. (The instrumental line width $G_{app} = 0.79(2)$ mm/s). The crystalline films spectra have isomer shifts $\delta \sim 3.49–3.54$ mm/s; for amorphous films $\delta \sim 2.03–2.09$ mm/s was obtained.

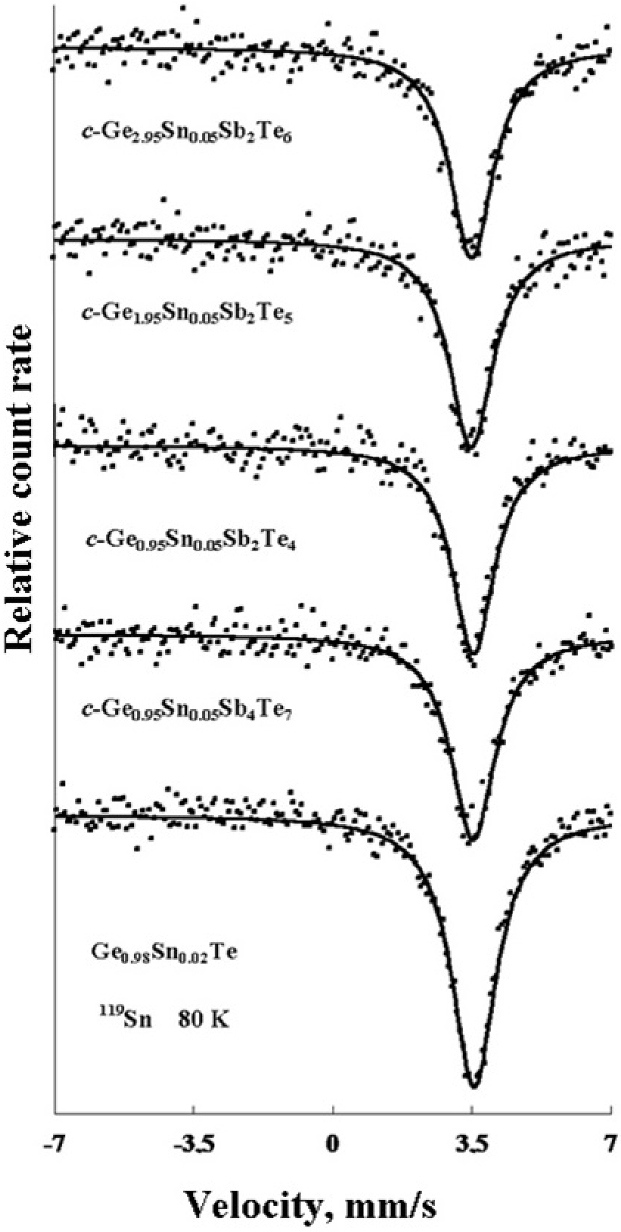

Fig. 1. Mössbauer spectra of ^{119}Sn impurity atoms in Ge(Sn)Sb crystalline films and in the $Ge_{0.98}Sn_{0.02}Te$ crystalline compound

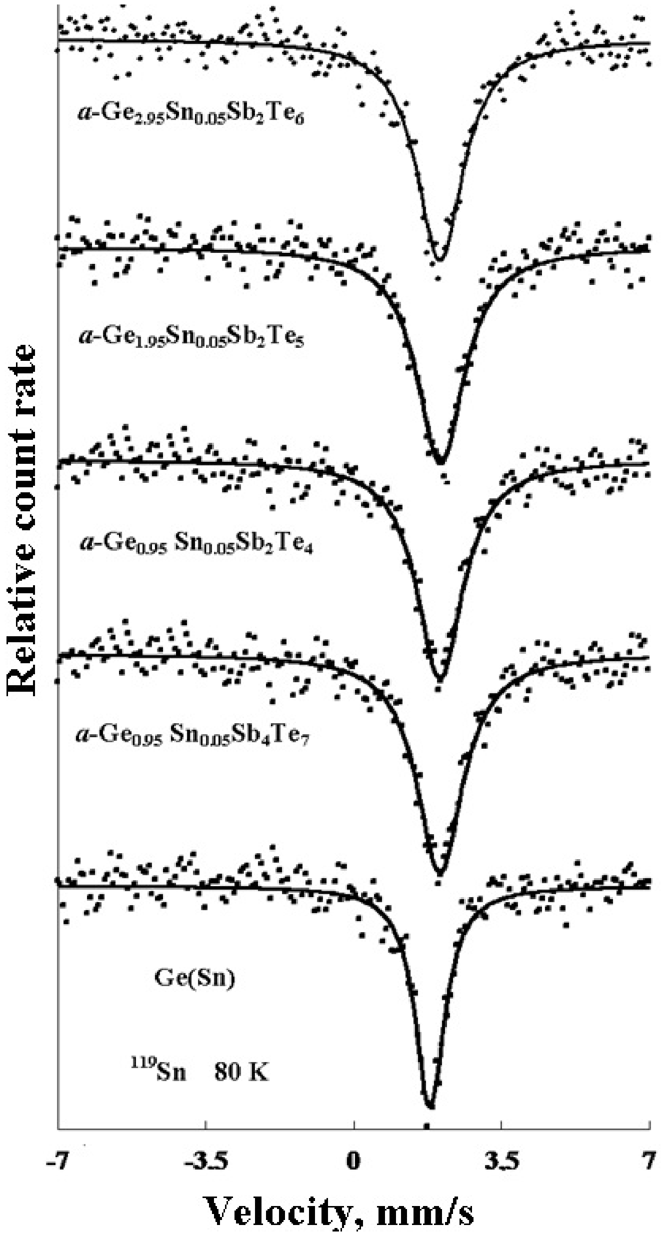

Fig. 2. Mössbauer spectra of ^{119}Sn in Ge(Sn)Sb amorphous films and in the crystalline germanium GeSn

The ^{119}Sn impurity atoms spectra of GeSbTe crystalline films correspond to the ionic compounds of divalent tin. Fig. 1 shows the ^{119}Sn impurity atoms spectrum in the $Ge_{0.98}Sn_{0.02}Te$ compound for which δ = 3.55(3) mm/s and G = 1.36(2) mm/s were obtained. These parameters correspond to divalent six-coordinated tin which isovalently replaces the divalent six-coordinated germanium atoms in the cationic node of the GeTe crystal lattice. GeTe compound crystallizes in a rhombohedrally distorted NaCl-type lattice, hence the broadening of the ^{119}Sn impurity atoms spectrum in the $Ge_{0.98}Sn_{0.02}Te$ solid solution. The broadening of ternary compounds spectra is also related with the presence of a high concentration of stoichiometric vacancies in the cationic sublattice of these compounds.

The data of Mössbauer spectroscopy on ^{119}Sn impurity atoms for Ge(Sn)SbTe crystalline films comply with the results of the X-ray diffraction studies of metastable vacancy-disordered cubic GeSbTe crystalline compounds. Divalent tin Sn^{2+} (electronic configuration is $5s^2p^x$) replaces divalent germanium Ge^{2+} (electronic configuration is $4s^2p^x$) in positions 4 *b* of the rhombohedrally distorted NaCl-type crystal lattice, and there are only tellurium atoms in the nearest environment of six-coordinated germanium atoms. The latter circumstance explains the closeness of the isomer shifts of the ^{119}Sn spectra in the GeSbTe crystalline compounds to the isomer shift of the ^{119}Sn spectrum in the SnTe compound (δ = 3.54(1) mm/s and G = 0. 94(2) mm/s) and also to the isomer shift of the ^{119}Sn impurity atom in the GeTe compound. The broadening of the spectra of *c*-GeSbTe ternary compounds compared to the spectral width of SnTe is due to the rhombohedral distortion of the lattices of *c*-GeSbTe compounds (six Ge-Te bonds at sites with octahedral symmetry are divided into three short and three long bonds, as in a GeTe crystal) as well as to a high concentration of randomly distributed stoichiometric vacancies in the cationic sublattice (Lotnyk et al. 2016; Sun et al. 2007; Urban et al. 2013; Wang et al. 2017; Zhang et al. 2016; Zheng et al. 2019).

The first problem that Mössbauer spectroscopy can solve is the determination of the valence state and local coordination number of germanium atoms in GeSbTe amorphous films. The isomer shifts of the ^{119}Sn spectra of Ge(Sn)Sb amorphous films have values close to the values of the isomer shifts of the spectra of impurity tin atoms ^{119}Sn in monocrystalline germanium (δ = 1.79(1), see Fig. 2) and also close to the measured shift of the spectrum of gray tin α-Sn (δ = 2.10(1)) that form the area of isomer shifts of tetravalent tin compounds with a tetrahedral sp^3 system of chemical bonds. Thus, impurity tin atoms in the structure of Ge(Sn)Sb amorphous films isovalently replace tetravalent germanium atoms, which form a tetrahedral system of chemical bonds (the local coordination number of germanium atoms in amorphous films is four).

The second problem solved using Mössbauer spectroscopy data is the determination of the chemical nature of atoms in the nearest environment of germanium atoms in GeSbTe amorphous films. It should be noted that, if germanium atoms are also present in the nearest environment of germanium atoms (i. e. the formation of Ge-Ge chemical bonds), the isomer shift of the ^{119}Sn spectra of amorphous films should be ~ 1.80 mm/s (as for the spectrum of impurity tin atoms in monocrystalline Ge). At the same time, the spectra of all amorphous films have isomer shifts within $\delta \sim 2.06–2.09$ mm/s. Note that the isomer shifts of the spectra of ^{119}Sn impurity atoms in the $Ge_{1.45}Sn_{0.05}Te_{8.5}$ glassy alloy are of the same range. Here the germanium (tin) atoms are tetravalent, forming a system of sp^3 bonds (their coordination number is four) and having tellurium atoms in the local environment (Seregin et al. 1977; Seregina et al. 1977). This conclusion can be confirmed by the fact that the isomer shift of the ^{119}Sn spectra of Ge(Sn)SbTe amorphous films monotonically increases from 2.03(1) mm/s for the $Ge_3Sb_2Te_6$ compound (contains 27.3 at.% of Ge) to 2.07(1) mm/s for the $GeSb_4Te_7$ compound (contains 8.3 at.% of Ge). Based on all the above, it should be concluded that there are tellurium atoms in the local environment of germanium atoms in the Ge(Sn)SbTe and GeSbTe amorphous films.

Kolobov et al., based on the results of XAFS to describe the order–disorder transition in $Ge_2Sb_2Te_5$ compound films, supposed that a crystalline film amorphization is accompanied by a germanium atom jump from octahedral positions in a crystalline film to tetrahedral positions with four Te atoms in the local environment (Kolobov et al. 2004). However, Baker et al. (Baker et al. 2006; Paesler et al. 2007), also using the EXAFS data, concluded that germanium atoms in $Ge_2Sb_2Te_5$ amorphous films form the Te_3Ge-$GeTe_3$ structural units, where predominant formation of Ge-Ge bonds can be seen. The structure of $Ge_2Sb_2Te_5$ and $GeSb_2Te_4$ amorphous films was also studied using the EXAFS method, in combination with high-energy X-ray diffraction and neutron diffraction, by the authors of (Jóvári et al. 2008). Ge-Ge and Ge-Sb bonds were shown to be present while Te–Te and Sb–Sb bonds were not found. Germanium atoms have a fourfold coordination. Finally, the local structure of the $Ge_2Sb_2Te_5$ amorphous phase was studied using anomalous X-ray scattering near the absorption K-edges of germanium, antimony, and tellurium atoms (Stellhorn et al. 2020). A half of the Ge atoms were found to have an octahedral environment similar to that in a crystalline phase. The remaining half of germanium atoms has tetrahedral symmetry and forms an energy barrier between the amorphous and crystalline phases, providing a long lifetime for the amorphous modification.

The Mössbauer spectroscopy data obtained by us comply with the ideas of the authors of (Kolobov et al. 2004) about the local structure of germanium atoms in $Ge_2Sb_2Te_5$ amorphous films and allow us to extend these results to other GeSbTe amorphous compounds. Tetravalent germanium atoms form a tetrahedral system of chemical bonds in the structural network of the amorphous matrix and have only tellurium atoms in their nearest environment. The conclusion of the authors of (Jóvári et al. 2008) that germanium atoms in $Ge_2Sb_2Te_5$ and $GeSb_2Te_4$ amorphous compounds have fourfold coordination is also confirmed (with the only clarification that this is true for all the GeSbTe amorphous films).

Conclusions

The local environment of atoms in $Ge_3Sb_2Te_6$, $Ge_2Sb_2Te_5$, $GeSb_2Te_4$ and $GeSb_4Te_7$ crystalline and amorphous films was determined by Mössbauer spectroscopy on the ^{119}Sn isotope. The data of Mössbauer spectroscopy on ^{119}Sn impurity atoms for crystalline films comply with the results of the X-ray diffraction studies: divalent tin replaces divalent germanium in a rhombohedrally distorted NaCl-type lattice.

Impurity tin atoms in the structure of GeSnSbTe amorphous films isovalently replace tetravalent germanium atoms, which form a tetrahedral system of chemical bonds (the local coordination number of germanium atoms in GeSbTe amorphous films is four), and the local environment of germanium contains mainly tellurium atoms.

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Conflict of Interest

The author declares that there is no conflict of interest, either existing or potential.

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