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VIBRATIONAL PROPERTIES OF SINGLE CRYSTAL $SnGeS_3$

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The polarized far-infrared spectra and nonpolarized Raman spectra of ternary sulphide $SnGeS_3$ are presented in the range from 20 to 450 cm^{-1}. 22 *IR* and 20 Raman modes of $SnGeS_3$ are observed. Using a Kramers-Kronig analysis, the optical constants and dispersion relation were obtained. A factor group analysis has been performed to identify the symmetries of the observed modes. The discussion on the vibrational properties is given with respect to the crystal structures of $SnGeS_3$ (the chains of GeS_4 tetrahedra which are linked together by sharing corners).

1. Introduction

$SnGeS_3$ is a semiconducting compound, obtained by using thermal annealing of mixtures of SnS and GeS_2 at 500° C, and by sublimation method[1]. This compound belongs to the group of ternary-sulphides - semiconducting materials with layered structure, whose properties still are not well known.

$SnGeS_3$ crystallizes in monoclinic system with unit cell parameters $a = 0.7269$ nm, $b = 1.022$ nm, $c = 0.6873$ nm, $\beta = 105.45°$, $Z = 4$ and a space group $P_{2_1/c}$[2,3]. Fig. 1 shows different projections of the structure as well as the

location of the four symmetry element of the space group $P_{2_1/c}$. The coordination of S and Ge follows strictly the 8-N rule, each Ge atom being tetrahedrally surrounded by four S atoms and each S bonded to two Ge atoms. Approaching the structure from the molecular unit standpoint, one can build up structure of $SnGeS_3$ by GeS_4 tetrahedra, connected via corners, which form $(GeS_2S^{2-}_{2/2})_\infty$ -chains along the $\vec{c}$-axis. The unit cell of $SnGeS_3$ consists of two such chains with two corner-connected GeS_4 tetrahedra. The Sn-atoms connect the tetrahedral chains to bend a layer parallel to the bc plane.

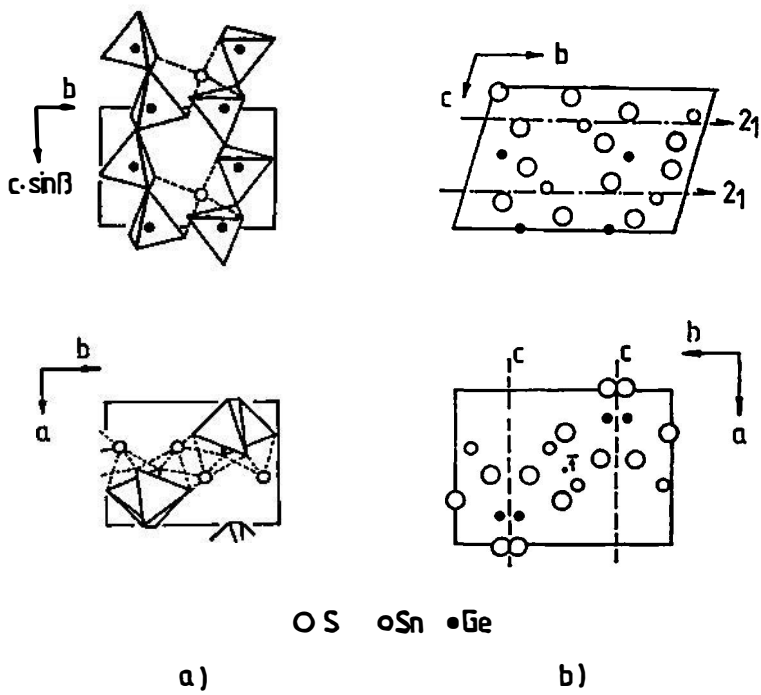

Fig. 1. Crystal structure of $SnGeS_3$ shown with the coordination tetrahedra (left) and crysta symmetry operations of the $P_{2_1/c}$ space (right) in the a) (100) and b) (001) planes.

As this compound was obtained as s single crystal, for the first time, in 1974[2)] it is obvious that its physical properties are not well known. Melting temperature of $SnGeS_3$ is 609°C, energy gap is $E_g = 2.23$ eV and electrical conductivity is in order 10^{-8} Ωm[1)]. Besides that, $SnGeS_3$ attracts attention because it is a photoconductor with the greatest spectral sensitivity at about 500 nm[1)].

The remainder of the paper is organized as follows: After mentioning the experimental details in Section 2, the results of *IR* spectra are presented in Section 3, together with a factor group analysis (*FGA*) and Kramers-Kronig analysis (*KKA*) of the reflectivity data. Finally, in Section 4, we discuss the results with the help of molecular unit structure models.

2. Experimental details

The single crystals of $SnGeS_3$ were grown by the vapour phase transport techniques. Details of the crystal growth process have already been published elsewhere[3]. Freshly cleaved samples were used for the reflectivity measurements with light parallel to the $\vec{b}$ and $\vec{c}$-axis. Near normal incidence polarized far infrared reflectivity measurements were made in the range 20—500 cm^{-1}, using the Bruker *IFS* 114 spectrometer.

Raman spectra at 4.2 K were taken in the back scattering geometry with the Spex or Jarrel-Ash double monochromator employing holographic gratings, a cooled *RCA C* 31034 A02 photomultiplier, and associated photon counting electronics. The 514.5 and 501.7 nm lines of an argon ion laser with the typical power of 100 mW were used as excitation sources.

3. Experimental results and analysis

3.1. Factor group analysis (*FGA*)

As shown in Fig. 1, the unit cell of $SnGeS_3$ consists of four formula units. The crystal symmetry is monoclinic with the space group $P_{2_1/c}$. Since there are 20-atoms per unit cell (with site symmetry C_1) this gives rise to 60 vibrational modes, which decompose into the following irreducible representations in the center of the Brillouin zone:

$$\Gamma = 15\,A_g + 15\,A_u + 15\,B_g + 15\,B_u. \tag{1}$$

The acoustic modes are $1\,A_u + 2\,B_u$, A_g (B_g) - modes are Raman active and A_u (B_u) - modes are infrared active. The Raman tensors corresponding to the Raman-active phonons A_g and B_g are

$$\underset{A_g}{\begin{pmatrix} a & 0 & d \\ 0 & b & 0 \\ d & 0 & c \end{pmatrix}}, \quad \underset{B_g}{\begin{pmatrix} 0 & e & 0 \\ e & 0 & f \\ 0 & f & 0 \end{pmatrix}} \tag{2}$$

where a, b, c, d, e, f are the only non-zero, independent components of the Raman tensors wich are allowed by symmetry for the $q = 0$ optical phonons. The matrices of equation (2) are referred to the present choice of unique axis $c_2^1 \,||\, b$ (second setting - Fig. 1. b); the basis functions for the four irreducible representations of C_{2h} shoud be adjusted to conform with this choice. This adjustment requires that y and z be interchanged in the character tables given in much of the literature[4]. Accordingly the basis functions in the second-setting case are

$$A_g : xx, yy, zz, xz$$
$$B_g : yz, xy$$
$$A_u : T_y$$
$$B_u : T_x, T_z.$$

The matrices of equation (2) are consistent with these basis functions.

In Table 1 is given a *FGA* of the Γ - point lattice modes. From Table 1 it is evident that the total number of Raman active modes is 30 and of infrared active modes is 27, 14 for the case when the electrical field vector $\vec{E}$ is parallel to the *b*--axis ($E \parallel b$) and *13* for the case $E \parallel c$.

Table 1

Irreducible representation	Transformation properties	Selection rules	Zone center modes		
			All	Acoustic	Optic
A_g	α_{xx}, α_{yy}, α_{zz}, α_{xz}	Raman	15	0	15
B_g	α_{xy}, α_{yz}	Raman	15	0	15
A_u	T_y	$IR(E \parallel b)$	15	1	14
B_u	T_x, T_z	$IR(E \parallel a,c)$	15	2	13

Group theoretical analysis of the zone-center lattice vibrations of $SnGeS_3$. T_i and α_{ik} are the vector and tensor components which transform according to the given irreducible representation.

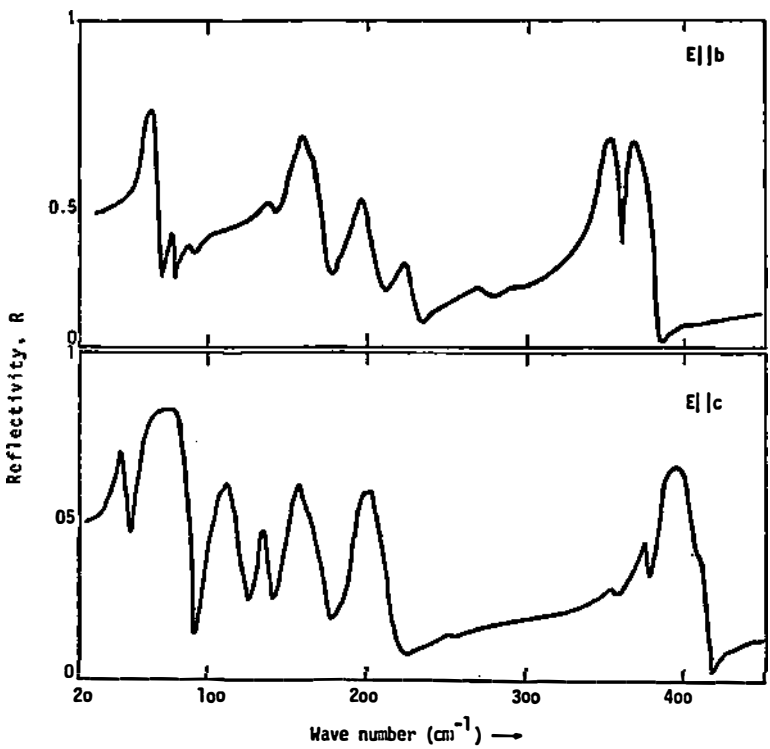

Fig. 2. Room temperature far-infrared reflectivity spectra of $SnGeS_3$.

3. 2. Experimental results

Room temperature reflectivity spectra in the range from 20 to 450 cm^{-1} for $E \parallel b$ and $E \parallel c$ polarization are given in Fig. 2. For the light polarized in the $E \parallel c$ direction there are 11 reststrahlen peaks, and for $E \parallel b$ direction 10 peaks are observed.

The Raman spectra of $SnGeS_3$ at 4.2 K for nonpolarized light is given in Fig. 5, and 20 different lines are observed.

3.3. Kramers-Kronig analysis (*KKA*)

Assuming a constant value of reflectivity below 20 cm^{-1} and above 450 cm^{-1}, a Kramers-Kronig analysis (*KKA*) was performed to obtain the phase angle of the complex reflectivity. The optical constants were then calculated from the Fresnel's formula. The frequencies of the *TO*-modes and their associated *LO*-modes are taken to be the peak positions of Im $(\tilde{\varepsilon})$ and the dielectric-loss function $[-\mathrm{Im}(1/\tilde{\varepsilon})]$, respectively. The values of the *TO* and *LO* frequencies, the static - and high - frequency dielectric constants ε_0 and ε_∞ are shown in Table 2.

Table 2

	ω_{TO}	ω_{LO}	ε_0	ε_∞
$E \parallel b$	62	69	11.5	4
	74	77		
	82	89		
	132	136		
	158	174		
	196	206		
	222	230		
	272	274		
	350	360		
	364	382		
$E \parallel c$	38	49	40	5
	60	89		
	110	122		
	136	138		
	156	172		
	196	216		
	250	252		
	354	356		
	374	378		
	386	406		
	408	414		
$\omega_{min.\ trans.}$	440			

Phonon frequencies (cm^{-1}) and the dielectric constants of $SnGeS_3$ determined from a *KKA* of the reflectivity data.

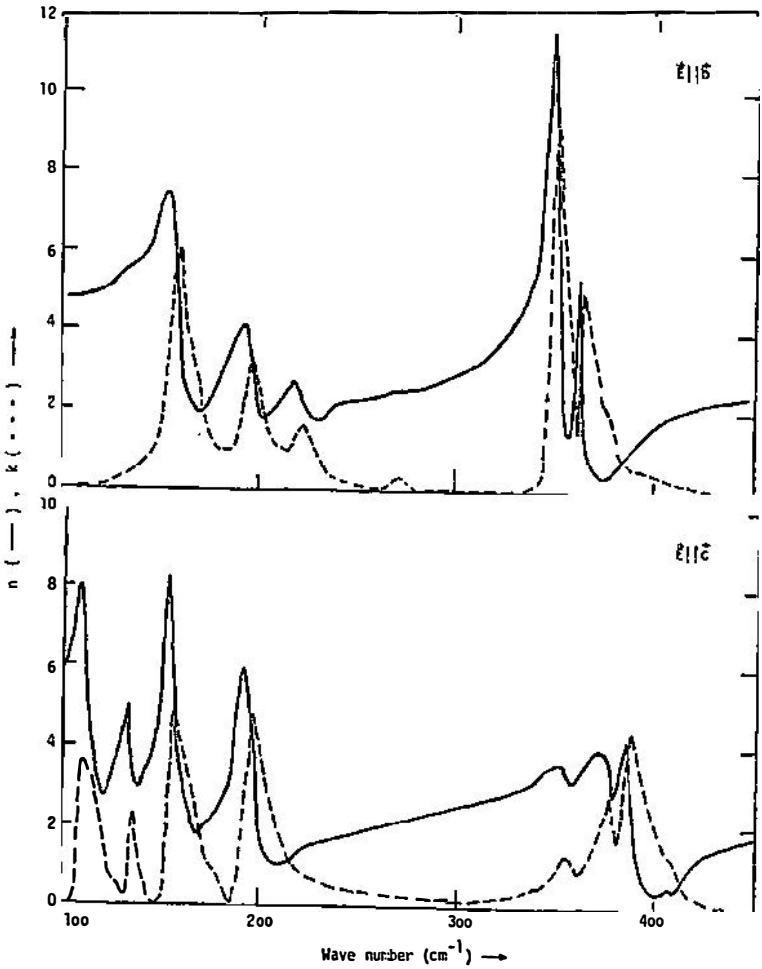

Fig. 3. Real (n) and imaginary (k) part of the complex refractive index of $SnGeS_3$ obtained from the *KKA* of the infrared reflectivity data.

The values of the static dielectric constant ε_0 was obtained using a *LST* relation

$$\varepsilon_0 = \varepsilon_\infty \prod_{j=1}^{N} \frac{\omega_{LOj}^2}{\omega_{TOj}^2}. \tag{3}$$

The values given for ε_∞ are the $\omega = 450\ \mathrm{cm}^{-1}$ values of ε_1.

The change of the real (n) and imaginary (k) part of the index of refraction and also the real (ε_1) and imaginary (ε_2) parts of the complex dielectric function together with the imaginary part of ε^{-1}, i. e. the dielectric loss function for $SnGeS_3$ are given in Figs. 3 and 4, respectively. These diagrams were obtained using a *KKA*.

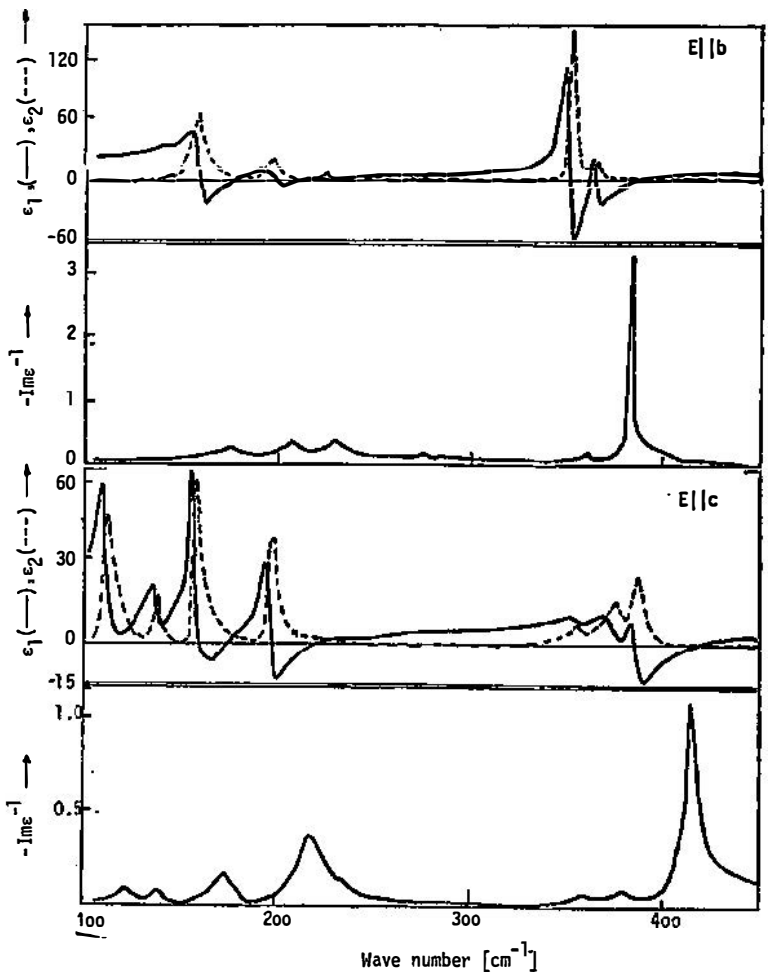

Fig. 4. Real ε_1 and imaginary ε_2 parts of the complex dielectric function and dielectric loss function -Im$(1/\varepsilon)$ obtained from the *KKA* of the infrared reflectivity data of $SnGeS_3$.

4. *Discussion*

According to the *FGA* (Table 1) it was determined that 30 of 60 vibrational modes of $SnGeS_3$ were Raman active, while 27 were infrared active modes. As it can be seeen in Fig. 2, only 21 infrared active modes (10 A_u + 11 B_u) were distinctly observed, which makes 6 less than the theoretically expected number. Unobserved oscillators are probably of quite weak intensity, so they mask by the level of noise (in the wave range from 20 to 200 cm^{-1}), or were masked by some of very strong oscillators (in the wave range above 350 cm^{-1}). In order to obtain more informations on $SnGeS_3$ infrared active phonons, measurements of trans-

mission coefficients were also performed. However, in the transmission spectra, beside the modes already observed, existence of only one more mode at 440 cm^{-1} was stated. Thus, the total number of the infrared active phonons, experimentally observed, is 22. Frequencies of these modes are given in Table 2.

The Raman spectrum of $SnGeS_3$, shown in Fig. 5, was determined using nonpolarized light at 4.2 K. 20 Raman lines were clearly observed, which means 10 less than the theoretically expected number.

Appearance of the vibrational spectra (Fig. 2 and Fig. 5) makes us suppose that the vibration of GeS_4-tetrahedral chains play a dominant role in the vibrational properties of $SnGeS_3$. Namely, in Fig. 2 and Fig. 5, two regions of the spectrum can be distinctly noticed: A spectral region above 350 cm^{-1}, resulting from bond stretching vibrations of the GeS_4 tetrahedra, and a spectrum below 250 cm^{-1}, resulting from bond bending tetrahedral vibrations.

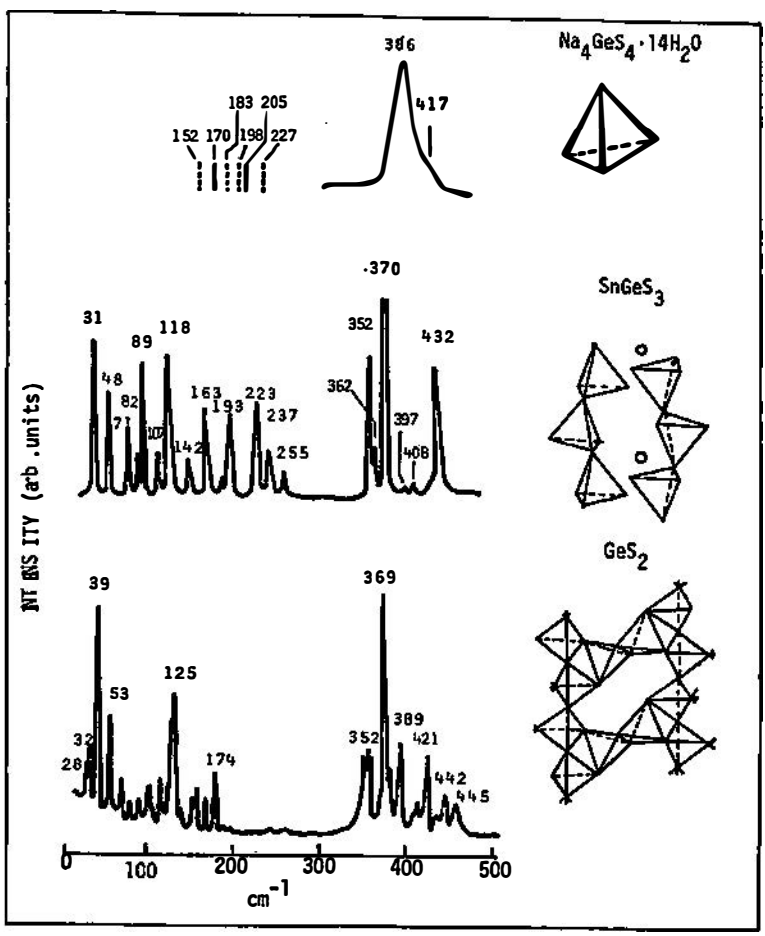

Fig. 5. Raman spectra of GeS_4^{4-} ion[5] (top), $SnGeS_3$ (in middle) and A_g component of the Raman spectra of GeS_2[8] (bottom).

As it can be seen in Fig. 1, a dominant property of $SnGeS_3$ crystal structure are two GeS_4 tetrahedra (in a unit cell) connected via corners, thus forming a Ge_2S_7 molecule. In a unit cell of $SnGeS_3$ there are two such molecules, mutually connected via tin atoms. In order to consider contribution of GeS_4 tetrahedra vibration on the vibrational properties of $SnGeS_3$, we shall briefly consider vibrational properties of an isolated GeS_4 tetrahedra, and vibrational properties of GeS_2, a compound in whose structure the GeS_4 tetrahedral chains are present, like in $SnGeS_3$.

A GeS_4 tetrahedra has T_d point-symmetry, which for distribution of normal modes gives:

$$\Gamma_{GeS_4} = 1A_1(R) + 1E(R) + 2F_2(R, IR). \quad (4)$$

A_1 and E modes are only Raman active, while F_2 modes are active both in Raman infrared spectrum. Modes at the highest frequencies (ν_1 (A_1) and ν_3 (F_2)) result from bond stretching vibrations, while modes at lower frequencies (ν_2 (E) and ν_4 (F_2)) result from bond bending vibration of GeS_4 tetrahedra. Vibrational properties of isolated GeS_4 tetrahedra have been poorly researched in the literature. It was determined with certainty that the ν_1 and and ν_3 modes of GeS_4 tetrahedra are at 386 and 417 cm^{-1}, respectively[5], while localization of bond bending modes of GeS_4 tetrahedra are insufficiently reliable because of disagreement in the literature data[6]. We shall first consider the bond stretching modes of GeS_4 tetrahedra.

In Fig. 5 (quite on the top), Raman spectra of GeS_4^{4-} ion in solution $Na_4GeS_4 \cdot 14\ H_2O$ was given[5]. Nonpolarized Raman spectra of $SnGeS_3$ was given in the middle of Fig. 5, while A_g component of the Raman spectra of GeS_2 was given at the bottom of the same figure. ν_1 and ν_3 modes of an isolated GeS_4 tetrahedra at coupling of tetrahedra via common corner in $SnGeS_3$ or common corner and common edge as in GeS_2, shift toward shorter wave numbers and decompose into several surrounding modes (Fig. 5). Since the modes in $SnGeS_3$, in the bond stretching region, appear at almost the same frequencies as in GeS_2, we come to a conclusion that these modes result exclusively from tetrahedral vibrations of Ge-S atoms, not from vibrations of Sn-Ge and Sn-S atoms. The Raman mode of $SnGeS_3$ of the strongest intensity is at 370 cm^{-1}. That means that the ν_1 (A_1) mode of GeS_4 tetrahedra (386 cm^{-1}) shifts, at coupling of the tetrahedra via a common corner, toward shorter wave numbers for 16 cm^{-1}.

In the spectral region below 250 cm^{-1}, resulting from bond bending vibrations of GeS_4 tetrahedra, there is a great number of the modes. Comparing the Raman spectra of $SnGeS_3$ and GeS_2[8], in this region of the spectra it can be noticed that only the mode at 82 cm^{-1} in $SnGeS_3$ has not an identical mode in the Raman spectra of GeS_2 (Fig. 5)[8], and could be ascribed to bond vibrations of Sn-S atoms, since this mode is present at 85 cm^{-1} also in SnS[7].

An analysis of infrared spectra of $SnGeS_3$ and GeS_2 lead to similar conclusions. Namely, all observed oscillators in $SnGeS_3$ in the wave range of 350 to 450 cm^{-1} were also noticed in GeS_2[8].

Acknowledgments

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VIBRACIONE OSOBINE MONOKRISTALNOG $SnGeS_3$

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U ovom radu prikazani su polarisani daleki infracrveni spektri i nepolarisan Raman spektar ternarnog sulfida $SnGeS_3$ u talasnom opsegu od 20 do 450 cm^{-1}. 22 infracrveno i 20 Raman aktivnih modova je uočeno. Optičke konstante i disperzione relacije su određene korišćenjem Kramers-Kronigove analize. Identifikacija uočenih modova izvršena je u skladu sa prezentiranom *Factor grupa analizom*. Diskusija vibracionih osobina povezana je sa kristalnom strukturom $SnGeS_3$ (lanci GeS_4 tetraedara koji su međusobno povezani preko zajedničkog roglja).