RATTLING-INDUCED SUPPRESSIONOF PHONON TRANSPORT IN In_2O_3 WITH Sn AND Ga

SUPRIMAREA INDUSĂ DE VIBRAȚII A TRANSPORTULUI FONONIC ÎN In_2O_3 CU Sn ȘI Ga

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Indium oxide based compounds have been intensively investigated as perspective semiconducting materials for high-temperature thermoelectric applications [1]. Different additives like Sn, Ga, Zn, Sb etc. were used [2-3] in such compounds to improve their thermoelectric properties. The In_2O_3has a complex crystal latticewith 40 atoms in a primitive cell. As a consequence one could expect the reduction of phonon thermal conductivity due to phonon hybridization, accompanied bydecrease of phonon group velocities and increase of phonon-phonon scattering phase space [4].In Ref. [5]we have reported on theoretical investigations of electronic properties of In_2O_3 with Sn-, Ga- and O-based point defect complexes, employing density functional theory (DFT). It has been shown that defect complexes strongly influence the electronic band structure and position of indium and oxygen atoms. However, the impact of different defect complexes on thermal properties of In_2O_3 requires additional investigations.

The first principles calculations were performed within DFT formalism as implemented in the Quantum ESPRESSO code [6, 7]. The indium tin oxide (ITO) was modeled based on 40-atom In_2O_3 bixbyite primitive cell by substituting one In atom at b-site with a Sn atom, which corresponds to 6.25 at. % Sn-doping. The schematics of the ITO primitive cell is shown in Figure 1a.Adding to the ITO lattice one Ga atom at an intersite in close vicinity of a Sn atom resulted in formation of a cage-like structure for Sn_b-Ga_i point defect as shown in Figure 1b.

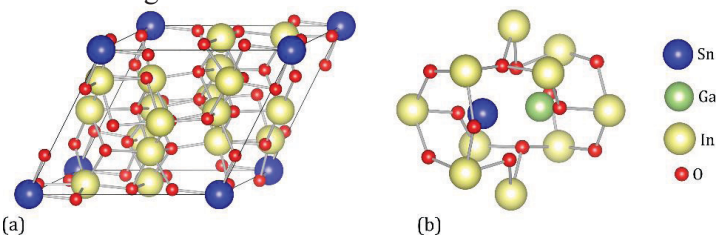

Fig. 1. (a) Schematic view of ITO primitive cell. (b) A cage-like structure containing Sn_b-Ga_i point defect in ITO-Ga_i crystal lattice

A clear evidence of a rattling nature of Sn-Ga point defect is provided by the temperature dependence of the atomic mean square displacement (MSD). In Figure 2 is shown the MSD in a wide temperature range for different atomsin In_2O_3-Sn_b-Ga_i crystal lattice.

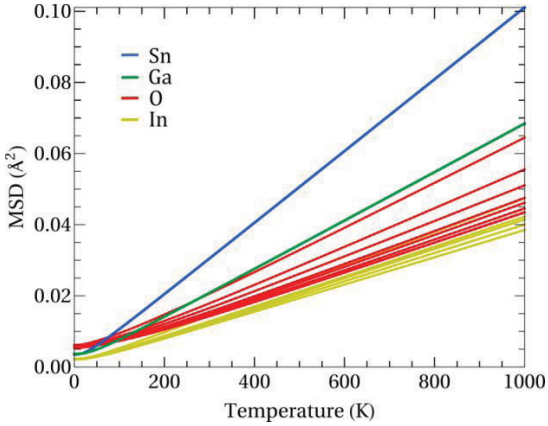

Fig. 2. Temperature dependence of atomic mean square displacement in In_2O_3 with Sn_b-Ga_i

The Sn and Ga atomic vibrations differ by a steeper temperature slope, characteristic for rattling atoms.These localized rattling vibrations hybridize with propagating high-velocity heat carrying acoustic vibrations of In atoms, thus playing an important role in suppressing the heat carrying capability of In_2O_3 with Sn_b-Ga_i.

To get insight into the thermal properties of In_2O_3 with Sn_b-Ga_iwe have calculated the phonon thermal conductivity$\kappa_{ph}\kappa_{ph}$ within linearized Boltzmann transport equation (BTE) approach taking into account all possible three-phonon scattering channels [8]. In Figure 3we show the room temperature mean free paths (MFP) of phonons (Figure 3a) and cumulative $\kappa_{ph}\kappa_{ph}$ (Figure 3b) in In_2O_3 without defects (black), with Sn_b defect (red) and Sn_b-Ga_i defect (blue).

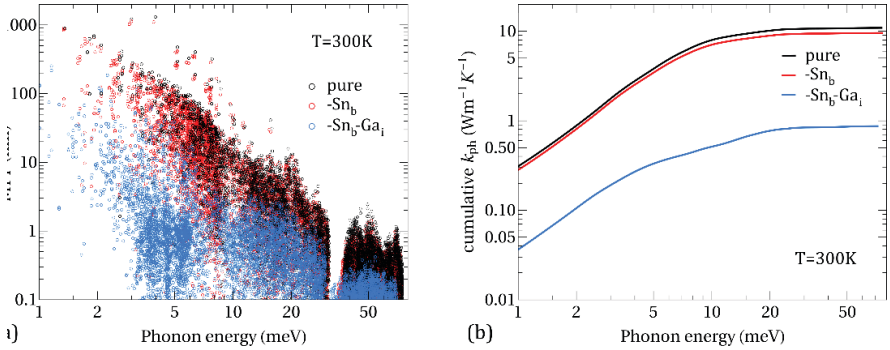

Fig. 3. Energetic distribution of: (a) phonon mean free path and (b) cumulative phonon thermal conductivity at 300 K in In_2O_3 without defects (black), with Sn_b defect (red) and Sn_b-Ga_i defect (blue)

It can be seen thatfor the whole range of energies both phonon MFP and thermal conductivity in In_2O_3 with Sn_b-$Ga_i$is 5 to 20 times lower at 300 K than in pure In_2O_3 or In_2O_3 with only Sn_b.It implies that Sn and Ga rattling modes induce the thermal transport suppression not only in the In-dominated low-frequency part of the spectrum but in theO-dominatedhigh-frequency part as well.

In conclusion, our theoretical modeling within DFT and BTE approaches taking into account all possible three-phonon scattering channels demonstrated that rattling vibrations have a strong impact on heat carrying capability of In_2O_3 with Sn_b-Ga_i point defect, with ~20 timessuppression of phonon thermal conductivity at room temperature in comparison with pure In_2O_3 or ITO.The obtained theoretical results demonstrate the possibility of engineering the thermal conductivity in indium oxide basedcompounds byGa doping and may lead to their practical applications in thermoelectricity.

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