

Raman and infrared spectroscopic study of the defect spinel $\text{In}_{21.333}\text{S}_{32}$

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In this paper, the polycrystal defect spinel $\text{In}_{21.333}\text{S}_{32}$ (JCPDF No: 84-1385; Sys: Cubic; Lattice: Face-centered) was prepared utilizing the melt-slowly cooling method and its unpolarized and polarized Raman spectra together with the infrared transmission one were studied in detail. Based on microstructural features of defect spinel $\text{In}_{21.333}\text{S}_{32}$ (the random distribution of vacancies and indium atoms on tetrahedral sites as well as the strong distortion of octahedral sites) and the polarized spectroscopic characterization, the two strongest peaks at 305 cm^{-1} and 245 cm^{-1} were ascribed to the so-called clustering modes, i.e., the A_{1g} symmetric stretching vibrating mode (ν_1) of tetrahedral InS_4 and octahedral InS_6 respectively. In addition, the ascriptions of the distinct peaks or valleys on Raman and infrared spectra of defect spinel $\text{In}_{21.333}\text{S}_{32}$ were further proposed in this paper.

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1. Introduction

Indium (III)-sulfide, In_2S_3 , is currently intensively studied in view of applications in photovoltaic devices, with the aim to replace CdS for environmental reasons [1]. Thin films of In_2S_3 deposited on photo-conducting metal oxides allow expanding the light-sensitive domain of the latter [2]. Moreover, the optical band gap of the In_2S_3 films themselves can be varied by an appropriate choice of the synthesis conditions [3,4]. In order to establish the exact dependence of the quality of materials upon the growth conditions, Raman scattering is now, as before, a very valuable “in situ” tool of assessment because of its high sensitivity [5, 6]. On the one hand, it can give a direct indication of the crystalline quality of the material. Moreover, it is one of the few techniques capable to provide information concerning the local ordering in the crystal lattice, and therefore, it may be extremely useful for investigating crystalline disorder. On the other hand, the Raman spectra also contain valuable information concerning secondary phases, lattice strains and chemical composition. Therefore, Raman spectroscopic study of crystal In_2S_3 has its practical importance.

As to the defect spinel crystalline In_2S_3 , the cation distribution can be written as $(\text{In}_{0.67}\square_{0.33})[\text{In}_2]\text{S}_4$ (round brackets: tetrahedral or A-site, square brackets: octahedral or B-site, \square : unoccupied site) with ordered (β -type) or random (α -type) distribution of cations and vacancies on tetrahedral sites [7,8]. The octahedral sites in the inverse spinel lattice are strongly distorted by the displacement of the anions in [111] direction away from their crystallographic $32e$ position in space group $\text{Fd}\bar{3}m$, while

the T_d symmetry of the tetrahedral sites is rather well conserved.

Based on group theoretical treatment and actual Raman scattering study of normal spinels such as MCr_2S_4 ($M = \text{Mn, Fe, Co, Cd}$ and etc.), the ascription of vibrational mode within the Raman scattering and IR transmitting spectra has been clearly done and well understood [9-11]. However, when it comes to the inverse or partial inverse indium spinels, the IR and Raman spectra are more complicated and not fully understood so far due to the facts that the bands are broadened and partly more than five Raman bands (predicted by group theory) were observed originated from the lack of full translation symmetry because of the random distribution of the cations [10, 11].

In this work, we investigated the characterizations and their ascription of vibrational spectra including Raman scattering and Infrared transmission of the prepared polycrystal defect spinel $\text{In}_{21.333}\text{S}_{32}$.

2. Experiment

Polycrystal defect spinel $\text{In}_{21.333}\text{S}_{32}$ was synthesized by direct reaction of a stoichiometric mixture of the elements in an evacuated silica tube at $1100\text{ }^\circ\text{C}$ during 10 h, followed by cooling to room temperature through directly shutting down the power. The reaction led to a reddish rod that the powder X-ray diffraction proved to be the defect spinel phase polycrystalline $\text{In}_{21.333}\text{S}_{32}$ (JCPDF No:84-1385; Sys: Cubic; Lattice: Face-centered; S.G.: $\text{Fd}\bar{3}m(227)$) (see Fig. 1). Raman scattering (RS) and Fourier-transform infrared (FTIR) transmission spectra

were recorded at room temperature. The Raman measurements were performed in a 180° backscattering geometry using an inVia Laser Confocal Raman Microscope made by Renishaw PLC. The 632.8 nm line of a He-Ne laser was used and the spectral resolution was of the order of 1 cm^{-1} . For the avoidance of local laser damage that could easily occur under the microscope, a laser power not exceeding an approximate level of 2 mW was used. In addition, two polarization configurations were used to record the Raman spectra; one was designed as HH, the other as HV. And I_{HH} is the Raman intensity measured with both the incident radiation and scattered radiation polarized in the scattering plane, whereas, I_{HV} is the Raman intensity measured with the incident radiation polarized in the scattering plane and the scattered radiation analyzed perpendicular to the scattering plane.

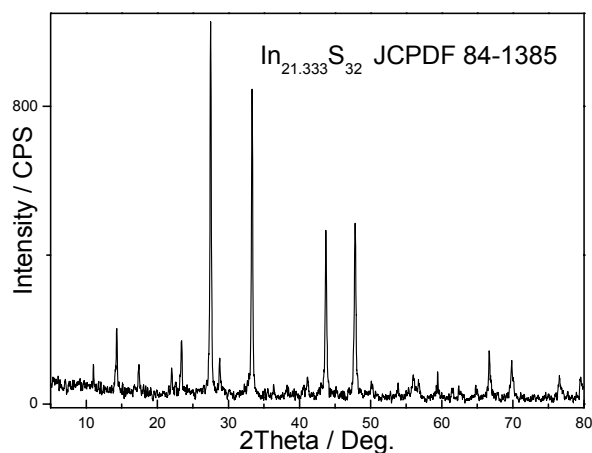


Fig. 1. Power X-ray diffraction pattern of the prepared $\text{In}_{21.333}\text{S}_{32}$.

FTIR transmission spectra were recorded using a Nicolet Nexus Fourier Transform Infrared Spectrometer under the N_2 gas atmosphere. Each FTIR spectrum is the average of 64 scans at a spectral resolution of 4 cm^{-1} . The samples were ground, then dispersed in CsI, and pressed at 5 kPa into pellets to obtain far-infrared spectra in the range of $150\text{--}600 \text{ cm}^{-1}$.

3. Results and discussion

The whole cubic cell of the spinel structure contains 56 atoms and is largely redundant when determining the number of vibrations of the lattice according to group theoretical treatment since only two octants of the cell, which lie along the main body diagonal, are really different. Considering the reduced cell, which contains only 14 atoms and is equivalent to the smallest Bravais cell, the total number of vibration modes at the centre of the Brillouin zone, described by the irreducible representation of the O_h point group [12], is

$$\Gamma = A_{1g} + E_g + 3F_{2g} + 5F_{1u} + 2A_{2u} + 2E_u + F_{1g} + 2F_{2u}.$$

Five of these modes ($A_{1g} + E_g + 3F_{2g}$) are Raman active, four F_{1u} modes are infrared active, and the remaining F_{1u} mode is an acoustic phonon. All other modes are silent. The statement reported in some literatures, namely that some of the vibrational bands are due to the octahedral unit of the structure and other to the tetrahedral one is wrong [5]. As revealed from lattice dynamical calculations all atoms and all bonds of the spinel structure are involved in each of the Raman or IR allowed phonon modes.

However, when it comes to inverse spinels with an inverse cation distribution, the Raman and IR spectra are more complicated and not fully understood so far. For example, the bands are broadened and more than five Raman scattering peaks (as predicted by group theory) are observed for CdIn_2S_4 [11]. These findings probably arise from the lack of full translation symmetry in inverse spinels due to the random distribution of the indium on the octahedral and tetrahedral sites. However, as an alternative explanation it must be born in mind that the additional bands are defect-induced modes also due to the breakdown of the translation symmetry.

In Fig. 2, the unpolarized Raman spectrum of the prepared polycrystalline $\text{In}_{21.333}\text{S}_{32}$ sample is represented together with the IR (CsI plate) transmittance one. To further verify the assignment of modes observed in the Raman and IR spectra, the polarized measurement was conducted (see Fig. 3).

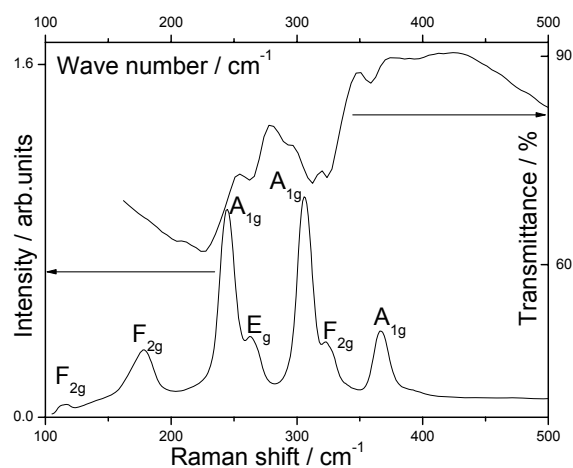


Fig. 2. Raman and FTIR transmission (CsI plate) spectra of the $\text{In}_{21.333}\text{S}_{32}$ polycrystal sample.

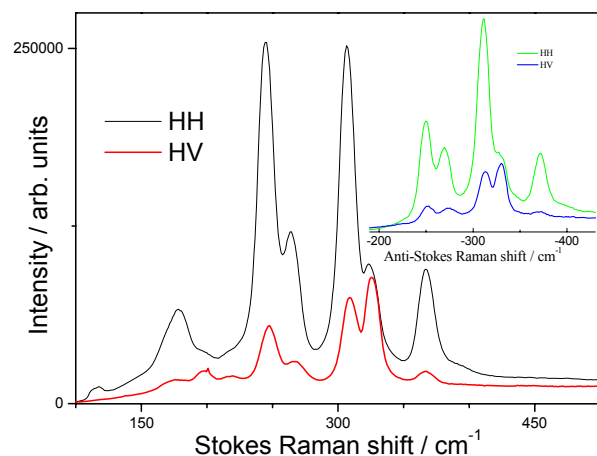


Fig. 3. Stokes and anti-Stokes polarized Raman spectra of the polycrystal $\text{In}_{21.333}\text{S}_{32}$.

According to the research of Lutz et al [11-14], the high-energy polarized Raman peak at 366 cm^{-1} can be clearly ascribed to the A_{1g} mode, the peak at 262 cm^{-1} to the E_g mode, and the peaks at $117, 179, 322\text{ cm}^{-1}$ to the F_{2g} mode. In Raman spectra of various inverse spinel-type indium sulfides MIn_2S_4 (such as $\text{M} = \text{Cd}, \text{Mn}, \text{Co}$), the various F_{2g} modes obviously display two-mode behavior, whereas the A_{1g} and E_g modes show one-mode behavior. The two-mode behavior is caused by replacing the bivalent metal atoms on the tetrahedral site by trivalent ones and vacancies, while the wavenumbers of the A_{1g} and E_g Raman bands are not influenced by the amount of bivalent metal atoms present because of the fact that motions of metal ions are not involved in the vibrational modes of the Raman-allowed bands of spinels apart from those of tetrahedrally coordinated metal ions in the case of F_{2g} modes. Earlier, according to Raman single-crystal experiments [11], this E_g mode was ascribed to the Raman bands of MIn_2S_4 ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{and Cd}$) in the range of $175\text{--}185\text{ cm}^{-1}$. Later, however, based on lattice dynamical calculations and the expected one-mode behavior [13], the phonon modes of species E_g are reassigned to be located at a place close to 250 cm^{-1} , suggesting that the previously reported results of the single-crystal studies are caused by resonance Raman phenomena.

Furthermore, based on the research of the Kringe et al about the Infrared spectroscopy of spinel-type chromium indium sulfide solid solution [15], the bands of strong absorption at 226 and 264 cm^{-1} were ascribed to the $F_{1u}(2)$ mode and the bands at 312 and 323 cm^{-1} to the $F_{1u}(1)$ one. And the larger effective dynamical charges of cations in spinel-type indium sulfides mainly originated from their stronger ionicity in comparison with the corresponding chromium ones leads to the behavior of distinct splitting of these two F_{1u} modes.

The distinct characterization of Raman spectrum of polycrystalline $\text{In}_{21.333}\text{S}_{32}$ is the presence of two strong

peaks at about 306 and 245 cm^{-1} in addition to the Raman active modes predicted by the space group analysis for an ideal normal spinel structure.

Firstly, the strongest peak at 305 cm^{-1} is proposed to be ascribed to the symmetric stretching vibrating mode (ν_1) of InS_4 tetrahedra based on the following considerations. Recent In K-edge EXAFS spectroscopic studies have revealed that majority of In atoms are present in the four-coordinated and In^{3+} state in In-Ge sulfide glasses [16]. And this four-coordinated state of most In atoms was further confirmed by the evolution of Raman spectra especially the prominence at 306 cm^{-1} that was undoubtedly ascribed to the ν_1 mode of InS_4 tetrahedra close to the ν_1 mode of GeS_4 tetrahedra at 340 cm^{-1} following the addition of In_2S_3 within the $(1-x)\text{GeS}_2-x\text{In}_2\text{S}_3$ pseudo-binary glasses [17,18]. In addition, according to the strong polarized characteristic of this Raman active mode shown in Fig.3 indicating that this mode is an A_{1g} symmetry one and the well-conserved randomly distributed tetrahedral site of In atoms in defect spinel $\text{In}_{21.333}\text{S}_{32}$, we feel it reasonable to ascribe the strongest peak at 305 cm^{-1} to a so-called clustering mode, i.e., the ν_1 symmetric stretching vibrational mode of InS_4 tetrahedra. Finally, according to spectral characterization of InCl_4 tetrahedra that all of the four modes ($\nu_1, 314\text{ cm}^{-1}$ at 575 K and 297 at 1000 K ; $\nu_2, 93\text{ cm}^{-1}$; $\nu_3, 349\text{ cm}^{-1}$; $\nu_4, 114\text{ cm}^{-1}$) are Raman-active while only the ν_3 and ν_4 modes are IR-active [19], the band of IR absorption at 358 cm^{-1} was assumed to be the ν_3 mode of tetrahedra InS_4 based on the similarity of atomic weight of S and Cl.

Similarly, the second strongest peak at 245 cm^{-1} was presumed to be originated from another clustering mode, i.e., the ν_1 symmetric stretching vibrational mode of InS_6 octahedra. To start with, based on the polarizing measurements, this additional Raman-active band should correspond to an A_{1g} symmetry mode. Furthermore, according to the Refs [12], in the region $230\text{--}260\text{ cm}^{-1}$, the additional Raman band beyond the group theoretical forecast comes out in the Raman spectra of partial inverse spinels, for example MnIn_2S_4 at 247 cm^{-1} , CdIn_2S_4 at 232 cm^{-1} , MgIn_2S_4 at 256 cm^{-1} . That's to say, the appearance of these bands is independent of composition of samples. Finally, the ν_1 mode of InCl_6 octahedra appears at 274 cm^{-1} [20]. Therefore, the second strongest peak at 245 cm^{-1} of defect spinel $\text{In}_{21.333}\text{S}_{32}$ together with the corresponding Raman bands of partial inverse spinels was assumed to be a so-called clustering (octahedral InS_6) mode. In addition, the shift of this mode toward lower wave number compared with InCl_6 octahedra maybe originate from the strong distortion of octahedral sites in the inverse spinel lattice which has been confirmed by X-ray absorption spectra [1]. Based on the comparable spectroscopic features of InCl_6 octahedra, that ν_1, ν_2 and ν_5 are Raman active while the other two ν_3 and ν_4 are IR active ones and the bands observed in IR spectra exhibit broadening and splitting especially the ν_3 (f_{2u}) mode in the region $200\text{--}300\text{ cm}^{-1}$ [20], the splitting IR absorptive bands at $204, 240$ and 290 cm^{-1} was ascribed to the ν_3 mode of octahedral InS_6

and this large splitting was assumed to be due to the strongly distorting of octahedral sites in defect spinel $\text{In}_{21.333}\text{S}_{32}$.

In fact, early in 1987 [21], the clustering mode was clearly identified to elucidate the additional Raman bands beyond the group theoretical prediction based on the recursion-method calculations of the densities of vibrational states for phonons in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloys. It can be rationally presumed that the above-mentioned two strong peaks are so-called clustering modes caused by high density of states of distinct phonon branches at $q \neq 0$, which is Raman allowed because of the increasing breakdown of the translation symmetry in defect spinel $\text{In}_{21.333}\text{S}_{32}$ that can be confirmed by the random distribution of vacancies and indium atoms on tetrahedral sites and the strong distortion of octahedral sites. Furthermore, their much stronger intensities compared with the A_{1g} one at 366 cm^{-1} of spinel exclude the possible ascriptions to the Raman-inactive F_{2u} ones that can also be explained by the lowering in the symmetry caused by the disordering in the cation sublattice of defective spinel.

4. Conclusion

In summary, polycrystalline $\text{In}_{21.333}\text{S}_{32}$ (JCPDF No: 84-1385) was synthesized by direct reaction of a stoichiometric mixture of the elements in an evacuated silica tube. Through considering the so-called clustering modes, the two strongest peaks located at 305 and 245 cm^{-1} were assumed to be due to the symmetric stretching vibrating of polyhedra InS_4 and InS_6 respectively. Furthermore, all the vibrational modes within Raman and IR spectra of defect spinel $\text{In}_{21.333}\text{S}_{32}$ were proposed in this paper. Certainly, these ascriptions are needed to be further verified through other techniques. For examples, it is necessary to verify whether there exists a secondary tetragonal phase in the prepared sample which also may lead to the IR band at 357 cm^{-1} [22] and a single-crystal sample should be prepared to further testify the results of polarized Raman spectra.

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