Available online at www.sciencedirect.com
ScienceDirect
Spectrochimica Acta Part A 69 (2008) 629–641
SPECTROCHIMICA ACTA PART A
www.elsevier.com/locate/saa

Polarized IR reflectance spectra of the monoclinic single crystal $K_2Ni(SO_4)_2{\cdot}6H_2O$: Dispersion analysis, dielectric and optical properties

Vladimir Ivanovski [a,b,*], Thomas G. Mayerhöfer [b], Jürgen Popp [b,c], Vladimir M. Petruševski [a]

[a] *Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Sts. Cyril and Methodius University, Arhimedova 5, 1000 Skopje, Macedonia*
[b] *Institut für Physikalische Chemie, Friedrich-Schiller Universität Jena, Lessingstraße 10, D-07743 Jena, Germany*
[c] *Institut für Physikalische Hochtechnologie e.V., Albert-Einstein-Str. 9, D-07745 Jena, Germany*

Received 7 March 2007; received in revised form 23 April 2007; accepted 7 May 2007

Abstract

Polarized IR reflectance spectra of $K_2Ni(SO_4)_2{\cdot}6H_2O$ single crystal (belonging to the group of Tutton salts) were recorded at near-normal incidence. From the dispersion analysis performed on the spectra recorded from the *ac* crystal plane, mode parameters: transversal frequency, oscillator strength, attenuation constant and the orientation of the transition moment were determined. The polarized spectrum along the *b* crystallographic axis was also recorded and a dispersion analysis performed. Comparison between the spectroscopically obtained transition moment directions with those obtained from the structure data for various modes is discussed. All dielectric tensor component values were obtained for the whole mid-IR frequency range. Also, the real and the imaginary parts of the complex indexes of refraction for the waves with wave vector in the direction of the *b* crystallographic axis and in the *ac* plane (when the direction of the electric vector is oriented along the *b* axis) were found as functions of frequency.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Tutton salt; IR reflectance spectroscopy; Polarized radiation; Dispersion analysis; Dielectric properties; Optical constants

1. Introduction

Tutton salts represent a large family of isomorphous compounds with a common formula $M'_2M''(XY_4)_2 \cdot 6H_2O$ where M' stands for univalent ions like: K^+, $NH_4{}^+$, Rb^+, Cs^+; M'' for: Ni^{2+}, Co^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+}, Cr^{2+}. X = S or Se when Y = O, but X = Be when Y = F. The investigations of Tutton salts have been performed using various experimental techniques in obtaining different goals. The copper and chromium Tutton salts have been widely investigated, mostly in connection to the Jahn-Teller effect of the Cu^{2+} and Cr^{2+} atoms in the CuO_6 and CrO_6 distorted octahedrons [1–6]. The tasks, concerning the IR and Raman investigations, were focused on revealing the hydrogen bonding network and on investigations of the vibrational characteristics in different frequency regions. Thus the stretching and deformation vibrations of water molecules, the vibrations of the sulfate ion in different K^+ and $NH_4{}^+$ Tutton salts, as well as the internal vibrations of the water complex octahedron [7–15] were studied. All of the IR investigations performed so far (except for [16]), employ either pressed pellet or mull techniques. Naturally, using these techniques it is not possible to make a clear-cut distinction between the A_u and B_u type mode phonons. Furthermore, due to the closeness of the frequencies of the mode components, the corresponding bands are expected to be overlapped in the studied spectra. Thus, the task of finding all mode components due to the site and unit-cell group splitting is practically impossible in the above way. On the other hand, in Raman experiments, monoclinic single crystals of Tutton salts have been investigated using a number of various scattering geometries. However, because the space group of Tutton salts is centrosymmetric (space group $P2_1/a$ [17]), modes of different symmetries will be triggered by employing IR or Raman spectroscopy. In short, the literature lacks important IR data that can be obtained only with polarized radiation. Nevertheless, even if polarized light is used in the experiment, problems with band overlap may still exist. In order to overcome these, a varying polarization in the *ac* crystal plane is the only possible solution so far. In this way different modes will be activated at different polarization directions. This means that two overlapped bands can be

* Corresponding author at: Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Sts. Cyril and Methodius University, Arhimedova 5, 1000 Skopje, Macedonia. Tel.: +389 2 3249913; fax: +389 2 3226865.
E-mail address: vladimir@iunona.pmf.ukim.edu.mk (V. Ivanovski).

1386-1425/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2007.05.014

distinguished in a complex band profile through changes of their intensity. Again, one should be aware of some other effects, like the appearance of the extra bands in the overlapping regions [18].

It should be mentioned that obtaining the vibrational, dielectric and optical characteristics from the recorded IR spectra of the monoclinic single crystals is not as straightforward as in the case of orthorhombic or crystals with higher symmetries. Namely, the dielectric properties of a monoclinic crystal are described by a second-rank tensor where some of the cross terms are present and the tensor can not be diagonalized for all frequencies (all modes) at the same time, i.e. its eigenvectors are frequency dependent. As already pointed out in Ref. [19], the change of the band profile with the change of the polarization direction (particularly for two or more overlapping bands) can be quite peculiar. Thus the band position, the number of bands and the direction of the transition moments can be hardly evaluated just from the observation of the change of the reflectance band profile with the change of the polarization direction. In order to overcome this novel imposed problem, a dispersion analysis (DA) has to be performed on the recorded polarized spectra (see e.g. Ref. [20] for details).

In this work, polarized IR reflectance spectra of $K_2Ni(SO_4)_2{\cdot}6H_2O$ Tutton salt (K–Ni–S abbreviation will also be used hereafter) in the range from 6000 to 400 cm^{-1} have been recorded with polarization along the *b* crystallographic axis, and using varied polarization in the *ac* crystal plane. Complete DA of the reflectance spectra was performed using equations firstly introduced in the work of Belousov and Pavinich [21] and modified as presented in Ref. [19]. In this way transversal frequencies together with oscillator strengths and attenuation constants have been obtained for each of the investigated mode components. It is also very important to mention that the directions of the transition moments have been determined, allowing comparisons between the spectroscopic data and the crystallographic ones to be carried out. The complete optical and dielectric properties of the K–Ni–S single crystal are obtained for the whole mid-IR region by acquiring the real and the imaginary parts of the complex dielectric tensor components and the complex index of refraction correspondingly.

2. Experimental

A single crystal of K–Ni–S was obtained by a slow evaporation of the equimolar aqueous solution of K_2SO_4 and $NiSO_4{\cdot}7H_2O$. The single crystal was then oriented. The direction of the *b* axes was found employing polarized IR radiation (as explained elsewhere [16]). The directions of the *a* and *c* axes with respect to the morphology of the crystal were found using an optical goniometer. The crystal was then polished so that a surface parallel to the crystallographic *ac* plane was obtained, and another one, parallel to the *b* crystallographic axis. The *X*-polarized spectra (c.f. Fig. 1) were recorded from these planes so that the polarization is either in the *ac* crystallographic plane (when the wave vector is along the *b* crystallographic axis), or parallel to the *b* axis (when the wave vector lies in the *ac* crystallographic plane).

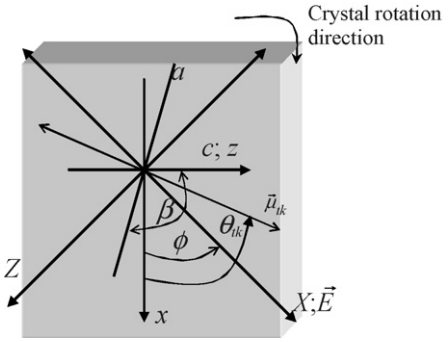

Fig. 1. Graphical representation of the experimental conditions for spectra recorded from the *ac* crystal face. *a* and *c* crystallographic axes (*b* axis is perpendicular to the view), *β*-crystallographic angle; *xyz*—internal right-handed crystal-fixed orthogonal system (*z* along *c* axis, *y* along *b* axis); *XYZ*—external right-handed orthogonal system defined with polarization direction (*X*) and incidence plane (*YZ*). *ϕ*—angle of rotation; θ_{tk}—angle between the *x* axis and the transition moment direction $\vec{\mu}_{tk}$ of the *k*th transversal phonon.

The experimental setting for the spectra recorded from the *ac* crystallographic plane is presented in Fig. 1. Here the connection between the crystallographic axes, the internal coordinate system *xyz*, polarization direction *X* and the direction of rotation is presented for the case when the spectra are recorded from the *ac* crystal plane and under assumption of normal incidence. The radiation is supposed to impinge normal to the *ac* crystal surface from above, with a wave vector along the *b* crystallographic axis.

The polarized IR spectra were recorded on a Bruker 66 IFS spectrometer using Seagull reflectance cell at an angle of 5°, and a fixed angle reflectance accessory of 8° with 2 cm^{-1} spectral resolution. A KRS5 polarizer has been employed. For comparison, polarized spectra were also recorded on a Perkin-Elmer System 2000 FTIR using 16° incidence angle. For obtaining spectra at different polarization angles in the *ac* plane it was the crystal that was rotated around the *b* axis, and not the polarizer. The fitting of the reflectance spectra recorded from the *ac* crystallographic plane was done using four reflectance spectra, recorded at $\phi = 0°$, 45°, 90° and 135° (cf. Fig. 1). For the fitting purposes only the spectra recorded under near-normal incidence (angles of 5° or 8°) were taken into account. This is because the theory that is behind the equations used for the DA treatment assumes normal incidence on the reflectance plane. The fitting was performed using programs developed by the authors, based on the Mathematica program package [22].

3. Theoretical background

The dielectric tensor fixed within the crystal can be represented using the following equation:

$$\tilde{\varepsilon}_{x,z} = \begin{pmatrix} \varepsilon_{xx}^{\infty} & \varepsilon_{xz}^{\infty} \\ \varepsilon_{xz}^{\infty} & \varepsilon_{zz}^{\infty} \end{pmatrix} + \sum_{k=1}^{N} \begin{pmatrix} \cos^2\theta_{tk} & \cos\theta_{tk}\sin\theta_{tk} \\ \cos\theta_{tk}\sin\theta_{tk} & \sin^2\theta_{tk} \end{pmatrix} \times \frac{S_{tk}^2}{\omega_{tk}^2 - \omega^2 - i\omega\gamma_{tk}} \quad (1)$$

Download English Version:

https://daneshyari.com/en/article/1235336

Download Persian Version:

https://daneshyari.com/article/1235336

Daneshyari.com