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Investigation of gyrotropic properties for $Hg_3X_2Cl_2$ (X=Se, Te) crystals

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ABSTRACT

This paper focuses on optical activity investigations of $Hg_3X_2Cl_2$ (X = Se, Te) crystals. To understand better the nature of gyrotropy occurrence, relation to the crystal structure of $Hg_3X_2Cl_2$ (X = Se, Te) crystals and contribution of interband transitions to optical rotation the detailed theoretical analysis is conducted. The gyration tensor of $Hg_3Se_2Cl_2$ crystals is calculated. The theoretical results are confirmed by experimental observation of optical activity. Nanomaterials based on $Hg_3X_2Y_2$ (X = S, Se, Te; Y = F, Cl, Br, I) gyrotropic crystals have tremendous potential in addressing the two major issues faced by our society: the searching for new energy sources and improving healthcare. Obtained data suggest that the phenomenon of optical activity should be taken into account in the studies concerning optical diagnostic methods in medicine.

1. Introduction

$Hg_3X_2Y_2$ (X = S, Se, Te; Y = F, Cl, Br, I) crystals belong to the corderoite family. The synthesis process of $Hg_3X_2Y_2$ cubic chalcogenide-halogenides is described as well as their polymorphism is investigated in the papers [1–5]. They are described by the $T^5 - I2_13$ space symmetry group that confirmed a presence of optical activity and electrooptical effect for these crystals which makes them perspective nanomaterials for nonlinear optics and optoelectronics. Interest in them is caused by such optical properties as photoconductivity, high refractive index and transparency in visible and IR-range [6–10]. It is interesting to note that the main structural feature of $Hg_3X_2Y_2$ mercury chalcogenide-halogenides is the tendency to formation of various polymorphic modifications due to the great conformational capacity of mercury-chalcogen component.

$Hg_3X_2Y_2$ crystals are of high interest for both researchers and engineers due to their chemical and physical properties. They are of great interest for practical applications in electronic and acoustical-optical devices: modulators, elements for dynamic holography, recording and information storage, deflectors and other devices based on the phenomena of light beams interaction.

These crystals have numerous potential applications in different fields, including biomedical science. Studied crystals are expected to contribute in the development of nanobiophysics and personalized medicine for health monitoring and prevention. $Hg_3X_2Y_2$ crystals can be efficiently used for enhancement of the optical processes in biomolecules by nanostructured surfaces on their basis. The optical rotation primary application of biological molecules involves determination of secondary structures of proteins and nucleic acids. Besides that, the optical rotatory dispersion and circular dichroism are widely used in biochemistry.

In the present work, an interpretation of crystal gyrotropy from the band structure calculations for $Hg_3X_2Cl_2$ (X = Se, Te) crystals is discussed in details. The gyration tensor calculations are performed. So, the main aim of this research is theoretical investigation of optical activity for $Hg_3X_2Cl_2$ (X = Se, Te) crystals.

1.1. Structure of $Hg_3X_2Cl_2$ crystals

$Hg_3X_2Cl_2$ (X = Se, Te) gyrotropic crystals are characterized by the structure with spiral chains. The atoms are located on the upward or downward double spirals in the structure [Fig. 1]. There are some groups of atoms in the structure of $Hg_3X_2Y_2$ crystals, which act as an optically active chromophore. $[HgX_2Cl_4]$ octahedra form spiral chains with triple spiral axis in the (111) direction of elementary cube.

Rotation power and its sign are determined by the specific atoms interaction in the materials structure which having desymmetric elements. A characteristic feature of all compounds is the presence of two sets of octahedral spirals with different radii and twisting directions. They are located side by side, oriented in the same direction and consistently alternated. The spiral which is

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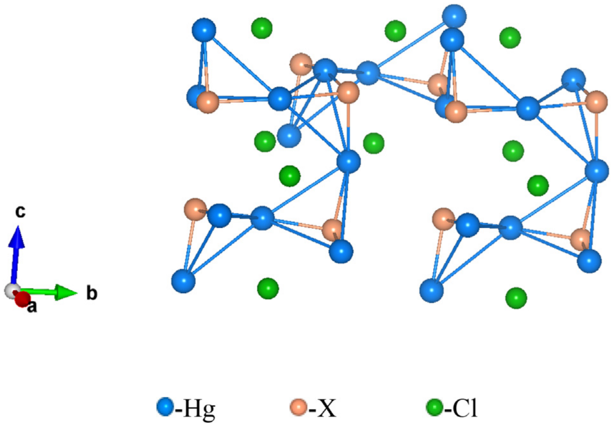

Figure 1. Structure of $Hg_3X_2Cl_2$ crystals.

twisted counterclockwise has a larger radius. Step of both spirals is equally [11]. Structural parameters of $Hg_3X_2Y_2$ crystals are presented in Table 1.

There are three spirals of each type along the (111) direction. Spirals radii are growing in $Hg_3Te_2Cl_2$–$Hg_3Se_2Cl_2$ structures. If spirals in $Hg_3Te_2Cl_2$ crystals are at some distance from each other, but they are overlap each other over 0.17 Å in $Hg_3Se_2Cl_2$ crystals [11]. Spirals interaction of opposite direction is increased and changes of rotation sign is due to this fact. Sign of $Hg_3Te_2Cl_2$ crystal rotation is caused by the strong influence of X^{VI} and Y^{VII} atoms on the symmetry of local crystal field and the polarization medium as a result.

1.2. Calculation method

The gyration tensor must comply with certain requirements that stem from the crystal symmetry. Optical activity of crystals is characterized by the gyration tensor. In general it includes symmetric and antisymmetric parts. According to optical activity theory the nature of light wave polarization in an optically active crystals includes normal component of gyration tensor in $\vec{k}$ vector direction. It is fully determined by symmetry of G part and gyration tensor consider as a symmetrical [11,12]. Pointing surface of gyration tensor for case of studied crystals describes by next matrix:

$$G=\begin{bmatrix} g_{11} & 0 & 0 \\ 0 & g_{22} & 0 \\ 0 & 0 & g_{33} \end{bmatrix} \qquad (1)$$

Pointing surface diameters of gyration tensor are nonzero only in spirals directions. The pointing surface symmetry of gyration tensor for body-centered cubic crystals T^5 $-I2_13$ describes by the $\infty\infty$ symmetry class of optical activity. The eigenvalues of gyration tensor are $g_{11}=g_{22}=g_{33}=g$ and non-diagonal elements are zero for this case. All enantiomorfous substances can exist in two versions: if the light rotates clockwise, then the light exhibits rotation to the right and if the light rotates counterclockwise, then the light exhibits rotation to the left. The most striking demonstration of crystals optical activity is the axial rotation of polarization plane. It is possible in enantiomorfous crystals of cubic system in any direction, and specific rotation are equally for the light of given frequency in all directions. These conclusions are consistent with gyration tensor review of studied crystals, which describes by the T class of symmetry.

Table 1
Structural parameters of $Hg_3X_2Cl_2$ (X = Se, Te) crystals.

Chemical formula	$Hg_3Se_2Cl_2$	$Hg_3Te_2Cl_2$
Space group	$I2_13$	$I2_13$
Structural type	α-$Hg_3S_2Cl_2$	α-$Hg_3S_2Cl_2$
Formula units per cell	4	4
Ratio of anions radii (X^{2-}/Hal^-)	1.07	1.17
a (nm)	0.906	0.933
b (nm)	0.906	0.933
c (nm)	0.906	0.933

According to phenomenological theory of optical activity for homogeneous medium the interrelation between $\vec{D}$ electric induction vector and $\vec{E}$ vector of electric field tension for plane monochromatic waves has next view:

$$\vec{D}=\vec{\varepsilon}\vec{E}+i\left[\vec{g}\vec{k},\vec{E}\right], \qquad (2)$$

$$\vec{B}=\vec{\mu}\vec{H}+i\left[\vec{f}\vec{k},\vec{H}\right], \qquad (3)$$

where $\vec{B}$ - magnetic induction vector, $\vec{H}$ – vector of magnetic field tension.

Dielectric permittivity and gyration tensors are determined the light propagation in crystals in the framework of the macroscopic approach. In case of optical isotropic medium the $\vec{g}$ and $\vec{f}$ tensors reduce to a scalar multipliers [because $g_{11}=g_{22}=g_{33}=g$]. Wave vector and refractive index determine from equations [2,3]:

$$n^2\left(1-\frac{\omega^2}{c^2}gf\right)\pm\frac{\omega}{c}(\mu g+\varepsilon f)-\varepsilon\mu=0, \qquad (4)$$

And the equation solution equils:

$$n_\pm=n_0\pm\frac{1}{2}\frac{\omega}{c}(\mu g-\varepsilon f) \quad n_0=\sqrt{\varepsilon\vec{\mu}} \qquad (5)$$

Expression for rotation of polarization plane per unit path follows from (5):

$$\rho=\frac{\pi}{\lambda}\left(n^- - n^+\right)=\frac{1}{2}\frac{\omega}{c}\Delta n=\frac{1}{2}\frac{\omega^2}{c^2}(\mu g-\varepsilon f), \qquad (6)$$

If magnetic effects not take into account, namely $\mu = 1$and $f = 0$, expression (6) takes the form:

$$\rho=\frac{1}{2}\frac{\omega^2}{c^2}g=\frac{1}{2}\frac{\omega^2}{c^2}g_{33}=\frac{g_{33}\times\pi}{\lambda\times n}, \qquad (7)$$

Expression (7) is valid for crystals of cubic system.

2. Results and discussion

Optical activity effect represents a phenomenon which is one of the most sensitive to the structure features. The rotation of polarization plane caused by specific interatomic interaction in compounds [13]. Rotation sign of light polarization plane is associated with structural features of investigated crystals. Deformation degree of $[HgX_2Cl_4]$ octahedras in $Hg_3X_2Y_2$ structures is an important factor that determines the gyrotropy of $Hg_3X_2Y_2$ crystals. Atoms transition of $[HgX_2Cl_4]$ octahedra in any of excited electronic states makes contributions to gyrotropy caused by C_1 local group of symmetry. Hence, the direct interband transitions in $Hg_3X_2Y_2$ crystals are localized on $[HgX_2Cl_4]$ structural complex. As the concentration of these complexes in the studied crystals are the same, the deformation degree of complex caused by internal crystal field will determine the strength of transition rotation and optical activity value of crystals [11]. The value of the specific rotation is increased with deformation increasing. $Hg_3Te_2Cl_2$ octahedra is the