Peculiarities of the electronic and elastic properties of indium selenide in different structural modifications

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Abstract

This report compares three modifications of indium selenide (InSe) – β-InSe, ε-InSe, and γ-InSe – focusing on their electronic, mechanical, dielectric, optical, and light absorption properties.

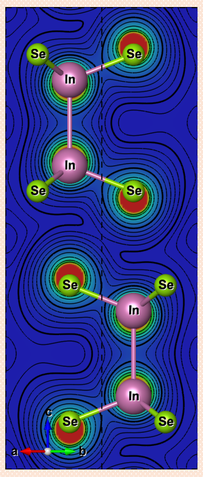
From the first-principles calculations of the band structure follow that the β-InSe and γ-InSe bulk crystals demonstrate the direct band gap (at the Γ and Z points in the Brillouin zone, respectively). At the same time, the ε-InSe polytype shows the indirect band gap. Mulliken charges analysis supports the distinct variations of their redistribution across the polytypes that can be attributed to the specialty of the crystallographic arrangements and provides a detailed understanding of the electronic distribution and bonding characteristics within β-InSe, ε-InSe, and γ-InSe.

The study also compared the optical characteristics of the three InSe modifications. The real and imaginary parts of the dielectric function, refractive indices, and absorption coefficients were calculated across different polarizations along crystal axes.

The mechanical stability conditions for the considered polytypes of indium selenide based on obtained elastic moduli have been analyzed. Other mechanical characteristics (elastic moduli, Young's moduli, Poisson's ratios) were also calculated for the β-InSe, ε-InSe, and γ-InSe bulk crystals. Analysis of these characteristics and the B/G ratio, an indicator of ductility, shows that γ-InSe and β-InSe have closer values than ε-InSe.

Energy band structure of the β-InSe crystal

Lattice parameters are equal: a=b=4.05 A^0, c=16.930 A^0



Relative coordinates of β-InSe atoms

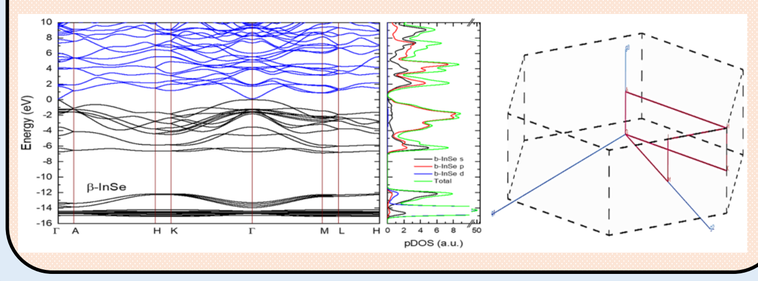
Atom	X	Y	Z
Se	0.33333	0.66667	0.89800
In	0.33333	0.66667	0.15700

D_{6h}^4

The electron configuration:
In: $4d^{10}\ 5s^2\ 5p^1$
Se: $3d^{10}\ 4s^2\ 4p^4$

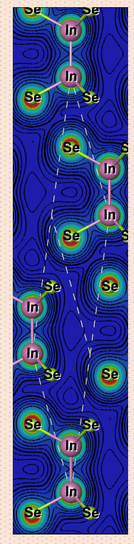
Sequence of band structure calculation:
Γ – A – H – K – Γ – M – L – H

Band structure for β-InSe:



Energy band structure of the γ-InSe crystal

Lattice parameters are equal: a=b=4.002 A^0, c=24.946 A^0



Relative coordinates of γ-InSe atoms

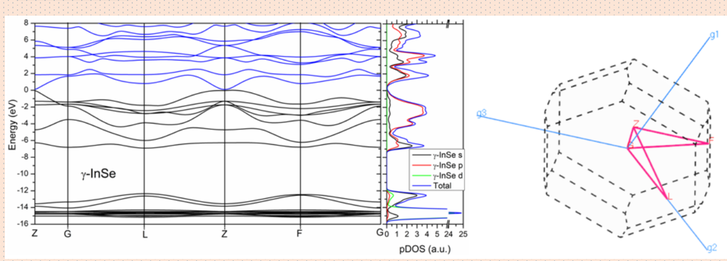
Atom	X	Y	Z
In	0	0	0
In	0	0	0.11102
Se	0	0	0.82834
Se	0	0	0.61666

C_{3v}^5

The electron configuration:
In: $4d^{10}\ 5s^2\ 5p^1$
Se: $3d^{10}\ 4s^2\ 4p^4$

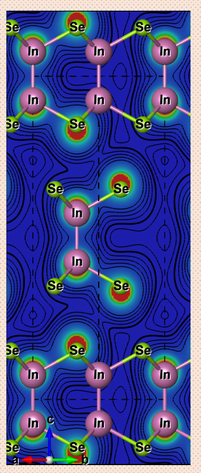
Sequence of band structure calculation:
Z – Γ – L – Z - F – Γ

Band structure for γ-InSe



Energy band structure of the ε-InSe crystal

Lattice parameters are equal: a=b=3.743 A^0, c=15.919 A^0



Relative coordinates of ε-InSe atoms

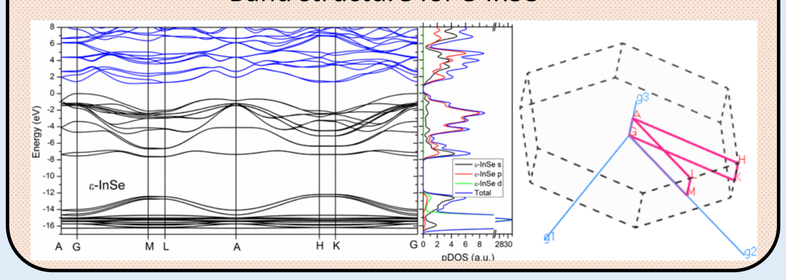
Atom	X	Y	Z
In	0	0	0.75
In	0.6667	0.3333	0.15
Se	0.6667	0.3333	0.575
Se	0.3333	0.6667	0.65

D_{3h}^1

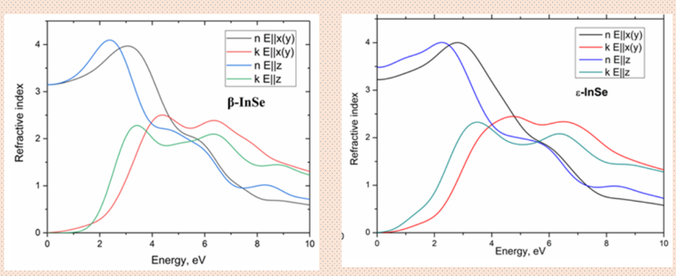
The electron configuration:
In: $4d^{10}\ 5s^2\ 5p^1$
Se: $3d^{10}\ 4s^2\ 4p^4$

Sequence of band structure calculation:
A – Γ – M – L - A - H - K - Γ

Band structure for ε-InSe



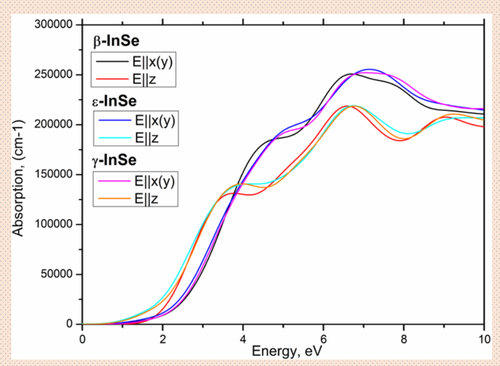
Refractive index vs photon energy for different modifications of InSe

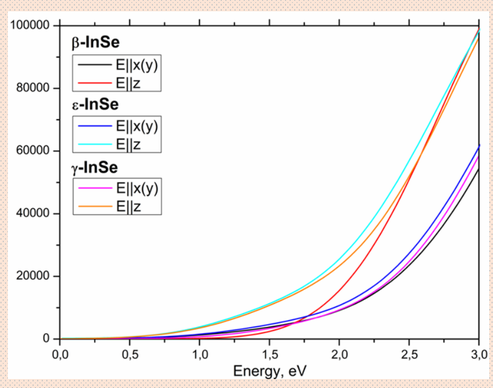


Comparison of Refractive Index for β-InSe, ε-InSe, and γ-InSe

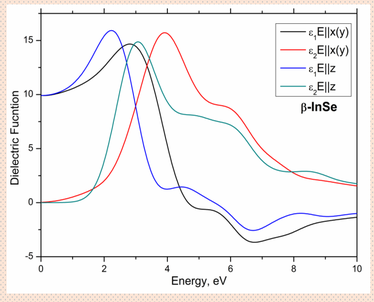
Refractive Index	β-InSe	ε-InSe	γ -InSe
n E ‖ x(y)	3,16	3.22	3.11
n E ‖ z	3,15	3.49	3.43

Absorption coefficient vs photon energy for InSe in different modifications





Comparison of Dielectric Properties of InSe Modifications



Comparison of the Real Part of the Dielectric Function (ε_1) at 0 eV

Real dielectric Function	β-InSe	ε-InSe	γ -InSe
ε_1 E ‖ x(y)	9,94	10.39	9.69
ε_1 E ‖ z	9,91	12.15	11.75

Comparative analysis of mechanical parameters for structural modifications of InSe

Parameters	β -InSe	ε-InSe	γ-InSe
Average sound velocity, (m/s)	1967	2085	2049
Bulk modulus, B (GPa)	37.56	38.54	43.81
Shear modulus G (GPa)	18.96	20.97	20.88
B/G ratio	1.98	1.84	2.10
Generalized anisotropy parameter	0.39	0.14	0.41
C_{11}, GPa	70.59	74.60	79.20
C_{12}, GPa	24.31	25.00	25.45
C_{13}, GPa	21.72	25.07	32.26
C_{14}, GPa			3.69
C_{33}, GPa	62.94	53.98	59.49
C_{44}, GPa	13.11	19.11	17.43
C_{66}, GPa	23.14	24.30	26.87
E_{xy}	0.27	0.23	0.14
$E_{x}z$	0.25	0.36	0.46
E_{yx}	0.27	0.23	0.14
E_{yz}	0.25	0.36	0.46
E_{zx}	0.23	0.25	0.31
E_{zy}	0.23	0.25	0.31
Young's Modulus X	58.61	59.68	59.68
Young's Modulus Y	58.61	59.68	59.68
Young's Modulus Z	53.00	41.49	39.60

Obtained elastic constants Cij for structural modifications of InSe satisfy the general stability criteria [1]:

for hexagonal crystal

$$\begin{cases} C_{11} > |C_{12}|; 2C_{13}^2 < C_{33}(C_{11}+C_{12}) \\ C_{44} > 0;\ C_{66} > 0 \end{cases}$$

for rhombohedral crystal

$$\begin{cases} C_{11} > |C_{12}|;\ C_{44} > 0 \\ C_{13}^2 < \frac{1}{2}C_{33}(C_{11}+C_{12}) \\ C_{14}^2 < \frac{1}{2}C_{44}(C_{11}-C_{12}) = C_{44}C_{66} \end{cases}$$

Born Criterion	β-InSe	ε-InSe	γ-InSe
$\frac{C_{11}}{\lvert C_{12}\rvert}$	2.9	2.98	3.11
$\frac{2C_{13}^2}{C_{33}(C_{11}+C_{12})}$	0.16	0.23	0.33

Thus, all structural poytypes of InSe are in a mechanically stable states!

The ratio C_{11}>C_{33} shows that the stiffness of the indium selenide when a uniaxial stress is applied along the principal axes X are greater than along Z axes.

The ratio C_{66} >C_{44} indicates that the displacements along the Z axis in the X plane are lighter than the displacements along the Y axis in the Z plane.

Values of the **Cauchy pressure** ($C_{12} - C_{44}$) which characterize the ductile nature of InSe polytypes

for **β -InSe** C_{12}- C_{44} **~11.2 GPa**
for **ε-InSe** C_{12}- C_{44} **~5.69 GPa**
for **γ-InSe** C_{12}- C_{44} **~8.02 GPa**

[1] F. Mouhat and F.-X. , Phys.Rev.B., 2014, V.90, p.224104-1-4.

Conclusion

For the first time, the investigation of the electronic, optical, and mechanical properties for the different structural modifications of indium selenide (β -InSe, ε-InSe, γ-InSe) has been carried out by the first-principle calculations. It is shown that the differences between the geometry of the crystalline polytypes of InSe directly influence their properties. Each modification exhibits unique characteristics and provides valuable insights for specific applications of selected materials in optoelectronics, photonics, and new devices so as transistors, photodetectors, and sensors. It is obtained that the β-InSe and γ-InSe bulk crystals are direct band materials, and ε-InSe is indirect band semiconductor.

From the analysis of the energetic dependencies of the optical characteristics follows that significant variations with anisotropy character in dielectric properties, refractive indices, and absorption coefficient spectra are observed for β-InSe, ε-InSe, and γ-InSe modifications.

The calculations of the elastic moduli and other mechanical characteristics for the materials of indium selenide demonstrate that all modifications are characterized by similar values of elastic moduli, average sound velocity, Bulk modulus, shear modulus G, and Young's modulus.

Estimations of the Cauchy pressure (C_{12} – C_{44}), and Pugh's ratio (B/G) ratio determine the ductile nature of considered polytypes, but ε-InSe has more lower values of these parameters . Universal anisotropy index characterizes structural modifications β-InSe, ε-InSe, γ-InSe as anisotropic. However, the degree of anisotropy is the lowest in the ε-InSe crystal.