



Theoretical study of structural features and optical properties of the $\text{Hg}_3\text{S}_2\text{Cl}_2$ polymorphs



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ABSTRACT

The interrelation between structural and optical properties of the $\text{Hg}_3\text{S}_2\text{Cl}_2$ polymorphs have been theoretically investigated. This paper presents the results of calculations of the refractive indices and reflection coefficients for (α) , (β) , (γ) – $\text{Hg}_3\text{S}_2\text{Cl}_2$ crystalline phases using the Harrison bonding-orbital method. The refractive indices in the spectral region far from the absorption edge were determined within the generalized single-oscillator model. The Hartree-Fock values for the valence levels were used for evaluation the energies of filled electronic states in $\text{Hg}_3\text{S}_2\text{Cl}_2$ crystals. By analyzing the polarizability and susceptibility χ it is possible to calculate the refractive index and reflection coefficient; moreover the performed calculations demonstrate a satisfactory agreement with experimental results.

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1. Introduction

$\text{Hg}_3\text{X}_2\text{Y}_2$ (X = S, Se, Te; Y = F, Cl, Br, I) compounds are crystallized in the corderoite structure and described by the $T^5 - I2_13$ space symmetry group. The crystal structure is one of the fundamental characteristics that substantially determines the main crystal properties. The main peculiarities of compounds under investigation are the high value of refractive indices [1–5] and optical activity [6], the ability to form continuous row of solid solutions that allows to variate their physical and chemical properties. They are interest, first of all, by the possibilities of practical application as the perspective nanomaterials for nonlinear optics.

The family of the mercury chalcogenhalogenides compounds presents a large variety of crystalline phases, known as (α) , (β) , (γ) – $\text{Hg}_3\text{S}_2\text{Cl}_2$. In the nature, α - $\text{Hg}_3\text{S}_2\text{Cl}_2$ and β - $\text{Hg}_3\text{S}_2\text{Cl}_2$ meet as corderoite minerals [7–10], γ - $\text{Hg}_3\text{S}_2\text{Cl}_2$ – as kenh suite mineral [11,12]. The crystal structures of α - $\text{Hg}_3\text{S}_2\text{Cl}_2$, $\text{Hg}_3\text{Te}_2\text{Cl}_2$, $\text{Hg}_3\text{Se}_2\text{Cl}_2$, $\text{Hg}_3\text{S}_2\text{F}_2$ and $\text{Hg}_3\text{Te}_2\text{Br}_2$ which isostructural to corderoite mineral α - $\text{Hg}_3\text{S}_2\text{Cl}_2$ are studied in Refs. [8–10]. Later in papers [13–17] the systematic research of pseudo-binary and pseudo-threefold systems of chalcogenides and chalcogenhalogenides of mercury are performed.

It should be noted that the compounds of mercury

sulphurhalides it is possible to prepare by passing carbon sulfur through solution of mercury salt in water or methanol [8]. In paper [6] it is offered a way of receiving mercury sulphurhalides by means of oxidation–reduction reactions. The most widespread is the way of the preparation from binary components in a stoichiometric ratio [6,16] with an insignificant excess of a halogen. Some specific reactions of mercury sulphurhalides preparation are considered in details in paper [1]. All this compounds are resistant crystal substances in air.

In this paper we presented the calculation results of the refractive indices of (α) , (β) , (γ) – $\text{Hg}_3\text{S}_2\text{Cl}_2$ crystalline phases using the Harrison bonding-orbital method. Such studies have not been carried out before for these type crystals.

2. Structure of (α) , (β) , (γ) – $\text{Hg}_3\text{S}_2\text{Cl}_2$ crystalline phases

The synthesis process of $\text{Hg}_3\text{X}_2\text{Y}_2$ cubic chalcogenhalogenides were described as well as their polymorphism was investigated in the papers [6–10]. $\text{Hg}_3\text{X}_2\text{Y}_2$ compounds are crystallized in the corderoite structure of α - $\text{Hg}_3\text{S}_2\text{Cl}_2$ [Fig. 1] and described by the $T^5 - I2_13$ space symmetry group. The structures of $\text{Hg}_3\text{X}_2\text{Y}_2$ compounds can be understood in the terms of the «modular» principle [19]. The halogen anion sublattice is close to the primitive cubic arrangement; this sublattice is body-centered by the X anions and face-centered by the Hg cations.

The main feature of synthesized and natural mercury

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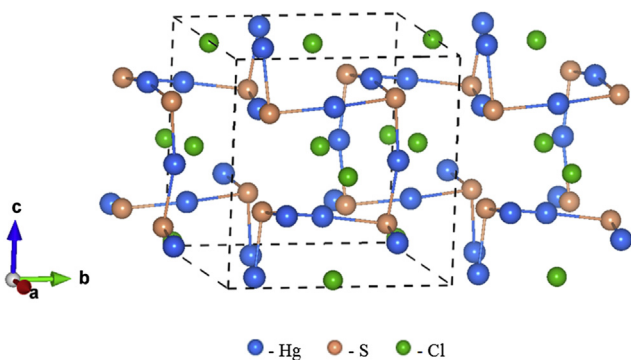


Fig. 1. Crystal structure of α - $\text{Hg}_3\text{S}_2\text{Cl}_2$.

chalcogenhalogenides is formation of numerous polymorphic modifications and existence of isomorphous substitutions in chalcogen and halogen anion sublattices. An example of them are mercury chalcogenhalogenides with the general formula $\text{Hg}_3\text{S}_2\text{Cl}_2$ – corderoite minerals α - $\text{Hg}_3\text{S}_2\text{Cl}_2$, β - $\text{Hg}_3\text{S}_2\text{Cl}_2$ and γ - $\text{Hg}_3\text{S}_2\text{Cl}_2$, which has variable structure depending on number of halogens entered into their structure. α - $\text{Hg}_3\text{S}_2\text{Cl}_2$ and β - $\text{Hg}_3\text{S}_2\text{Cl}_2$ phases are crystalline in the cubic and monoclinic structures and their symmetry are described by $I2_13$ and $\text{Pm}\bar{3}\text{n}$ space groups while in γ - $\text{Hg}_3\text{S}_2\text{Cl}_2$ phase the symmetry is described by Pbmm space group (the lattice parameters are shown in Table 1).

The structure of the α - $\text{Hg}_3\text{S}_2\text{Cl}_2$ type is realized in the cases, when the chalcogen anion size is more than the halogen anion size: S^{2-} (0.182 nm), Se^{2-} (0.193 nm), Te^{2-} (0.211 nm) > Cl^- (0.181 nm); Te^{2-} (0.211 nm) > Br^- (0.196 nm). The main feature of this structural type is existence of $(\text{Hg}_3\text{X}_2)_{2n}^{2+}$ infinite chains from $[\text{XHg}_3]$ trigonal pyramids connected by the mercury atoms which are joint for two pyramids. These chains are unite in three-dimensional framework in which octahedral emptiness the halogen ions are localized.

For β - $\text{Hg}_3\text{S}_2\text{Cl}_2$ the $[\text{SHg}_3]$ pyramids connected between itself in three-dimensional framework. Along threefold axes of a lattice the chains $(-\text{SHg}_3-\text{Cl}-\text{Hg}_3\text{S}-\text{Cl}-\text{SHg}_3-)$ with chlorine atoms in $[\text{ClHg}_{12}]$ structures, for which triangular planes are centered by sulfur atoms, are observed. The structure parameters of β - $\text{Hg}_3\text{S}_2\text{Cl}_2$ are presented in Table 1. Each S^{2-} is covalently bonded to three mercury atoms at distances of 2.36–2.40 Å and the $\text{Hg}-\text{S}-\text{Hg}$ angle varies from 94.8 to 98.0°. The structure contains linear covalently bonded $\text{S}-\text{Hg}-\text{S}$ groups and $[\text{SHg}_3]$ «umbrellas», which are similar to those in $\text{Hg}_3\text{X}_2\text{Y}_2$ mercury chalcogenhalogenides structures [18,19].

γ - $\text{Hg}_3\text{S}_2\text{Cl}_2$ crystalline phase was completely investigated as structure of order-disorder type, which is constructed from different polytypes, including blocks of symmetry of $\text{A}2/\text{m}$ or $\text{F}2/\text{m}$ and caused by existence of the center of symmetry [12,13]. The structure consists of equivalent layers, for which there are two

possible options of placement of rather previous layer. Pairs created by the previous and following layer in any of these two options are geometrically equivalent. The main feature of γ - $\text{Hg}_3\text{S}_2\text{Cl}_2$ structure are $(\text{Hg}_3\text{S}_2)_n^{2+}$ chains, in which loops of chlorine atoms are placed. These chains connect in the two-dimensional layers. Valence angles of $\text{Hg}-\text{S}-\text{Hg}$ in pyramids of γ - $\text{Hg}_3\text{S}_2\text{Cl}_2$ structure are equal 94–96°.

A special feature of all studied modifications of $\text{Hg}_3\text{S}_2\text{Cl}_2$ compounds is a stronger ordering of the anions in comparison with the cations, owing to the strong covalent $\text{Hg}-\text{S}$ bonds. These bonds form various configurations with the same fixed bond-lengths [18]. The less «fixed» halogen anions form regular sublattices in which the isomorphous $\text{Cl} \rightarrow \text{B} \rightarrow \text{I}$ substitutions are plausible over a wide range of compositions. At the same time, the presence of the «hinge-joint» bonds in the covalent $-\text{S}-\text{Hg}-\text{S}-\text{Hg}-\text{S}-$ radical results in the appearance of many polymorphic modifications.

3. Calculation method

It should be noted that the theoretical calculations of refractive indices of α - $\text{Hg}_3\text{S}_2\text{Cl}_2$, β - $\text{Hg}_3\text{S}_2\text{Cl}_2$ and γ - $\text{Hg}_3\text{S}_2\text{Cl}_2$ crystalline phases by using the Harrison bonding-orbital method [20,21] represent the scientific interest. The analysis of covalent and ionic crystals is almost always based on the description of conditions of an electron in a crystal in the form of a linear combination of atom orbitals. Using the Harrison bonding-orbital theory is irreplaceable for calculation of parameters, which describe the structure of energy bands, as well as for understanding the physical nature of this structure. This method supposes in neglect all matrix elements between the bonding and anti-bonding states. It allows to reduce a Hamiltonian matrix to two matrixes, one of which is constructed from valence band states, and another one is constructed from conductive band states. Using of Wannier functions provides to zeroing of matrix elements between the bonding and anti-bonding states in a matrix. As the result one can obtain the diagonal matrix elements, which correspond to Wannier energy levels, as well as matrix elements between the bonding states, responsible for splitting of these levels in bands.

The refractive index, as well as the dielectric susceptibility, depends on the dipole formed by the atoms bonds, and thus an actual task is definition of spatial distribution of a charge. The essence of a bonding-orbital method consists in the description of the localized charges on the basis of interactions between electronic orbitals of the atoms. All the calculations were performed for the optimized structures, moreover the theoretical calculation compares with experimental data.

4. Results and discussion

The refractive index in the spectral region far from the absorption edge was determined within the generalized single-oscillator model. It makes possible to determine the energies of filled electronic states using the Hartree-Fock values for the valence levels in complex crystals [20,21]. The approach becomes particularly useful when it is simplified by including only nearest-neighbor couplings and using universal parameters, which allows direct prediction of all properties.

There are two types of chemical bonds in investigated crystals: the covalent bonds between atoms of mercury and halides, and ionic bonds between atoms of mercury and halogens. Character of a chemical bond depends on a total energy of a crystal and on the sum of energy of all filled energy bands. Many interesting aspects of a chemical bond are related with the defects, distortions of the crystal lattice or impurities. As $\text{Hg}-\text{S}$ are the main chemical bonds, such interpretation of structures reflects physical and chemical properties of the studied crystals.

Table 1
Crystal data of (α), (β), (γ) – $\text{Hg}_3\text{S}_2\text{Cl}_2$ phases.

| Chemical formula | α - $\text{Hg}_3\text{S}_2\text{Cl}_2$ | β - $\text{Hg}_3\text{S}_2\text{Cl}_2$ | γ - $\text{Hg}_3\text{S}_2\text{Cl}_2$ |
|--|---|--|---|
| Space group | $I2_13$ | $\text{Pm}\bar{3}\text{n}$ | Pbmm |
| Formula units per cell | 4 | 32 | 8 |
| <i>a</i> (nm) | 0.8905 | 1.7925 | 0.9328 |
| <i>b</i> (nm) | 0.8905 | 1.7925 | 1.6820 |
| <i>c</i> (nm) | 0.8905 | 1.7925 | 0.9081 |
| β (deg) | 92 | 94.8–98.0 | 94–96 |
| Z | 4 | 6 | 6 |
| Ratio of anions radii ($\text{X}^{2-}/\text{Hal}^-$) | 1.005 | 1.005 | 1.005 |
| Structural type | own | own | own |

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