

# Raman spectra of amorphous phase change materials from first principles

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## ABSTRACT

We computed the Raman spectra of amorphous GeTe, GST and Sb<sub>2</sub>Te<sub>3</sub> from ab initio phonons and the empirical bond polarizability model. Models (200-300 atoms) of the amorphous phases were generated by quenching the melt by means of ab-initio molecular dynamics simulations. The calculated spectra are in very good agreement with experimental data and can be assigned mostly to vibrations of defective octahedra. The spectrum of a-GeTe shows also features assigned to vibrations of Ge in tetrahedral geometry.

**Key words:** ab-initio simulations, Raman spectra, structural properties, amorphous phases

## 1. INTRODUCTION

Raman spectroscopy is a useful tool to monitor structural transformations. In the case of phase change materials it has been used to discriminate between different amorphous structures which can be generated by incomplete crystallization or by different means (rf sputtering or ion irradiation) [1]. At this aim, an assignment of the Raman spectra of amorphous Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> (GST) and GeTe has been proposed on the basis of the structural model introduced by Kolobov *et al.* from the analysis of x-ray absorption fine structure (EXAFS) [2]. The average coordination of Ge atoms inferred from EXAFS data decreases from 6-fold in the crystal to a 4-fold coordination of Ge atoms in both a-GST and a-GeTe. Consequently, the Raman spectra have been interpreted in terms of vibrations of GeTe<sub>4-n</sub>Ge<sub>n</sub> tetrahedra (where n = 0,...,4) [3]. However, while a 4-fold coordination can be reliably inferred from EXAFS, bonding angles are subject to large uncertainties. Recent ab initio molecular-dynamics simulations [4-6] of a-GST, a-GeTe and a-Sb<sub>2</sub>Te<sub>3</sub> showed that indeed Ge atoms are mostly 4-fold coordinated, but only approximately one third of Ge atoms display tetrahedral coordination (one fourth in a-GeTe), whereas the majority of Ge and all Te and Sb atoms are in a defective octahedral environment with bond angles typical of the octahedral geometry but coordination lower than six, i.e. mostly four for Ge and Sb and three for Te (Fig. 1). Moreover, three Ge-Te or Sb-Te bonds are shorter than the others giving rise to a 3+n coordination in defective octahedra, ruled by p-bonding. Based on ab-initio calculations we here propose a different assignment of the Raman spectra of GeTe and GST.

## 2. THEORY

Models (from 216 to 298 atoms large) of the amorphous phases of GeTe, GST and Sb<sub>2</sub>Te<sub>3</sub> were generated by quenching from the melt within density-functional-based molecular dynamics simulations as described in Ref. [4,5]. Cubic GST was modelled by a 270 cubic supercell with Ge and Sb and 20 % of stoichiometric vacancies distributed randomly on one sublattice of the rocksalt lattice. The Raman spectra were computed from ab-initio phonons and empirical polarizabilities within the the Bond Polarizability model [5] whose parameters were fitted to the fully ab-initio Raman spectra of reference crystalline systems [7] and small models of the amorphous phases.

## 3. RESULTS & DISCUSSION

The theoretical and experimental Raman spectra of a-GeTe, a-GST and a-Sb<sub>2</sub>Te<sub>3</sub> are reported in Fig. 1. No experimental Raman data are available for a-Sb<sub>2</sub>Te<sub>3</sub> to our knowledge. The agreement between theory and

experiments is very good. Inspection on the phonon displacements reveal that the main peaks at  $110$  and  $175 \text{ cm}^{-1}$  in a-GST and the two peaks at  $129$  and  $152 \text{ cm}^{-1}$  in a-GST are due to vibrations of defective octahedra. The weaker structures above  $200 \text{ cm}^{-1}$  in a-GeTe are due instead to vibrations of  $\text{GeTe}_{4-n}\text{Ge}_n$  tetrahedra. Similar structures are present also in the spectrum of a-GST but their intensity is much lower than that of the main Raman peaks at lower frequency which are dominated by vibrations of the more polarizable Sb-Te bonds. As a consequence the contribution of tetrahedra to the Raman spectrum of a-GST is hidden by the larger Raman cross section of octahedra. The Raman spectrum of  $\text{Sb}_2\text{Te}_3$  is actually very similar to the spectrum of a-GST. For sake of comparison the Raman spectrum of crystalline cubic GST is also given in Fig. 1. Note that, as opposed to the common behaviour of most materials, the Raman spectrum of the crystalline cubic GST phase is broader than the spectrum of the amorphous phase. This is actually due to the presence of disorder in the form of 25 % of vacancy sites in one sublattice of c-GST which makes the spread in Ge-Te and Sb-Te bond lengths actually larger in c-GST than in a-GST [4].

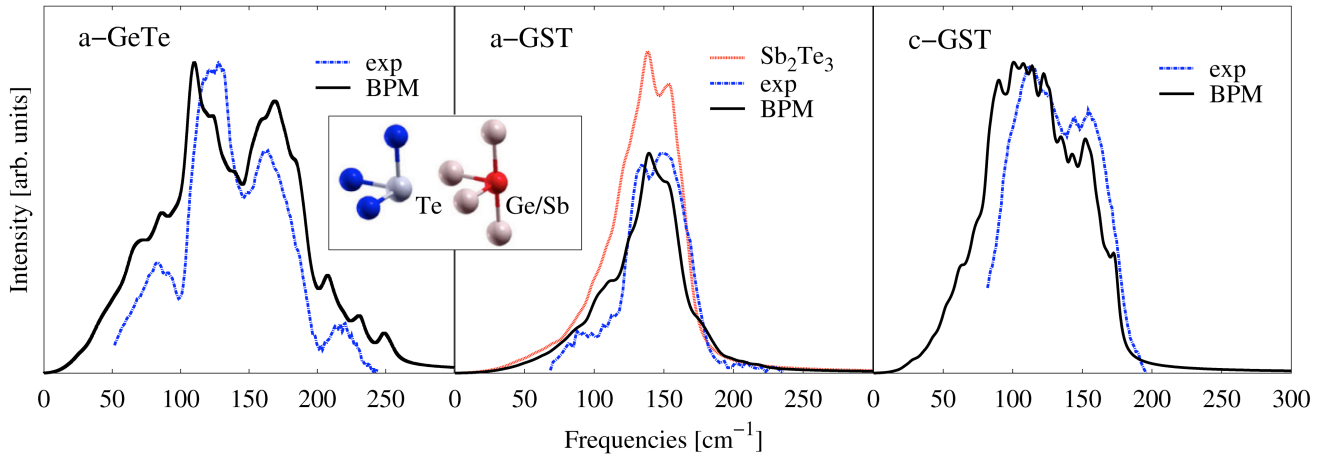


Fig. 1 Theoretical Raman spectra of amorphous GeTe, GST and  $\text{Sb}_2\text{Te}_3$  and of cubic GST. The experimental data come from Ref. [3] for GeTe and Ref. [1] for GST. The vertical scale (arb. units) differ in the three different panels. Theoretical data on a-GeTe are from Ref. [5]. The geometry of the defective octahedral environment of Ge and Te is shown in the inset.

#### 4. CONCLUSION

Based on ab initio calculations, we have provided an assignment of the Raman spectrum of a-GeTe, a-GST and a- $\text{Sb}_2\text{Te}_3$  to vibrations of specific local structures in the amorphous network. The good comparison with experimental Raman spectra validate the structural models emerged from ab-initio simulations and provides a compelling evidence of the existence of both defective octahedra and tetrahedra.

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