Bulgarian Chemical Communications, Volume 47, Special Issue B (pp. 80–83) 2015

Impurity absorption in uniaxial gyrotropic crystals of magnesium sulfite hexahydrate

A. Hristova[1]*, T. Dimov[2], I. Iliev[2]

[1] *Faculty of Engineering, 'N. Y. Vaptsarov Naval Academy, 73 Vasil Drumev str., 9026 Varna, Bulgaria*
[2] *Faculty of Science, Konstantin Preslavski University of Shumen, 115 Universitetska str., 9700 Shumen, Bulgaria*

There have been studied the features of absorption of uniaxial gyrotropic crystals Magnesium sulfite hexahydrate, doped with impure Co-ions ($MgSO_3.6H_2O$:Co). The experiment have been conducted using linear polarized light $\vec{E}\|\vec{c}$ and $\vec{E}\perp\vec{c}$ ($\vec{c}$ is the optical axis of the crystal) in the visible spectra range from 400 nm to 650 nm, where is the Co-ion's absorption band. Impurities cause the appearance of additional structures in the spectra of the crystal, which have been described and analyzed on qualitative level. The linear dichroism in the absorption of impurity ions inside the crystal lattice has been analyzed.

Key words: Magnesium sulfite hexahydrate ($MgSO_3.6H_2O$), absorption spectra, linear dichroism

INTRODUCTION

The crystals of Magnesium sulfite hexahydrate ($MgSO_3.6H_2O$) belong to the crystallographic class C_3 (without center of symmetry). The single cell of the crystal contains octahedron $Mg(H_2O)_6^{2+}$ and pyramidal ion SO_3^{2-}. Single crystals magnesium sulfite hexahydrate, pure and doped, are obtained for the first time in the world practice using doctor Kovachev's original method in the Laboratory for Crystal growth at the Faculty of Physics of Sofia University. The growth of monocrystals with relatively big size (40–50 mm) is performed using reaction in an aqueous solution in interaction of alkaline sulfites and soluble Magnesium salts. Samples of such great size (Fig. 1) allo one to explore in details the physics characteristics of the crystal. This exploration is being done at the Laboratory for optical properties of crystals in the Department of Experimental Physics (Faculty of Science of the University of Shumen).

Fig. 1. $MgSO_3.6H_2O$:Co single crystal.

Of particular interest in crystal optics are the cases of introducing impurity atoms. Impurities in the crystal cause changes in the electrical, magnetic and optical properties. The ions Co^{2+} are in the same isomorphous order with Mg^{2+} and replace them in the crystal lattice of magnesium sulfite hexahydrate ($MgSO_3.6H_2O$). Co-ion is located in octahedral surroundings of six water molecules [1]. Crystals Magnesium sulfite hexahydrate doped with cobalt ($MgSO_3.6H_2O$:Co) are extremely suitable for experimental proof of theoretical reasoning. The absorption spectrum of the examined crystal contains absorption band of Co -ion in the visible part of the spectrum (in the interval (450–550 nm).

The anisotropy of the crystal is due to the type of the particles in the crystal lattice, their mutual disposal and the nature of their chemical connection. The linear dichroism is a result of the anisotropy of the crystal and is determined by the difference of the absorption coefficients of the linear polarized light ($\vec{E}\perp\vec{c}$ and $\vec{E}\|\vec{c}$). The research of the dichroism spectrum allows us to find hidden electronic transitions and to determine their polarization.

The presented experiment in the current paper is sequel of the intial researches of the dichroism in $MgSO_3.6H_2O$:Co [2]. An attempt is made to explain the absorption of cobalt ions, embedded in a uniaxial gyrotropic crystal of magnesium sulfite hexahydrate ($MgSO_3.6H_2O$:Co). There is information that these crystals possess nonlinear optical properties [3], which gives the opportunity to apply them in the laser technologies.

* To whom all correspondence should be sent:
antonina05@abv.bg

THEORETICAL CONSIDERATIONS

The incidence of linear polarized light in uniaxial, optically inactive crystal, excite and distribute two linear polarized orthogonal waves. In optically active and absorbing uniaxial crystal the waves are elliptical polarized and are not orthogonal. This orthogonal deviation is usually weak and could be ignored [4]. The coefficients of absorption of uniaxial crystal are determined using the equation of Bouget-Lambert:

$$\alpha_{\perp,\parallel} = \left(\frac{1}{d}\right) \ln\left(\frac{I_0}{I_{\perp,\parallel}}\right) \qquad (1)$$

where I_0 is the intensity of the falling and $I_{\perp,\parallel}$ are the intensities of the passed light trough sample with thickness d. $I_{\perp,\parallel}$ correspond to polarization of the falling light $\vec{E}\perp\vec{c}$ and $\vec{E}\parallel\vec{c}$ ($\vec{E}$ is the electric vector of the falling light).

The optical spectra give the opportunity to collect information about the thin spectral structure and impurity levels in the forbidden band of the crystal. The electronic band structure of the crystal is presented in [5].

EXPERIMENTAL SETUP AND MATERIALS

The sample of $MgSO_3.6H_2O$:Co is flatly parallel plate with thickness $d = 4.6$ mm. It is cut by the crystal in such manner that the light propagates of it in th dirrection $10\bar{1}0$ (Fig. 2). The crystals are suitable for taking down absorption spectra because the walls are parallel and optically smooth. The optical axis of the crystal lies on a plane which is perpendicular to the direction of propagation of light.

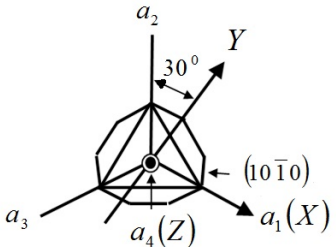


Fig. 2. Crystallographic (a_1, a_2, a_3, a_4) and crystallophysics (X, Y, Z) axes of $MgSO_3.6H_2O$:Co.

The crystal samples are oriented using a system of two polarizers = "polarizer P – crystal CR – analyzer A". The leaking directions, of polarizers P and A, are orthogonal. Monochromator SPM-2 and polarization prisms Glan-Taylor are used. The light beam is given by the monochromator SPM-2, it becomes parallel using a system of lenses L and passes through

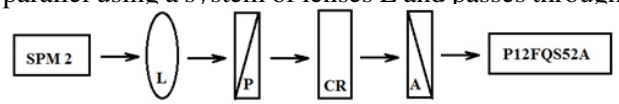


Fig. 3. Experimental scheme.

the polarizer P. Linearly light falls on the crystal sample. During the absorption measurement the analyzer A is removed and the intensity $I(\alpha)$ of the light is measured using a photomultiplier P12FQS52A with dark current 10^{-9}A (Fig. 3).

Absorption spectra (Fig. 4) of pure and doped Magnesium sulfite hexahydrate have been taken in the spectral interval 400–650 nm. In this interval are the absorption band of Co-ion and the forbidden zone of the pure $MgSO_3.6H_2O$.

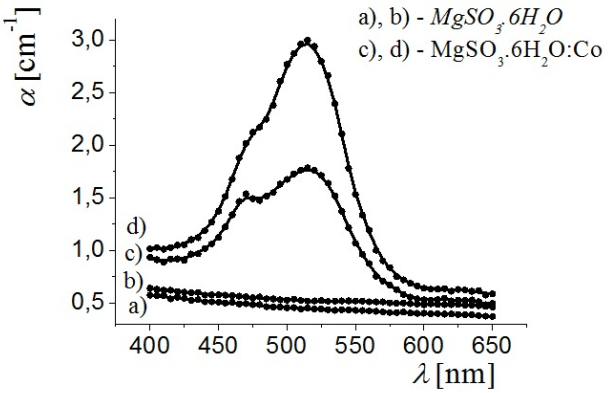


Fig. 4. Absorption spectra of pure and doped Magnesium sulfite hexadydrate Lines a) and c) – for $\vec{E}\parallel\vec{c}$; Lines b) and d) – for $\vec{E}\perp\vec{c}$.

EXPERIMENTAL RESULTS AND DISCUSSIONS

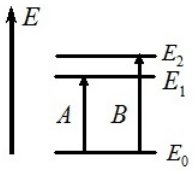
The analyze of the Fig. 4 spectra shows that the presence of Co-impurities in the crystal leads to appearance of absorption bands in the forbidden band of the pure $MgSO_3.6H_2O$. The two peaks in the absorption spectrum of doped with cobalt crystal $MgSO_3.6H_2O$:Co correspond to two energetic transitions A and B (Table 1) of the electrons in the d-zone of Co-ion.

Absorption band of Co-ion for both polarizations consists of two maxima, divided using a computer program (Fig. 5). The two derived Lorentzian curves that correspond to the two maxima, show that:

1. The values of the absorption coefficients $\alpha_{\max}$ are the same for both polarizations ($\vec{E}\parallel\vec{c}$ and $\vec{E}\perp\vec{c}$) in the transition B.

Table 1. Values of the absorption coefficients and schema of the energetic transitions in the *d*-zone of *Co*-ion.

	$\vec{E} \parallel \bar{c}$		$\vec{E} \perp \bar{c}$	
	Transition A	Transition B	Transition A	Transition B
E, [eV]	2.39	2.67	2.40	2.65
α_{max}, [cm^{-1}]	1.62	0.92	2.70	0.97



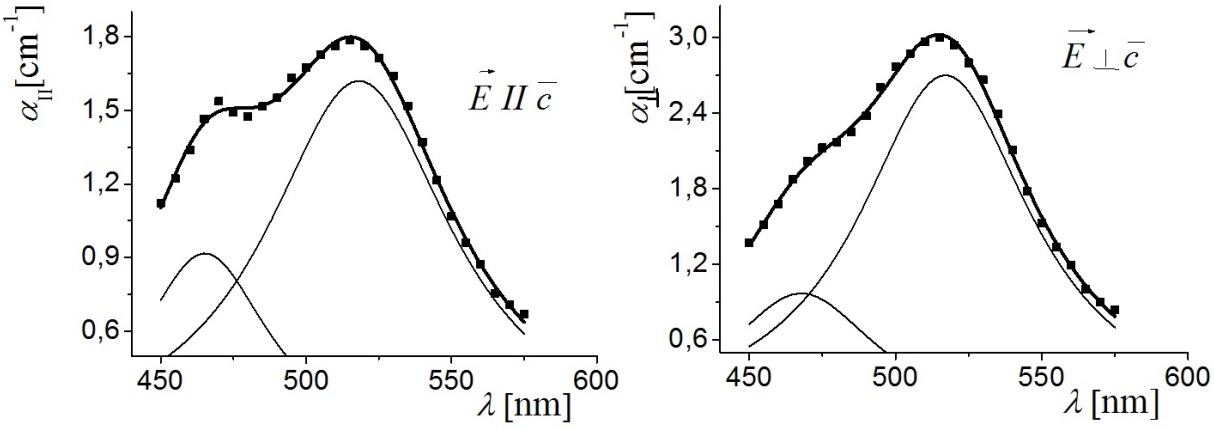


Fig. 5. Components decomposition of the absorption coefficients $\alpha_{\parallel}$ and $\alpha_{\perp}$ in the absorption band of Co-ion.

2. In the transition *A* the absorption coefficients α_{max} are different for the two polarizations (Table 1).

Fig. 6 shows the linear dichroism for the two absorption curves. It has high value in the spectral range, in relation to transition *A*. Moreover, it is not constant and depends on the length of the light wave λ. This allows us to assume that the moment of the transitions *A* and *B* are not parallel [6].

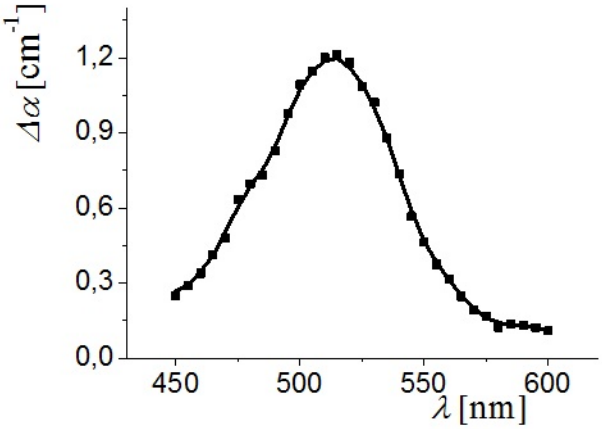


Fig. 6. Spectrum of the linear dichroism $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$ for $MgSO_3.6H_2O$:Co.

CONCLUSION

1. There have been measured the absorption spectra of pure and doped with cobalt Magnesium sulfite hexahydrate in the visible part of the spectrum from 400nm to 650nm with linear polarized light ($\vec{E} \| \bar{c}$ and $\vec{E} \perp \bar{c}$).
2. The computer's calculation show that the absorption band, connected with the doped Co-ion, could be considered with great authenticity as composed of two Lorentzian curves.
3. Due to the anisotropy of the crystal have been established and analyzed linear dichroism in the investigated region of the spectra.
4. The spectral dependency of the linear dichroism shows that the moments of electronic *d*-transitions are not parallel.

Acknowledgments: *The authors are very grateful to Tsanio Kovachev from the Faculty of Physics of Sofia University for the provided samples. Part of the present work has been supported by Grant 08-226/12.03.2014 from Konstantin Preslavsky University, Shumen.*

REFERENCES

[1] Z. Bunzarov, S. M. Saltiel, T. Kovachev, L. Ljutov and D. Russev, *Proc. of SPIE* **3052**, 197–200 (1996).

[2] Zh. Bunzarov, I. Iliev, T. Dimov, P. Petkova, Tz. Kovachev et al., "Circular dichroism in magnesium sulfite hexahydrate doped with cobalt" in *Proc. SPIE 7501, International Conference on Ultrafast and Nonlinear Optics 2009*, 75010X (November 11, 2009).

[3] L. Pavlov, I. Hadjichristov, S. Lazarov, Ts. Kovachev, Zh. Bunzarov, I. Buchvarov, I. Nikolov and M. Iliev, "Nonlinear X(2) and X(3) spectroscopy of Magnesium Sulfite Hexahydrate single crystal" in *Proc. of SPIE* **6604**, 1P1–1P4 (2007).

[4] A. Konstantinova, B. Grechushnikov, B. Bokut and E. Valiachko, *Optical Properties of the Crystals*, Nauka i Tekhnika, Minsk, 1995 (in Russian).

[5] A. P. Litvinchuk, Zh. Bunzarov and M. N. Iliev, *Electronic structure, optical properties, and lattice dynamics of* $MgSO_3.6H_2O$.

[6] Ch. Cantor and P. Schimmel, *Biophysical Chemistry*, Part II, Mir, Moskva, 1984, p. 28.

ПОГЛЪЩАНЕ И ОПТИЧНА АКТИВНОСТ В ЕДНООСНИ ЖИРОТРОПНИ КРИСТАЛИ ОТ МАГНЕЗИЕВ СУЛФИД ХЕКСАХИДРАТ

А. Христова[1], Т. Димов[2], И. Илиев[2]

[1] *Инженерен факултет, Висше военноморско училище "Н.Й. Вапцаров", ул. "Васил Друмев" №73, 9026 Варна, България*
[2] *Факултет по природни науки, Шуменски университет "Епископ Константин Преславски", ул. "Университетска" №115, 9700 Шумен, България*

(Резюме)

Изследвани са особеностите на поглъщане на едноосни жиротропни кристали магнезиев сулфид хексахидрат, дотиран с примесни Co-йони ($MgSO_3.6H_2O$:Co). Експериментът е извършен с линейно поляризирана светлина $\vec{E} \perp \vec{c}$ и $\vec{E} \parallel \vec{c}$ ($\vec{c}$ е оптичната ос на кристала) във видимия диапазон от 400 nm до 650 nm, където е абсорбционната ивица на Co-йон. Примесите предизвикват появата на допълнителни структури в спектъра на кристала, които са описани и анализирани на качествено ниво. Анализиран е линейният дихроизъм в поглъщането на примесните йони в кристалната решетка.