Nanoscale physics

Modelling and first-principles calculation of low frequency quasy-localized vibrations of soft and rigid As-S nanoclusters

R.M. Holomb, P.M. Ihnatolia, O.V. Mitsa, V.M. Mitsa

Uzhhorod National University, Pidhirna Str., 46, 88000 Uzhhorod, Ukraine.
E-mail: holomb@gmail.com

Nowadays the non-crystalline chalcogenides in glassy and thin film forms are important photonic media for both practical usage and fundamental investigations. One of the most intriguing fundamental phenomenon in physics of disordered solids is the excess contribution to the low frequency (LF) vibrational states with respect to the predictions of the Debye theory. This contribution seen as a broad peak in the inelastic (neutron and Raman) scattering intensity around 1 THz. The peak intensity (usually referred to as the Boson peak (BP)) in the 2-10 meV energy range is proportional to the density of states ($g(\omega)$) by the rule of $g(\omega)/\omega^2$ while the Debye theory in this spectral region predicts the constant intensity [1]. The relaxational and vibrational properties of non-crystalline solids in the LF (<100 cm^{-1}) region may contribute to the understanding of anomalous properties at low temperatures, the glass transition and other phenomena observed in disordered materials. While the relaxation dynamics can be described by the mode coupling theory, the vibrational excitations are still unsettled and subject of intense investigation and discussions.

In this work we present the results of modelling of different As-S nanoclusters representing the medium range order structures of As-S glasses and first-principles calculations of low frequency Raman active vibrations. It was established that there is no vibrational contribution from a single AsS_3 pyramidal structural units and rigid cage-like As-S nanoclusters. However, the low frequency Raman modes calculated for gas phase medium range order branchy- and ring-like As-S nanoclusters are found to be located in the spectral region of BP observed in the Raman spectra of As-S glasses. Further modelling includes the model of 12-membered ring incorporated in continuous media. The stepwise fixing of the ring in space (by introducing fictive heavy terminal atoms) revealed the localization of the Raman active vibrational modes at extremely low frequency range (2-5 cm^{-1}). It was established that the mode localization and the red-shift of low energy vibrations is depending on degree of freedom of the ring in space.

1. *Holomb R., Mitsa V.* Boson peak of As_xS_{1-x} glasses and theoretical calculations of low frequencies clusters vibrations // Solid State Commun. – 2004. – **129**, №10. – P. 655-659.