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# INFRA R ED SPECULAR REFLECTANCE SPECTRA OF PRESSED POLYCRYSTALLINE SAMPLES OF ALUMS – COMPARISON WITH SINGLE CRYSTAL SPECTRA

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Abstract: Vibrational properties of several alums were analyzed by employing polarized specular reflectance IR spectroscopy. A polycrystalline sample in a form of pellet was used for that purpose. Due to the cubic crystal system in which these crystals crystallize, the same equations for the reflectance and dielectric function were employed when conducting the dispersion analysis as those used for single crystals. Very good fit results were obtained for the investigated polycrystalline samples. Apart from this, dispersion analysis on single crystal reflectance spectra was also performed. Vibrational parameters, like the oscillator strength $S$, attenuation constant $\gamma$ and the frequency of the transversal phonons $\omega_t$ obtained from the fit of the polycrystalline samples, were compared with the corresponding data obtained from the dispersion analysis performed on single crystal specimens. The dielectric and optical properties of the alums were obtained and the LO–TO splitting for each of the modeled bands was calculated.

**Key words**: alums; specular reflection spectroscopy; dispersion analysis; polycrystalline pressed pellets; optical and dielectric properties

## INTRODUCTION

Alums are a large group of compounds that have been studied extensively. Alums occur naturally in various minerals. Potassium alum, is found in the minerals kalinite, alunite and leucite. These salts have particular ability to form a vast family of isomorphous compounds with a common formula $M'M'''(RY_4)_2\cdot12H_2O$, where M' stands for a univalent ion: $Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$, $Tl^+$, $NH_4^+$, $CH_3NH_3^+$, $N_2H_5^+$, $NH_3OH^+$ or $C(NH_2)_3^+$; M''' for: $Al^{3+}$, $Ga^{3+}$, $In^{3+}$, $Sc^{3+}$, $Ti^{3+}$, $V^{3+}$, $Cr^{3+}$, $Fe^{3+}$, $Co^{3+}$, $Mo^{3+}$, $Ru^{3+}$, $Rh^{3+}$ and $Ir^{3+}$; $R$ = S or Se when $Y$ is O, and $R$ = Be when $Y$ = F. Alums crystallize in the cubic crystal system adopting the space group $Pa\bar{3}$ and having four formula units ($Z$ = 4) per unit cell. There are three types of alums: $\alpha$, $\beta$ and $\gamma$ (Lipson, 1935). In the structure of the alums, half of the water molecules are coordinated to the M' ion, and the other half are coordinated to the M''' ion, thus making the metal ions octahedrally coordinated. In the $\alpha$ alums the M' octahedron is being distorted while in the $\beta$ alums the octahedron is almost regular (Cromer et al., 1966). The $\gamma$ type alums differ from both $\alpha$ and $\beta$ in terms of the orientation of the O atom from the tetrahedral $SO_4^{2-}$ anion lying along the $C_3$ symmetry axis (Cromer et al., 1967).

The main reason for using the alums in this study is that their characteristics are adequate for this kind of analysis. The alums are relatively soft (as all other crystals obtained from water solution) and they can be easily sintered without applying temperatures higher than ambient. The main disadvantage for the reflection technique is that it becomes destructive (through preparation of a pallet) from nondestructive (by using of a single crystal).

The reflectance spectra of the alum single crystals have already been studied thoroughly and the vibrational characteristics discussed Ivanovski et al., 1999a, 1999b; Petruševski et al., 2001. The optical and dielectric properties have also been obtained in the past (Ivanovski et al., 1999) by using Kramers–Kronig method. However, this method has its drawbacks (Kuzmany, 2009; Palik, 1985) and has to be applied with caution.

The results presented in this work are a good base to extend the analysis for polycrystalline samples prepared in a certain way, enabling to obtain the optical, dielectric and vibrational properties out of polycrystalline samples. It is important to emphasize that this approach is just an approximation without taking into account the rigorous (and thus more complicated) theories of effective medium (Levy and Stroud, 1997). The concept of the effective medium theories lies on the self-consistent procedure according to which particles from one of the components are assumed to have usually spherical or ellipsoidal shape and are embedded in an effective medium (EM). The properties of this so-called effective medium are self-consistent (Bruggeman, 1937). According to the EM approximation, the particles have either spherical or ellipsoidal shape and have a random orientation in the matrix that has effective optical and dielectric properties. EM theories assume that the field around each particle inside the heterogeneous material is constant and both the matrix and the inclusions are treated symmetrically or asymmetrically, according to the approach, and they are both considered as particles (Pecharromán and Iglesias, 1994).

In this work, polarized IR specular reflectance spectra from twelve single crystals and polycrystalline alums have been recorded and analyzed by performing dispersion analysis. The alums used in this work are listed in Table 1.

Table 1

*Corresponding abbreviations used for the twelve synthesized single crystals and polycrystalline samples used in this work, together with the type of the alum*

| Alum | Abbreviation | Type |
|---|---|---|
| $NH_4Al(SO_4)_2 \cdot 12H_2O$ | AAlSD | A |
| $NH_4Cr(SO_4)_2 \cdot 12H_2O$ | ACrSD | A |
| $NH_4Fe(SO_4)_2 \cdot 12H_2O$ | AFeSD | A |
| $CsCr(SeO_4)_2 \cdot 12H_2O$ | CsCrSeD | A |
| $CsFe(SO_4)_2 \cdot 12H_2O$ | CsFeSD | B |
| $CsGa(SeO_4)_2 \cdot 12H_2O$ | CsGaSeD | A |
| $KAl(SO_4)_2 \cdot 12H_2O$ | KAlSD | A |
| $KCr(SO_4)_2 \cdot 12H_2O$ | KCrSD | A |
| $RbAl(SO_4)_2 \cdot 12H_2O$ | RbAlSD | A |
| $RbCr(SO_4)_2 \cdot 12H_2O$ | RbCrSD | A |
| $RbFe(SO_4)_2 \cdot 12H_2O$ | RbFeSD | A |
| $TlAl(SO_4)_2 \cdot 12H_2O$ | TlAlSD | A |

## 2. EXPERIMENTAL

One part of the investigated alums were commercially available, therefore the polycrystalline samples were prepared by recrystallization from their saturated water solutios. The other crystal samples were synthesized via slow evaporation out of water solutions from the corresponding salts ($M'_2SO_4 \cdot nH_2O$ and $M'''_2(SO_4)_3 \cdot mH_2O$) taken in stoichiometric ratio. The possibility for this kind of synthesis lays in the fact that double salts have lower solubility in water than the corresponding salts from which they are obtained. To avoid the possible efflorescence (since many alums are known to be efflorescent), the crystallization was done in refrigerator at temperature of about 5 °C.

The morphology of the grown single crystals resembled truncated octahedra with (111) planes best developed for $\alpha$ and (210) for $\beta$ alums. The crystals were powdered in a vibrating mill for time ranging from 30 s to 45 s. Afterwards, the powder was pressed at a pressure of nearly 1 GPa for 5 minutes to form a pellet. After pressing, the pellets were transparent (Figure 1a) with glossy and highly reflective surface (Figure 1b).

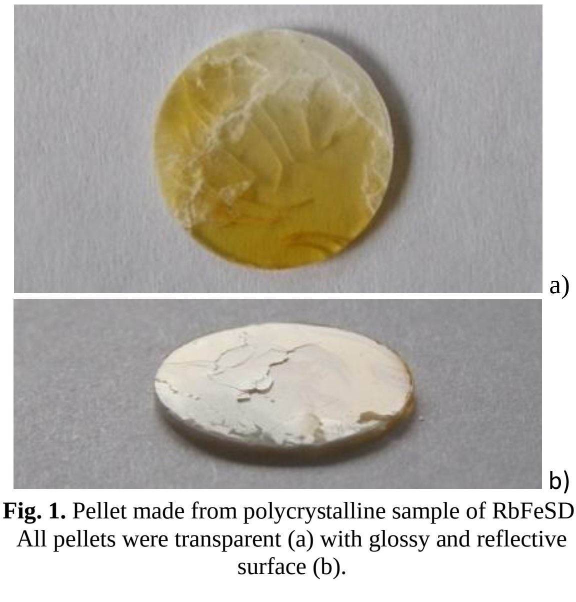

**Fig. 1.** Pellet made from polycrystalline sample of RbFeSD. All pellets were transparent (a) with glossy and reflective surface (b).

The reflectance spectra of single crystal alums were previously recorded using Perkin-Elmer fixed angle specular reflectance accessory with an incidence angle of 6.5° and non-polarized incident radiation in the region from 6000 to 370 cm$^{-1}$. The pellets were used to obtain the IR specular reflectance spectra. These spectra were recorded using Perkin-Elmer fixed angle specular reflectance accessory with an incidence angle of 16° and *s*-polarized radiation. The same technique (specular reflectance IR spectroscopy) was applied in both cases. All spectra were recorded with 4 $\text{cm}^{-1}$ resolution using a Perkin-Elmer System 2000 FTIR spectrometer.

The main modification of the specular reflectance IR spectroscopy technique is about the way the sample is prepared for analysis. Instead of using single crystal, reflectance spectra from polycrystalline samples were recorded by placing the pellet in the Perkin-Elmer specular reflecting accessory under an incidence angle of 16° and recording the spectra using the *s*-polarized radiation in the region from 6000 to 400 $\text{cm}^{-1}$. The *s*-polarization of the light employed in the investigations was obtained by the use of a KRS-5 grid polarizer.

Using incidence angle near normal (Ivanovski, et al., 1999a, 199b) have previously done, enables applying K–K relations for determination the optical and dielectric parameters. The already obtained results for single crystals (as previously described) were used for comparison with the parameters obtained via dispersion analysis. The reason for using the accessory with incidence angle of 16° instead of the accessory with 6.5° (as for the single crystals) when recording the polycrystalline samples, was the lower quality of the spectra obtained with the accessory having 6.5° angle.

## 3. RESULTS AND DISCUSSION

The reflectance spectra of alums (being cubic and crystallizing in $Pa\bar{3}(T_h^6)$ space group, thus optically isotropic), can be easily recorded, since the spectrum does not depend on the crystal surface from which it is obtained. In order to calculate the phase angle $\theta$, K–K relations can be used. These relations are valid for normal incidence angles and they can be used when the incidence is near normal (Nussenzveig, 1972), as in the case of the single crystals (only 6.5° deviation from normal incidence). When the deviation from normal incidence is greater, as in the experiments conduced for polycrystalline samples (16° deviation from normal incidence), the K–K relations can not give satisfactory result. K–K transformations enable direct calculation of the longitudinal optical (LO) and transversal optical (TO) frequencies of phonons without imposing any model for the dielectric function $\varepsilon$.

The advantage of using the dispersion analysis (DA) is that by using a proposed model for the dielectric function together with the reflection function obtained from the reflectance spectra, the optical and vibrational characteristics can be calculated. Also in this case it is not required to take into consideration the range of frequencies.

### 3.1. *Dispersion analysis*

All spectra, those from single crystals as well as those from pressed pellets, were fitted using downhill simplex iteration method. The starting number of oscillators present in the dielectric function [given with Eq. (4)], was gradually increased until a satisfactory fit was achieved (Figure 2).

The “good fit” results were also proven by the standard deviation as a statistical parameter. The number of oscillators that were used in the fitting procedure changes, depending on whether the alum contains metallic or nonmetallic cation or whether it has sulphate or selenate anion. The average value of the standard deviation was $18\cdot10^{-7}$ for the analyzed twelve alums.

The equation for the reflectance function of the *s*-polarized light used for the fitting of the recorded reflectance spectra of polycrystalline samples is dependent on the complex dielectric function $\varepsilon$ and the incidence angle $\alpha$ (Mayerhöfer, 2004):

$$R_s = \left|\frac{\cos\alpha - \sqrt{\varepsilon - \sin^2\alpha}}{\cos\alpha + \sqrt{\varepsilon - \sin^2\alpha}}\right|^2. \tag{1}$$

The non-polarized spectra of a single crystal also depends on the *p*-polarized reflectance $R_\text{p}$,

$$R_p = \left|\frac{\varepsilon\cos\alpha - \sqrt{\varepsilon - sin^2\alpha}}{\varepsilon\cos\alpha + \sqrt{\varepsilon - \sin^2\alpha}}\right|^2, \tag{2}$$

according to the equation (3) (Decius et al., 1979):

$$R = \frac{1}{2}(R_s + R_p). \tag{3}$$

The dielectric function present in Eq. (1) when no interaction between oscillators is present can be represented as a sum of Lorentz oscillators and is given by Eq. (4) (Mayerhöfer, 2004),

$$\varepsilon = \varepsilon_\infty + \sum_{k=1}^{N} \frac{S_k^2}{\omega_{k,\mathrm{t}}^2 - \omega^2 - i\gamma_k\omega} \,. \qquad (4)$$

In these equations, $S_k^2$ is the oscillator strength of the $k$-th oscillator, $\omega_{k,\mathrm{t}}$ – frequency of the $k$-th transversal optical phonon, $\gamma_k$ – damping constant of the $k$-th oscillator and $\varepsilon_\infty$ is the background dielectric constant.

Eqs. (1) and (2) are valid for an optically isotropic case. This is justified (Nussenzveig, 1972; Mayerhöfer, 2004) since the crystallites obtained by grinding are with dimensions of around 1 μm (Decius et al., 1979) and all of them have cubic symmetry.

With the downhill simplex iteration method applied on the reflectance $R_s$ [Eq. (1)] for pellets and reflectance $R$ [Eq. (3)] for single crystals in which [Eq. (4)] is included for $\varepsilon$, best fit values for the parameters $\omega_{k,\mathrm{t}}$, $S_k$ and $\gamma_k$ can be found. The values for these parameters concerning RbFeSD and CsFeSD are given in Table 2. These alums have been chosen as a reprezentatives for $\alpha$ and $\beta$ type alums. The CsFeSD was chosen because it was the only $\beta$ type alum investigated and there was no particular reason why RbFeSD was chosen.

For obtaining the longitudinal optical phonons, the energy loss function as given by the Eq. (5) can be used:

$$\text{Energy loss function} = -Im\left(\frac{1}{\varepsilon}\right). \qquad (5)$$

The frequencies of the LO phonons can then be easily obtained from the band maximum of the function presented in Figure 3 according to Eq. (5).

With the obtained data, the complex dielectric function and the complex refractive index can be determined using Eq. (4) and Eq. (6), therefore applying Eqs. (7) and (8), respectively:

$$\varepsilon = \varepsilon' + i\varepsilon'' \qquad (6)$$

$$\varepsilon' = \varepsilon_\infty + \sum_j^N \frac{S_j^2(\omega_j^2 - \omega^2)}{(\omega_j^2 - \omega^2)^2 + \omega^2\gamma_j^2}, \quad \varepsilon'' = \sum_j^N \frac{S_j^2\omega\gamma_j}{(\omega_j^2 - \omega^2)^2 + \omega^2\gamma_j^2} \qquad (7)$$

$$n^2 = \frac{1}{2}\left(\varepsilon' + \sqrt{(\varepsilon')^2 + (\varepsilon'')^2}\right), \quad k^2 = \frac{1}{2}\left(-\varepsilon' + \sqrt{(\varepsilon')^2 + (\varepsilon'')^2}\right) \qquad (8)$$

The corresponding data obtained for the dielectric and optical parameters are given in the Figures 4. The calculated LO–TO splitting for each of the fitted bands corresponding to modes assigned, mainly according to the ref. Nussenzveig, 1972, is given in Table 3.

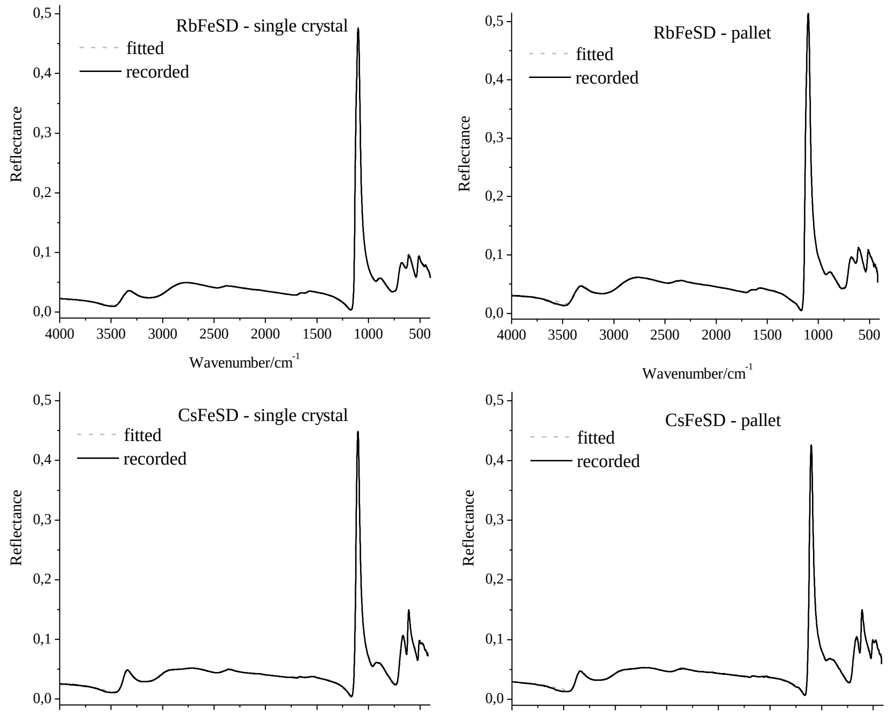

**Fig. 2.** Recorded and fitted spectra for RbFeSD and CsFeSD as representatives for the group of α and β type alums

Table 2

*Results from the fitting procedure by DA given as transversal frequency $\omega_t$, square root oscillator strength $S^2$ and damping constant $\gamma$. All parameters are in units of $cm^{-1}$. The abbreviations s.c. and p. stand for* ***s****ingle* ***c****rystal and* ***p****ellet, respectively*

| Assignment | RbFeSD | | | | | | CsFeSD | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\omega_t$ | | $S$ | | $\gamma$ | | $\omega_t$ | | $S$ | | $\gamma$ | |
| | s.c. | p. | s.c. | p. | s.c. | p. | s.c. | p. | s.c. | p. | s.c. | p. |
| $\nu(\mathrm{OH})^{\mathrm{I}}$ | 3360 | 3357 | 518 | 549 | 136 | 139 | 3361 | 3360 | 542 | 530 | 106 | 111 |
| $\nu(\mathrm{OH})^{\mathrm{III}}$ | 2892 | 2890 | 974 | 999 | 443 | 446 | 2998 | 2999 | 811 | 785 | 355 | 352 |
| $\nu(\mathrm{OH})^{\mathrm{III}}$ | | | | | | | 2761 | 2761 | 556 | 521 | 361 | 313 |
| Combination | 2395 | 2398 | 451 | 368 | 441 | 280 | 2404 | 2402 | 314 | 389 | 178 | 254 |
| Added for fit | | | | | | | 2130 | 2176 | 194 | 75 | 290 | 75 |
| $\delta(\mathrm{HOH})^{\mathrm{I,III}}$ | 1674 | 1673 | 70 | 54 | 394 | 65 | 1670 | 1673 | 60 | 54 | 72 | 54 |
| $\nu_3(\mathrm{SO_4})'$ | 1116 | 1117 | 39 | 48 | 11 | 15 | 1135 | 1146 | 51 | 92 | 20 | 84 |
| $\nu_3(\mathrm{SO_4})$ | 1086 | 1086 | 463 | 506 | 20 | 19 | 1090 | 1090 | 435 | 443 | 19 | 20 |
| $\omega(\mathrm{H_2O})^{\mathrm{III}}$ | 901 | 902 | 184 | 153 | 88 | 70 | 914 | 915 | 121 | 80 | 58 | 54 |
| $\omega(\mathrm{H_2O})^{\mathrm{I}}$ | 689 | 690 | 282 | 295 | 88 | 83 | 686 | 684 | 214 | 229 | 68 | 64 |
| $\nu_4(\mathrm{SO_4})$ | 611 | 611 | 180 | 186 | 53 | 49 | 611 | 610 | 199 | 201 | 29 | 30 |
| $\nu_3(\mathrm{M^{III}O_6})$ | 517 | 518 | 142 | 133 | 37 | 31 | 511 | 509 | 126 | 120 | 32 | 30 |

Prime (') refer to the disordered sulphate ions.

According to the results for the LO–TO splitting (Table 3) and the differences (Table 4), calculated for single crystals and polycrystalline samples, it is obvious that differences are not greater than 3 $cm^{-1}$ for the CsFeSD alum and not greater than 1 $cm^{-1}$ for the RbFeSD alum.

The permittivity function of the pellet is taken to be equal to the one of the pure alum without making assumptions of the air-surrounding medium (Serna, et al, 1987). This approximation can be made as a result of the isotropic nature of the analyzed compounds as well as the fact that the alums can be easily pressed and sintered which minimizes the presence of air (i.e. surrounding medium) in the pallet. The validity of this approximation is proved with the obtained results. In the case of unisotropic crystals the case is much more complicated and the relations for the permittivity function differ. In that case, this assumption does not work and different approach should be taken into consideration (Decius, et al., 1973).

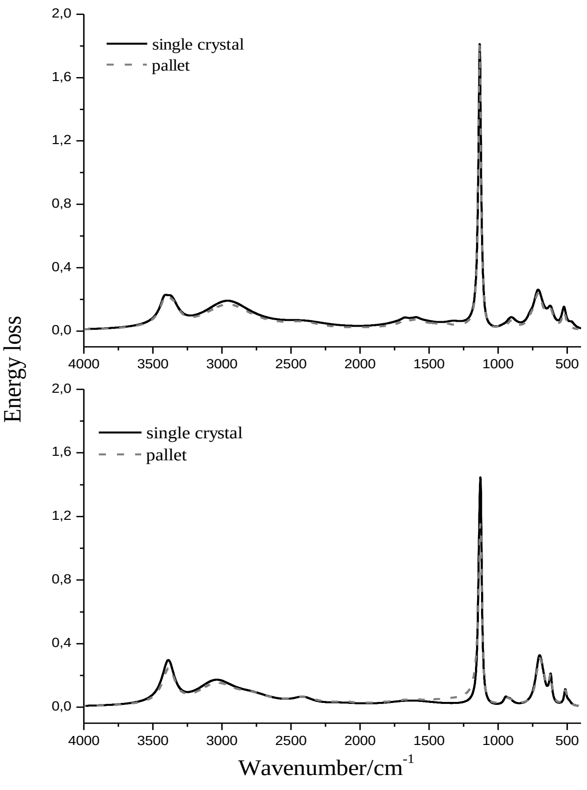

**Fig. 3.** Energy loss function for RbFeSD and CsFeSD used for obtaining the LO frequencies

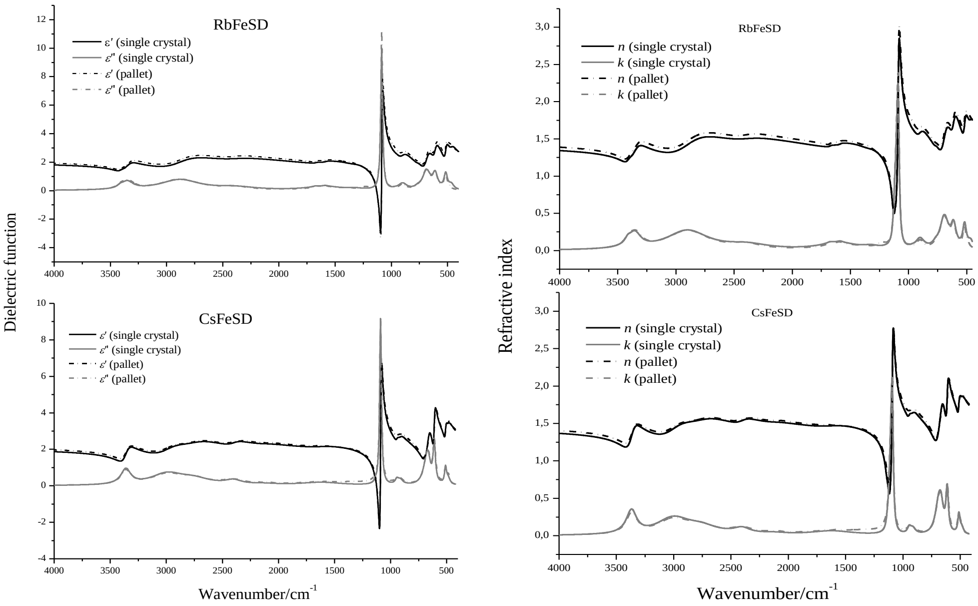

**Fig. 4.** (a) comparison of the real and imaginary part (*ε*' and *ε*'') from the complex dielectric constant and (b) the real and imaginary part (*n* and *k*) of the complex index of refraction from single crystal and pallet in the case of RbFeSD and CsFeSD.

Table 3

*LO–TO splitting in single crystals and pellets for RbFeSD and CsFeSD.*
*The abbreviations s.c. and p. stand for **s**ingle **c**rystal and **p**ellet, respectively.*

| Assignment | | RbFeSD s.c. | | RbFeSD p. | | CsFeSD s.c. | | CsFeSD p. | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\omega$/cm$^{-1}$ | LO–TO | $\omega$/cm$^{-1}$ | LO–TO | $\omega$/cm$^{-1}$ | LO–TO | $\omega$/cm$^{-1}$ | LO–TO |
| $\nu(OH)^{I}$ | $\omega_{t,1}$ | 3360 | 48 | 3357 | 47 | 3361 | 27 | 3360 | 24 |
| | $\omega_{l,1}$ | 3408 | | 3404 | | 3388 | | 3384 | |
| $\nu(OH)^{III}$ | $\omega_{t,2}$ | 2892 | 66 | 2890 | 66 | 2998 | 39 | 2999 | 36 |
| | $\omega_{l,2}$ | 2958 | | 2956 | | 3037 | | 3035 | |
| $\nu(OH)^{III}$ | $\omega_{t,3}$ | | | | | 2761 | 39 | 2761 | 39 |
| | $\omega_{l,3}$ | | | | | 2800 | | 2800 | |
| Combination | $\omega_{t,4}$ | 2395 | 23 | 2398 | 22 | 2404 | 15 | 2402 | 18 |
| | $\omega_{l,4}$ | 2418 | | 2420 | | 2419 | | 2420 | |
| | $\omega_{t,5}$ | | | | | 2130 | 3 | 2176 | 4 |
| | $\omega_{l,5}$ | | | | | 2133 | | 2180 | |
| $\delta(HOH)^{I,III}$ | $\omega_{t,6}$ | 1674 | 2 | 1673 | 3 | 1670 | 2 | 1673 | 2 |
| | $\omega_{l,6}$ | 1676 | | 1676 | | 1688 | | 1675 | |
| $\nu_3(SO_4)'$ | $\omega_{t,7}$ | 1116 | 17 | 1117 | 17 | 1135 | | 1146 | |
| | $\omega_{l,7}$ | 1133 | | 1134 | | | | | |
| $\nu_3(SO_4)$ | $\omega_{t,8}$ | 1086 | | 1086 | | 1090 | 38 | 1090 | 38 |
| | $\omega_{l,8}$ | | | | | 1128 | | 1128 | |
| $\omega(H_2O)^{III}$ | $\omega_{t,9}$ | 901 | 4 | 902 | 3 | 914 | 12 | 915 | 15 |
| | $\omega_{l,9}$ | 905 | | 905 | | 926 | | 930 | |
| $\omega(H_2O)^{I}$ | $\omega_{t,10}$ | 689 | 21 | 690 | 20 | 686 | 14 | 684 | 15 |
| | $\omega_{l,10}$ | 710 | | 710 | | 700 | | 699 | |
| $\nu_4(SO_4)$ | $\omega_{t,11}$ | 611 | 13 | 611 | 12 | 611 | 10 | 610 | 11 |
| | $\omega_{l,11}$ | 624 | | 623 | | 621 | | 621 | |
| $\nu_3(M^{III}O_6)$ | $\omega_{t,12}$ | 517 | 7 | 518 | 6 | 511 | 3 | 509 | 4 |
| | $\omega_{l,12}$ | 524 | | 524 | | 514 | | 513 | |

Prime (') refer to the disordered sulphate ions.

Table 4

*The difference between the LO–TO splitting of the bends obtained from the single crystal (s.c.) and the pallet (p.) for RbFeSD and CsFeSD. All values are given in cm$^{-1}$.*

| Assignment | RbFeSD s.c. | RbFeSD p. | LO–TO difference | CsFeSD s.c. | CsFeSD p. | LO–TO difference |
|---|---|---|---|---|---|---|
| | LO–TO | LO–TO | | LO–TO | LO–TO | |
| $\nu(OH)^{I}$ | 48 | 47 | 1 | 27 | 24 | 3 |
| $\nu(OH)^{III}$ | 66 | 66 | 0 | 39 | 36 | 3 |
| $\nu(OH)^{III}$ | | | | 39 | 39 | 0 |
| Combination | 23 | 22 | 1 | 15 | 18 | 3 |
| | | | | 3 | 4 | 1 |
| $\delta(HOH)^{I,III}$ | 2 | 3 | 1 | 2 | 2 | 0 |
| $\nu_3(SO_4)'$ | 17 | 17 | 0 | | | |
| $\nu_3(SO_4)$ | | | | 38 | 38 | 0 |
| $\omega(H_2O)^{III}$ | 4 | 3 | 1 | 12 | 15 | 3 |
| $\omega(H_2O)^{I}$ | 21 | 20 | 1 | 14 | 15 | 1 |
| $\nu_4(SO_4)$ | 13 | 12 | 1 | 10 | 11 | 1 |
| $\nu_3(M^{III}O_6)$ | 7 | 6 | 1 | 3 | 4 | 1 |

Prime (') refer to the disordered sulphate ions.

### 3.2. *Kramers–Kroning method*

The Kramers–Kroning relations make it possible to obtain the optical, dielectric and vibrational characteristics of the investigated specimen without proposing a model for the dielectric function. However, since integration for the frequency in the range $0 < \omega < \infty$ is required, which is experimentally impossible, it adds some amount of error to the result. Also, an adequate correction concerning the incidence angle should be performed (Bussemer et al., 1992).

If the measurement is done by employing radiation with near normal incidence angle (in our case 6.5°), then the phase angle $\theta$ can be calculated using Kramers–Kroning relations. Knowing the reflection function $R$ together with the phase angle $\theta$ enables the determination of the real $n$ and imaginary part $k$ of the complex index of refraction (Eqs. 9 and 10):

$$n = \frac{1-R}{1+2\sqrt{R}\cos\theta + R} \tag{9}$$

$$k = \frac{2\sqrt{R}\sin\theta}{1+2\sqrt{R}\cos\theta + R} \tag{10}$$

The dielectric parameters $\varepsilon'$ and $\varepsilon''$ can be obtained from the optical parameters $n$ and $k$, applying the relations:

$$\varepsilon' = n^2 - k^2, \qquad \varepsilon'' = 2nk, \tag{11}$$

that are later used for the calculation of the conductivity $\sigma$ and resistivity $\rho$ functions,

$$\sigma = \omega\varepsilon_0\varepsilon''_{\mathrm{r}} \tag{12}$$

$$\rho = \frac{\varepsilon''_{\mathrm{r}}}{\omega\varepsilon_0\left[(\varepsilon'_{\mathrm{r}})^2 + (\varepsilon''_{\mathrm{r}})^2\right]} \tag{13}$$

The maximums of the functions $\sigma$ and $\rho$ represent the frequencies of the TO and LO phonons, respectively (Pecharroman and Iglesias, 1994).

Since the purpose of this work is not to make assignation of the bands in the spectra, the assignment has been taken from previous work and it is in correlation with the obtained results. The aim of the presented results is to show that an excellent agreement between the spectra recorded from single crystals and polycrystalline pressed samples exists (Figure 5). This can be additionally confirmed by the vibrational parameters obtained from the performed DA (Table 1). The greatest difference in the values for the transversal frequencies is not more than 3 cm$^{-1}$ except for the inverted sulphate anions where a difference of 11 cm$^{-1}$ occurs. The greater differences for the values concerning the oscillator strength and the damping constants in the case of RbFeSD alum are due to the bigger reflectance occurring in this case. The differences in the case of CsFeSD alum are smaller since the intensity of the reflection is nearly the same.

Although single crystal and pellet spectra were recorded under different experimental conditions (different specular reflectance accessories having different incidence angle and at the same time using polarized and nonpolarized radiation), it appears that this difference can be neglected, at least for the visual comparison of the spectra (spectra from pellets were also recorded using 6.5° incidence angle accessory, giving unsatisfactory results).

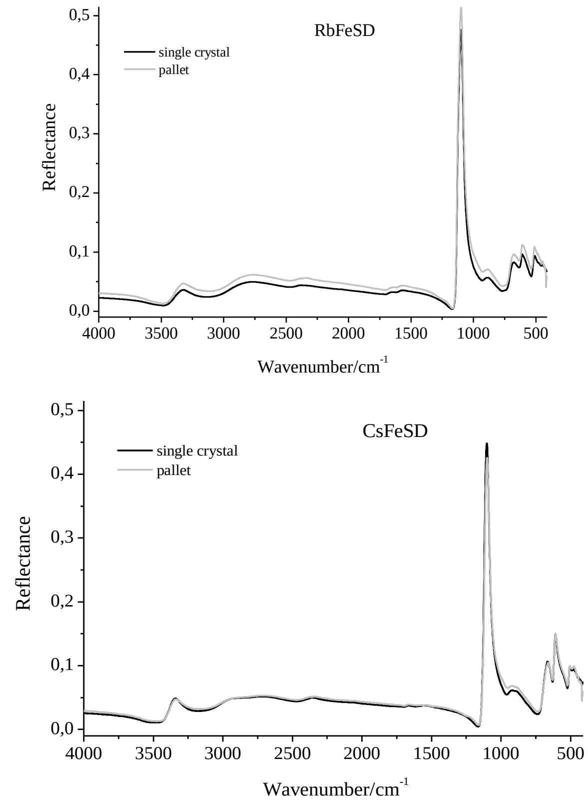

**Fig. 5.** Reflectance spectra recorded from single crystal and polycrystalline sample, depicting an excellent correspondence between the spectra

For one part of the investigated alums, the recorded spectra for the single crystal and for the pellet were almost identical as it can be seen in Figure 5 for the CsFeSD. In the other cases, the spectra representing the pressed pellet were with greater intensity than the spectra from the single crystal (Figure 5, RbFeSD). The intensity difference can be a result of the unequal surfaces between the two samples. Also the different polarization and inci-dence angle can influence the intensity of the reflection. The increasing of the reflection intensity occurs when the incidence angle is greater and when using mixed polarization the reflection intensity is smaller in comparison with the reflection measured when using s-polarization. In most of the cases it was shown that the prepared pressed pellets were more reflective than the single crystals. Beside the intensity differences of the reflectance bands, there is no difference between the band positions arising from the vibrataion of the oscillators. This was proven by the dispersion analysis.

Taking into consideration that LO–TO splitting is connected to the oscillator strength of the mode, it is expected the splitting to be greater for bands with larger reflectance. From the tables it can be noted that this conclusion is in agreement with the values presented therein, so the greatest splitting occurs for $\nu(\mathrm{OH})^{\mathrm{I}}$, $\nu(\mathrm{OH})^{\mathrm{III}}$ and $\nu_3(\mathrm{SO_4})$.

From the results presented in Table 4, one can conclude that there are differences between the values for LO–TO splitting obtained from the K–K analysis and the DA. The dispersion analysis gives results that are much better than those obtained by the K–K relations and this is due to the fact that K–K relations are derived for the frequency region from 0 to $\infty$. Also, the reason for the bad K–K results lies in the fact that the incidence angle of the radiation is not normal to the surface of the single crystal or pellet. On the other hand, as a prove of the weakness of the K–K analysis are the results obtained for the absorption coefficient derived from the K–K. The fact that the absorption coefficient function gets negative values in some regions for certain values of the wavenumber, is clear indication that the analysis itself has certain weakness that can be avoided by using the DA.

## 4. CONCLUSION

According to the reflection studies conducted on polycrystalline pressed samples, it can be concluded that the proposed method for preparing the samples is in agreement with the results obtained from single crystals. Often, the preparation and the growth of single crystals can be time consuming, so the advantage using this method is that less time is required for preparation of the samples for analysis. It should be noted however, that DA itself, using permittivity and reflectance function valid for single crystal, appears to be a rather good approximation for a polycrystalline sample when crystals that crystallize in the cubic crystal system are investigated.

The validity of the proposed method for preparation of the samples is shown via comparison of the recorded reflectance spectra obtained from the single crystals and pellets, the comparison of the dielectric functions and the index of refraction, as well as the energy loss function. One more prove about the relevance of the method is the calculated

LO–TO splitting of the bands. As seen from the results, the differences in the LO–TO splitting are not greater than 3 cm$^{-1}$ in the case of CsFeSD and are no more than 1 cm$^{-1}$ in the case of RbFeSD.

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## Резиме

# ИНФРАЦРВЕНА ОГЛЕДАЛНА РЕФЛЕКСИОНА СПЕКТРОСКОПИЈА НА ПОЛИКРИСТАЛНИ ПРЕСУВАНИ ТАБЛЕТКИ ОД АЛУМИ – СПОРЕДБА СО СПЕКТРИТЕ НА МОНОКРИСТАЛИ –

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**Клучни зборови:** стипси; огледална рефлексиона спектроскопија; дисперзиона анализа; поликристални пресувани таблетки; оптички и диелектрични параметри

Извршена е анализа на вибрационите карактеристики на неколку стипси користејќи огледална инфрацрвена рефлексиона спектроскопија со поларизирано зрачење. За оваа цел се користени поликристални примероци во облик на таблетки. Како резултат на тоа што кристалите на стипсите му припаѓаат на кубичниот кристален систем, може при

спроведување на дисперзионата анализа истите равенства да се користат за рефлектанцата и диелектричната функција, како оние кои се користат во случај на монокристали. Многу добри резултати се добиени за спроведената интерполација кај поликристалните примероци. Покрај тоа беше направена и дисперзиона анализа на рефлексионите спектри од монокристални примероци. Вибрационите параметри – јачината на осцилаторот $S$, константата на придушување $\gamma$ и фреквенцијата на трансверзалните фонони $\omega_t$, добиени од интерполацијата на поликристалните примероци, беа споредени со соодветните податоци добиени од интерполацијата на монокристалните примероци. Определени беа диелектричните и оптичките параметри на стипсите, а потоа беше пресметано и LO–TO расцепување за секоја од моделираните ленти..