Energy Band Spectra and Optical Properties of The In_6Se_7 Crystal with Substitutional Impurities

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Abstract

The study of the In_6Se_7 crystal is motivated by their potential application for electronic, thermoelectric, and optoelectronic devices. Doping of In_6Se_7 monoclinic crystal with various impurities allows creating a wide class of new compounds with unusual physical properties. In [1,2] was shown that substitution of In^+ site by Sn and Pb impurities can change the conduction type, charge concentration, tend to reduce the lattice thermal conductivity, and as in consequence, lead to the significant enhancement of the thermoelectric performance. Also, it is of interest to investigate the optical properties of In_6Se_7 doped by the Sn atoms.

According to the structural analysis, the In_6Se_7 crystal is one of the indium selenides crystallizing in the space group P2l/m, and where the In ions occupy different sites. Such crystal structure suggests that the incorporation of the Sn contents at these In sites is possible. Therefore we considered some models of the Sn atoms substitution for indium and calculated the electron spectra and optical parameters.

Using density functional theory (DFT) within local approximation for exchange-correlation interaction (LDA) we investigated the spatial distribution of electron density, band structures, and total and partial density of states in the In_6Se_7 and $In_{6-x}Sn_xSe_7$ crystals. We obtained the dispersive dependences of optical characteristics for both the undoped and doped In_6Se_7 crystal. The effect of the Sn impurities on the bandgap and optical parameters have been analyzed. It is shown that the Sn dopants play an important role in the controllable modulation of bandgap, dielectric constant, and refractive index in the considered crystals.

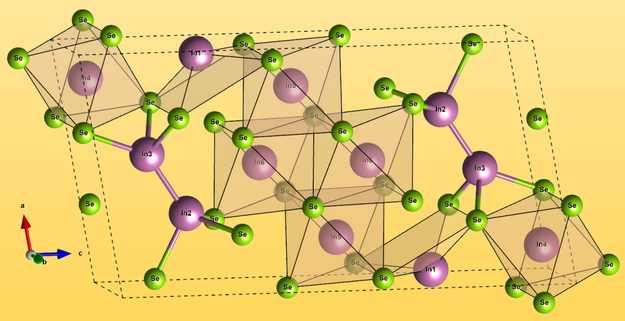
CRYSTAL AND BAND STRUCTURE OF THE In_6Se_7 NEW COMPOUNDS IN In–Se SYSTEM

In_6Se_7

Space group: P21/m.

Lattice parameters: *a* = 9.433 Å, *b* = 4.064 Å, *c* = 18.378 Å, β = 100.92°

The unit cell of In_6Se_7 crystal

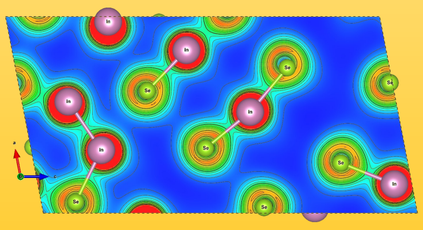


Atom	x	y	z	Site	Sym.
In1	0.02580	0.25	0.72820	2e	m
In2	0.67930	0.25	0.81286	2e	m
In3	0.43270	0.25	0.87581	2e	m
In4	0.85290	0.25	0.04719	2e	m
In5	0.17040	0.25	0.53376	2e	m
In6	0.48550	0.25	0.39523	2e	m
Se1	0.33680	0.25	0.00680	2e	m
Se2	0.74470	0.25	0.17940	2e	m
Se3	0.26040	0.25	0.27330	2e	m
Se4	0.97060	0.25	0.40720	2e	m
Se5	0.66980	0.25	0.53280	2e	m
Se6	0.37730	0.25	0.65910	2e	m
Se7	0.94320	0.25	0.90780	2e	m

Compound	*a*, Ang	*b*, Ang	*c*, Ang	β, deg	V0, Ang^3	E_{tot}, eV
In_5SnSe_7 (model 1)	9,49094	4,03009	17,3790	101,983	650,250	-18735,62590
In_5SnSe_7 (model 2)	9,60101	4,03857	17,4041	103,866	655,169	-18735,70060
In_5SnSe_7 (model 4)	9,39396	4,04241	17,7173	101,609	659,037	-18735,77520
In_5SnSe_7 (model 3)	9,48697	4,03430	17,5562	102,306	656,496	-18735,97700
In_5SnSe_7 (model 5)	9,34970	4,05380	17,7324	101,966	657,488	-18736,05270
In_5SnSe_7 (model 6)	9,51679	4,04658	17,5424	102,412	659,774	-18735,93156
In_6Se_7	9,43122	4,06481	17,6119	100,874	663,048	-21535,34110

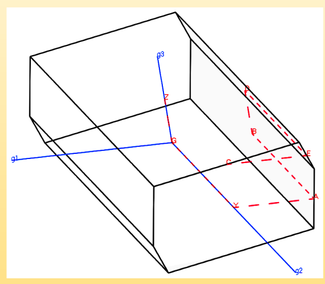
Lattice parameters, volume, total energy of the relaxed $In_{6-x}Sn_xSe_7$

Spatial distribution of electron density



1. J. Cui, M. Cheng, W. Wu, Z. Du, Y.Chao.// Appl. Mater. Interfaces- 2015.-V.8.- P 23175 –23180.
2. M. Cheng, Sh.Chen, Zh.Du, X. Liu, and J. Cui//Phys. Status Solidi A.-2016.- P, 1–7.

Energy bands structure and optical properties of the In_6Se_7



Brillouin zone

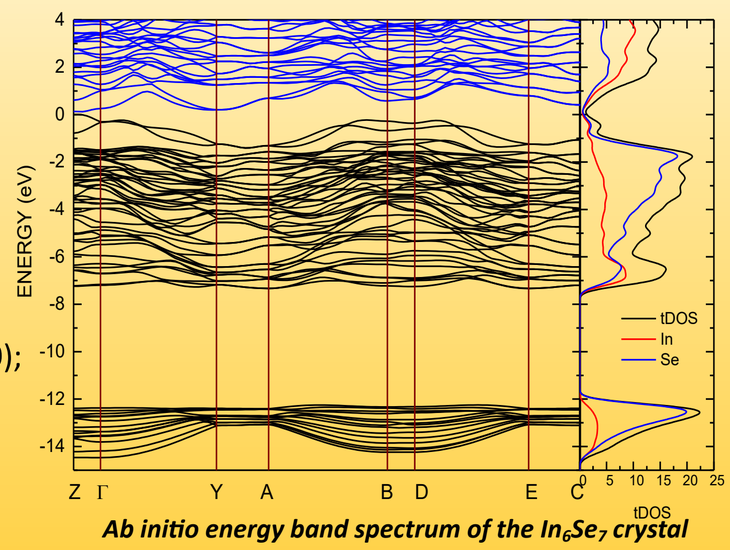
Points of high symmetry:

Z=(0,0,½); Γ=(0,0,0); Y=(0,½,0);

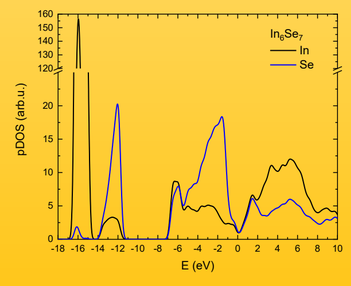
A=(-½,-½,0); B=(-½,0,0);

D=(-½,0,½); E=(-½,½,0);

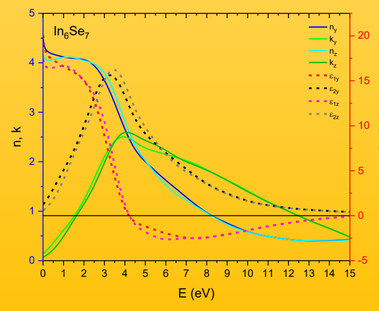
E_g^{calc} = 0.125 eV E_g^{exper}= 0.540 eV



Ab initio energy band spectrum of the In_6Se_7 crystal



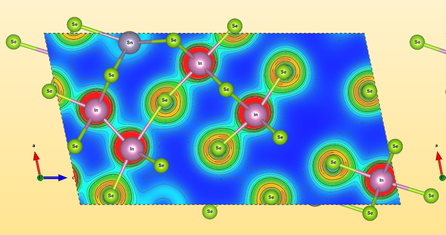
Partial density of electron states in pure In_6Se_7

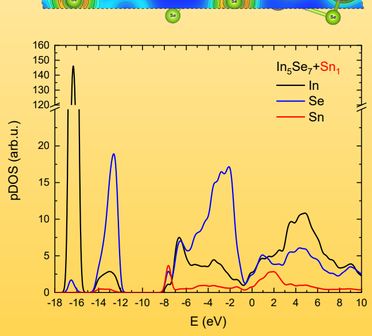


Energy dependence of optical characteristics in pure In_6Se_7

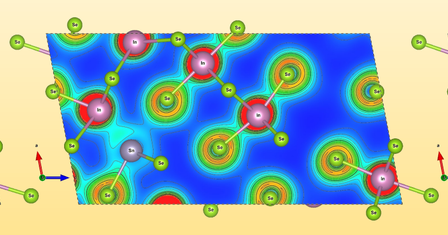
MODELING OF THE Sn IMPURITY-INDUCED CHANGES IN ELECTRONIC STATES OF In_6Se_7 CRYSTAL

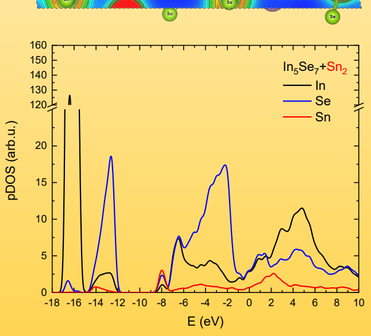
Model 1: Sn → In1



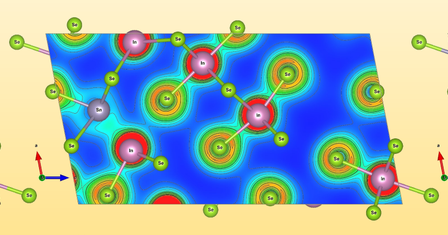


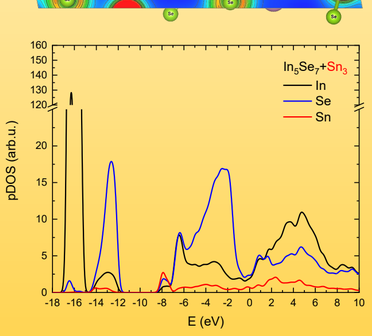
Model 2: Sn → In2



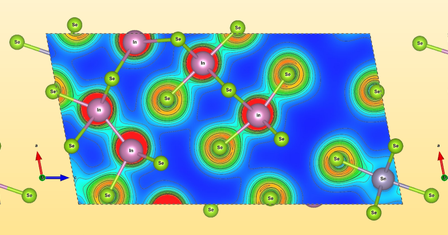


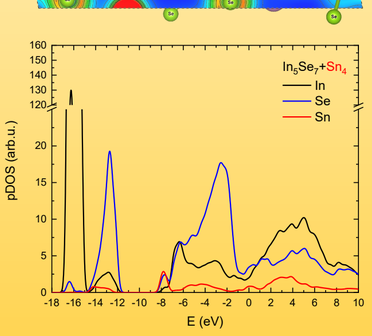
Model 3: Sn → In3



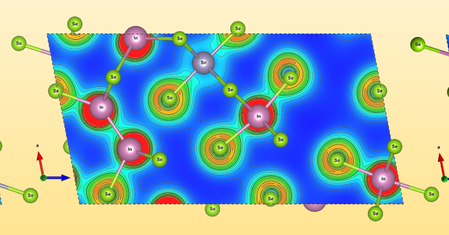


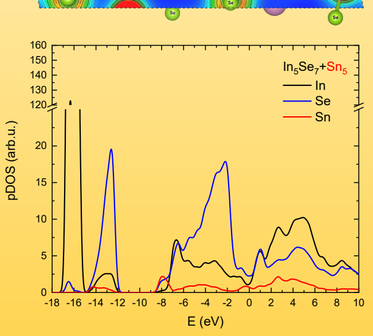
Model 4: Sn → In4



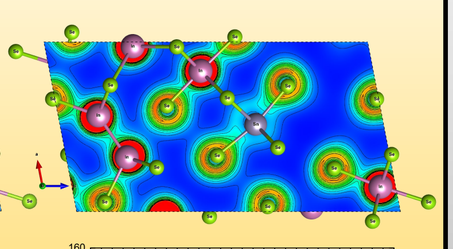


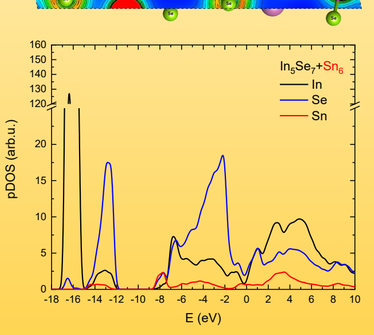
Model 5: Sn → In5



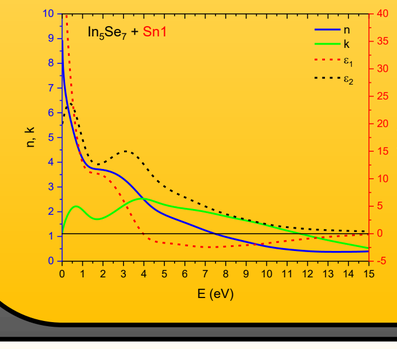


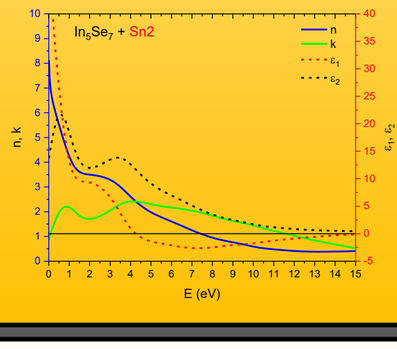
Model 6: Sn → In6

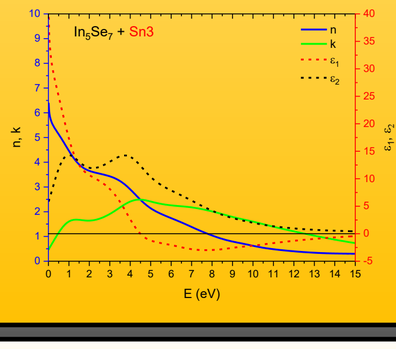


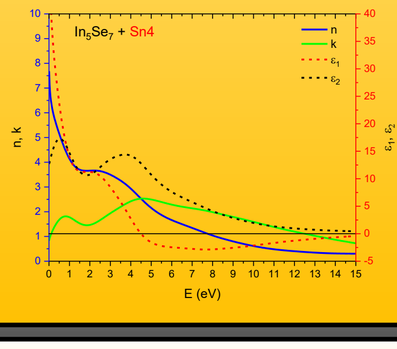


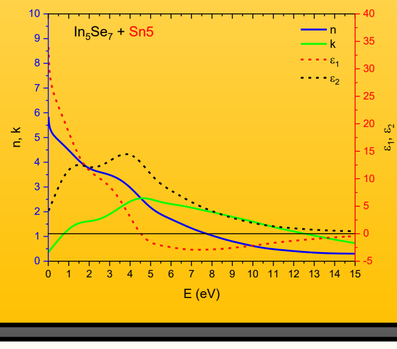
OPTICAL PROPERTIES OF $In_{6-x}Sn_xSe_7$ CRYSTAL.

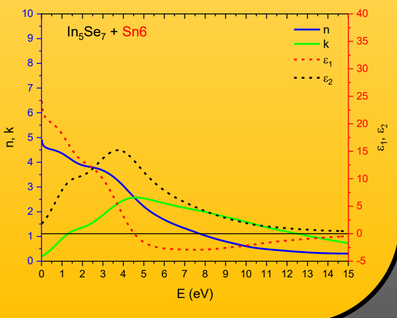












Conclusion: *In the framework of the density functional theory (DFT) using the local approximation for exchange-correlation interaction (LDA) the calculations of the spatial distribution of electron density, band structures, and the partial density of states in the In_6Se_7 and $In_{6-x}Sn_xSe_7$ crystals have been performed. The direct minimal energy gap is localized in Γ–Z direction for the pure crystal. For impurity crystals the tendency to the metallic state takes place.*

Six different models of $In_{6-x}Sn_xSe_7$ have been considered. The structural parameters and total energy values are obtained. Our analysis shows that model 5 is the most likely one. The doping by Sn atoms influences the topology of band structure and redistribution of the total and partial density of states. Additional peaks due the Sn states are observed at E ~ –8 eV and in the energy region E ~ 2–4 eV in energy dependences of the partial density of states. Also, the intensity of the peaks caused by In and Se states is slightly change.

We obtained the dispersive dependences of optical characteristics for both the undoped and doped In_6Se_7 crystal. We calculated the refractive indices and extinction coefficients, real and imaginary parts of the dielectric function, and the absorption coefficient for different polarizations along crystal axes for different models of $In_{6-x}Sn_xSe_7$.