

MINERALS FROM MACEDONIA VII. RAMAN SPECTRA OF SULFIDE MINERALS FROM THE ALLSHAR DEPOSIT (STIBNITE, REALGAR, ORPIMENT AND LORANDITE)

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In recent years, Raman spectroscopy (especially, the micro-Raman technique) has become one of the most frequently used experimental tools for characterization and/or identification of minerals. As a part of our extended study of minerals we have collected, separated, identified and characterized some of the sulfide minerals from different ore deposits from Macedonia. The first group of sulfide minerals studied by the micro-Raman technique consisted of four minerals from the first and second zone [1] of the ore deposit in the locality of Allshar (southern part of Macedonia, close to the Greek border). The studied minerals were orpiment (As_2S_3), realgar (As_4S_4), lorandite (TlAsS_2) and stibnite (Sb_2S_3). Stibnite (the only studied mineral from the first zone) is orthorhombic, space group $Pbnm$, $Z = 4$ [2]. The remaining three minerals (found in the second zone of the deposit) are monoclinic: realgar and orpiment crystallize in the same space group, $P2_1/m$, ($Z = 16$ and 4 , respectively) while lorandite crystallizes in the space group $P2_1/a$, with $Z = 8$ [2].

We have already studied the vibrational spectra of these minerals [3, 4], the Raman spectra of orpiment, realgar and lorandite being recorded on the Spectra Physics 1245 Raman spectrometer, using a He-Ne laser excitation [3]. In general, those spectra were of good quality, except for the appearance of numerous plasma lines. The Raman spectra reported in this work were recorded on the Jobin-Yvon LabRam Infinity spectrometer with 532 nm laser line of an Nd-YAG frequency-double laser are shown on Fig.1. Since most of the Raman bands appear in the $100\text{--}500\text{ cm}^{-1}$ spectral region, only these parts of the Raman spectra are shown on Fig.1. Note that Raman spectrum of polycrystalline stibnite presented in Fig. 1 differs from the Raman spectrum of the single crystal sample of stibnite reported in the literature [5]. Thus, the band at around 180 cm^{-1} in our spectrum is absent in the reported Raman spectra of stibnite, while the reported weak band at around 215 cm^{-1} has not been detected in our spectrum. The three bands above 240 cm^{-1} (a strong band at around 245 and the two less defined bands at 278 and 290 cm^{-1}) are present in both spectra but differ in intensity. The first one is the most intense in our spectrum, whereas the remaining two are the strongest in the reported Raman spectrum of single crystal [5]. This could be ascribed to different polarization effects and/or to the extent of grinding of our samples.

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first one is the most intense in our spectrum, whereas the remaining two are the most intense ones in the reported Raman spectrum of single crystal [5]. This could be ascribed to different polarization effects as well as to the extent of grinding of our samples.

The Raman spectra of realgar and orpiment (Fig.1) are of good quality, reproducible and in a fair agreement with those reported by us [3] and by other authors [6]. The spectral differences between realgar and orpiment are due to the presence of different structural constituents in the structures of these minerals. In general, their Raman spectra were interpreted in terms of As-S stretching and S-As-S bending mode [3]; the frequencies of the former ones being above 250 cm^{-1} , and those of the later between 250 and 100 cm^{-1} .

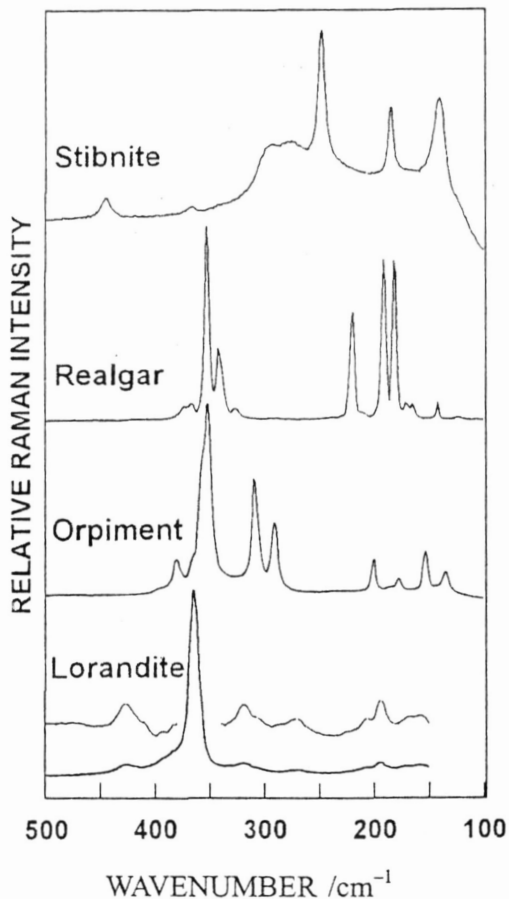


Fig. 1. The Raman spectra of stibnite, realgar, orpiment and lorandite

Only one strong band (at 363 cm^{-1}) appears in our Raman spectrum of lorandite, accompanied by additional weak bands at around $425, 320, 270, 205, 193$ and 170 cm^{-1} (Fig.1) and another strong band (below $\approx 100\text{ cm}^{-1}$) was detected in our Raman spectrum of lorandite recorded earlier [3]. Note that the Raman spectrum of synthetic weissbergite (TlSbS_2) [7] is very similar to the present Raman spectrum of lorandite and that the strong Raman band at 329 cm^{-1} in the spectrum of TlSbS_2 was thought to be associated with the strong Sb-S interaction in the *c* direction [7]. Assuming that the corresponding vibration is essentially localized in the Sb-S or As-S fragment of the crystal structure (a crude approximation) and taking into account the masses of Sb and As, the predicted frequency of the corresponding As-S vibration in lorandite would be expected to appear around 365 cm^{-1} , very close to the frequency of the strongest band observed in our Raman spectra of lorandite. This coincidence is not a proof that we are indeed dealing with *harmonic* vibrations of *diatomic* oscillators but is helpful in the assignment. The vibrations giving rise to the weaker bands are certainly of a more complex character.

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