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# Magneto-optical investigation of MgSO<sub>3</sub>·6H<sub>2</sub>O with polarized light

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## ABSTRACT

The crystals of magnesium sulphite hexahydrate (MgSO<sub>3</sub>·6H<sub>2</sub>O) belong to point group C<sub>3</sub> (no center of symmetry). They possess gyrotropy and nonlinear optical properties. The refractive index  $n_o$  and  $n_e$ , the angle of Faraday rotation  $\phi(\lambda)$ , the Verdet constant V( $\lambda$ ), the magneto-optic anomaly factor  $\gamma(\lambda)$  and the density of oscillators N of MgSO<sub>3</sub>·6H<sub>2</sub>O single crystals have been studied in the present work. The investigations were carried out in the spectral range 300 – 800 nm with linear polarized light  $\vec{E} \perp \vec{c}$ ,  $\vec{E} \parallel \vec{c}$  ( $\vec{c}$  is the optical axis of MgSO<sub>3</sub>·6H<sub>2</sub>O) propagated in the direction (10 $\bar{1}$ 0).

### 1. Introduction

For the first time in practice single crystals of MgSO<sub>3</sub>·6H<sub>2</sub>O have been grown only in the Laboratory for Crystal growth at the Faculty of Physics of Sofia University [1]. The crystal homogeneity was improved by automatization and optimization of the temperature control. Investigations were carried out to determine the optimum conditions for the increase of crystal size of MgSO<sub>3</sub>·6H<sub>2</sub>O. A method for hermetic capsulation of the crystals in special crystal holders-containers was developed. This is necessary to lessen the turbidity of the crystals in open atmosphere. The magnesium sulphite hexahydrate has some basic industrial applications: in the woodworking industry in the production of pulp and paper [2]; in the sulfur-cleaning installations for capturing sulfur dioxide separated from the combustion of industrial fuels [3]; in the food industry it serves to stabilize the food products [4]; in the wine industry to stop the alcoholic fermentation process [5]. The aim of this work is to investigate the optical characteristics of MgSO3.6H2O in the external magnetic field.

#### 2. Experimental details

Single-crystals of the compound can be obtained by a method which combines chemical reaction and polythermic growth from low-temperature water-based solutions. The chemical reactions include Mg and  $SO_3$  ions in the presence of  $HSO_3^-$  ions, the latter are brought in order to prevent mass crystallization. They apparently widen the metastable zone and hinder the process by increasing solubility (similarly to calcite). The ions  $HSO_3^-$  can be brought into the system by adding Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> as follows [6]:

 $MgCl_2 + Na_2SO_3 \rightarrow MgSO_3 + NaCl$ 

where, in order to prevent mass crystallization,  $HSO_3^-$  ions are added. They apparently widen the metastable zone and hinder the process by increasing solubility (similarly to calcite). The ions  $HSO_3^-$  can be brought into the system by adding Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> as follows:

$$Na_2S_2O_5 \rightarrow 2 Na^+ + S_2O_5$$

 $S_2O_5^{2-} + H_2O \rightarrow 2 \text{ HSO}_3^{--}$ 

It is best to start the crystallization process at a temperature of 46–53 °C. At higher temperatures MgSO<sub>3</sub>·6H<sub>2</sub>O is prone to turn into MgSO<sub>3</sub>·3H<sub>2</sub>O. Crystal growth lasts for 20–25 days, where the temperature is gradually lowered to ambient by a semi-automatic device. The present volume of the apparatus allows the growth of crystals with a maximum length of the basal edge of the three-cornered pyramid 30–40 mm. The growth method of MgSO<sub>3</sub>·6H<sub>2</sub>O was developed by assoc. prof. Tzanyo Kovachev and it has been patented. The investigations were carried out in the spectral range of 300 – 800 nm with linear polarized light  $\vec{E} \perp \vec{\tau}$ ,  $\vec{E} \parallel \vec{c}$  ( $\vec{\sigma}$  is the optical axis of MgSO<sub>3</sub>·6H<sub>2</sub>O) propagated in the direction (1010). The thickness of the sample is d = 10 mm.

The  $\varphi$ -modulation was realized using a Polarizer-Crystal-Analyzer system with a vibrating polarizer, i.e. (vP-C-A). P and A were placed in a crossed position before starting the P-vibration. The signal passing through the vibrating P-C-A, for small angles between P and A, was a linear function. The rotation angle was measured by the minimum value of the signal. In this way the minimum could be determined by the crossing point of two straight lines [7]. The accuracy of the rotation angle determination using the  $\varphi$ -modulation was about ~ 0.1°. The

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**Fig. 1.** The refractive index for MgSO<sub>3</sub>·6H<sub>2</sub>O in the spectral region 300 – 800 nm  $(\vec{E} \perp \bar{c})$  (perpendicular) and  $\vec{E} \parallel \bar{c}$  (parallel)).



Fig. 2. The imaginary part  $\varepsilon_2$  of dielectric constant in the spectral region 300 – 800 nm.

wave vector k was antiparallel to the vector of the magnetic induction B =  $\mu_0\mu$ H, where  $\mu_0$  is the permeability in vacuum,  $\mu$  is the permeability of the investigated sample and H is the intensity of the magnetic field.

#### 3. Results and discussion

The magneto-optic Faraday effect presents the connection between optics, magnetism and atomic physics. The effect occurs when the rotation of a linearly polarized wave passes through a thickness of a transparent medium. However, rotations of polarized light are not only limited to optically active materials, but also including some optically inactive materials exposed to high magnetic field. In magnetized medium the refractive indices for right- and lefthanded circularly polarized light are different. The precession of the angular momentum of an electron orbiting the nucleus leads to different indices of refraction for right- or left-handed polarized light. This leads to a rotation of plane polarized light.

The values of refractive index  $n_{\perp}$  and  $n_{\parallel}$  are calculated by the Sellmeier equation (Fig. 1):

$$t^{2,\perp} = 1 + \frac{1.1326\lambda^2}{\lambda^2 - 10546},\tag{1}$$

$$n^{2,\parallel} = 1 + \frac{1.2549\lambda^2}{\lambda^2 - 11125} \tag{2}$$

Two reference values for  $n_{\perp}$  and  $n_{\parallel}$  are taken from [8] for  $\lambda_1 = 532nm$ and  $\lambda_2 = 546nm$ . The inequality  $n_{\parallel} > n_{\perp}$  means that the density of crystal structure is bigger in the direction  $\vec{E} \parallel \bar{c}$  (Fig. 1). The dielectric constants  $\varepsilon_{\parallel}$  and  $\varepsilon_{\perp}$  are presented in the Fig. 2. The inequality  $\varepsilon_{\parallel} > \varepsilon_{\perp}$ gives the information that the quantity of the charge is bigger in the direction  $\vec{E} \parallel \bar{c}$  (Fig. 2).

The rotation angle  $\varphi$  and refractive index n are related by the formula [9]:

$$\varphi = \frac{\pi e_2}{\lambda n} d \tag{3}$$

where  $\varepsilon_2 = 2nk$  is the imaginary part of dielectric constant, d is the thickness of the investigated sample,  $\lambda$  is the wavelength and n is the refractive index. The extinction coefficient k can be present as follows:  $k = \alpha \lambda / 4\pi$ , where  $\alpha$  is the absorption coefficient.

The values of  $\varphi$  in the spectral region 300 – 800 nm are calculated by the Eq. (3) (Fig. 3). It shows that values of the magneto-optical rotation are bigger when  $\vec{E} \perp \vec{c}$ .

The rotation angle  $\varphi$  can be expressed also by the formula [10]:

$$\varphi(\lambda) = A/(\lambda^2 - \lambda_0^2), \tag{4}$$

where A is a constant determined from the matrix elements of the interband transitions,  $\lambda$  is the wavelength, and  $\lambda_0$  is the wavelength related to the interband transitions and corresponding to the natural frequency  $\omega_0$  of an effective harmonic oscillator. The reciprocal value of rotation angle can be expressed as a linear function of  $\lambda^2$ .

$$1/\varphi = B\lambda^2 + C \tag{5}$$

B and C in the Eq. (5) are specific crystals constants (Fig. 4). The deviations from the linear dependence are connected with the vibrations of water molecules in the crystal. Therefore, the linear correlation analyses in the investigated spectral region shows  $R^2 = 0.9319$  (perpendicular) and  $R^2 = 0.8165$  (parallel). The values of wavelength which related to the interband transitions are  $\lambda_0^{\perp} = 615nm$  and  $\lambda_0^{\parallel} = 519nm$  respectively.

The relationship between the rotation angle  $\phi$  and the Verdet



Fig. 3. The angle of Faraday rotation for MgSO<sub>3</sub>·6H<sub>2</sub>O in the spectral region 300 – 800 nm  $(\vec{E} \perp \bar{c} \text{ (perpendicular) and } \vec{E} \parallel \bar{c} \text{ (parallel))}.$ 

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