

VIBRATIONAL SPECTRA OF SOME SULFIDE MINERALS FROM ALŠAR

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ABSTRACT

The infrared spectra (recorded at room temperature and at the boiling temperature of liquid nitrogen) of three minerals (lorandite, orpiment and realgar) from the Alšar ore deposit are presented and briefly discussed. Also presented are the Raman spectra (room temperature only) of the investigated minerals.

INTRODUCTION

Among the minerals found in the ore deposit Alšar (or Allchar) in Macedonia (Yugoslavia), *lorandite*, a mineral with the composition corresponding to the formula $TlAsS_2$, is certainly the most interesting one. The importance of lorandite lies in the fact that it is rather reach in thallium and hence can be used as a suitable dosimeter for solar neutrinos. In fact, a large-scale international project called LOREX (from *Lorandite Experiment*) is presently under way [1].

Surprisingly enough, very little has been done on the vibrational properties of lorandite. To the best of our knowledge, the only contribution to this field is our previous report [2] where the room-temperature (RT) infrared spectra of natural lorandite have been presented and briefly discussed. In the meantime, we were able to obtain the Raman spectra of lorandite and to record the infrared spectra of lorandite at the boiling temperature of liquid nitrogen (henceforth abbreviated as LNT). Raman, as well as RT and LNT infrared spectra of two other sulfide minerals from Alšar, *realgar* (As_4S_4) and *orpiment* (As_2S_3) - were also recorded*.

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* In our previous communication [2] the RT infrared spectra of realgar and orpiment were presented but not discussed.

The crystal structures of all three presently studied minerals are known [3-6]. It was found [4,6] that lorandite is monoclinic, crystallizing in the space group $P2_1/a$ with four $Tl_2As_2S_4$ formula units in the unit cell. Realgar and orpiment are also monoclinic, the space group in which they crystallize being reported [3,5] as $P2_1/n$. Despite the fact that the three minerals crystallize in the same space group*, structural differences exist between them. Thus, realgar is built up of discrete As_4S_4 molecular units, whereas layers are encountered in the case of lorandite and orpiment. The basic structural motive in the structures of the latter two minerals, however, are the AsS_3 pyramids (two non-equivalent ones in the case of lorandite). Even the structure of realgar is, in some way, related to that of orpiment [3] and the interatomic distances and bond angles in these two minerals are similar. In the structure of lorandite, two of the sulfur atoms from each AsS_3 pyramid act as *bridges* between neighbouring As atoms, whereas the third sulfur atom of a given pyramid may be conveniently called *terminal* [2] since it does not participate in the As-S-As bonding. The terminal sulfur atoms are bonded to thallium atoms, however.

EXPERIMENTAL

The studied samples of lorandite, realgar and orpiment were natural minerals from Alšar. They were carefully separated from the ore samples in which they were found. The comparison of the spectra of the natural minerals with their synthetic analogues [7] showed no differences thus proving that the studied samples were indeed *pure* minerals.

The infrared spectra were recorded from CsI pellets on a Perkin-Elmer 580 infrared spectrophotometer. A VLT-2 variable-temperature cell cooled with liquid nitrogen was used to obtain the LNT spectra.

The Raman spectra from single crystal samples were obtained on a Spectra Physics 1245 spectrophotometer. A He-Ne laser operating at 632.8 nm with a power of 10 mW was used as a light source.

RESULTS AND DISCUSSION

The RT and LNT spectra of lorandite, orpiment and realgar are given in Fig. 1, whereas the Raman spectra are shown in Fig. 2. The plasma lines in the Raman spectra are marked by arrows.

* The space groups $P2_1/a$ and $P2_1/n$ differ only in the choice and orientation of the unit cell parameters of the space group which may alternatively be called C_{2h}^5 .

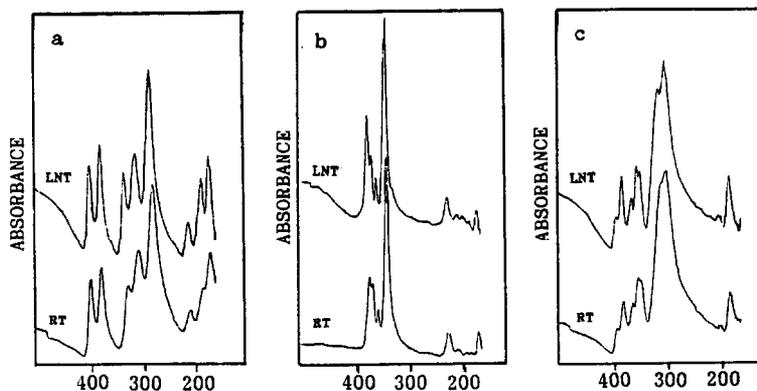


Fig. 1. Infrared spectra of lorandite (a), realgar (b) and orpiment (c)

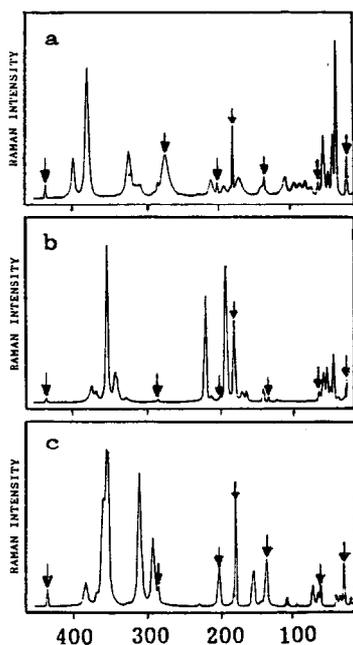


Fig. 2. Raman spectra of lorandite (a), realgar (b) and orpiment (c)

Spectra of orpiment and realgar

Despite the fact that our attention was directed mainly to the spectrum of lorandite, the discussion will be commenced by the brief analysis of the spectra of realgar and orpiment. The reasons for this are two-fold. Firstly, the spectra of the synthetic analogues of these two minerals have already been studied [8-10] and assigned so that the published results may serve as a good starting point for the assignment of the lorandite spectrum. Secondly, the comparison of the RT and LNT spectra of these minerals (which are structurally similar to lorandite but do not contain thallium) may give an indication as to the effect of the temperature lowering on the vibrations which, necessarily, are stretchings and bendings of units composed of arsenic and sulfur only.

As seen in Fig. 1 c, the bands in the spectrum of orpiment are only slightly affected by the temperature change from RT to LNT, their frequencies becoming somewhat higher (the magnitude of the shifts is 2 - 3 cm^{-1}) and their width decreasing. It should be noted that, generally speaking, the absolute values of the shifts for the bands at lower frequencies (related to the bending modes) are smaller

than those of the bands attributable to modes which are predominantly stretching in character. The situation is similar in the spectrum of realgar (Fig. 1 b), at least as far as the bands above 300 cm^{-1} are concerned. In this case, namely, the bands below 250 cm^{-1} have frequencies which are practically identical at RT and at LNT.

Our RT spectra of orpiment and realgar are in a fair agreement with the published infrared [9,10] and Raman spectra [8-10], although disagreements exist as far as the exact frequency values are concerned. In addition to that, a band at 359 cm^{-1} (not observed previously) has been resolved in the infrared spectrum of realgar and several hitherto unobserved bands (at 202, 182 and 158 cm^{-1}) are clearly seen in our infrared spectra of orpiment.

As expected (a symmetry center exists in the unit cell), the infrared and Raman frequencies do not coincide.

In view of the rather detailed analysis of these spectra available in the literature, we refrain from further discussion.

The spectra of lorandite

The changes in the infrared spectra of lorandite caused by the change of temperature from RT to LNT are comparable to those observed in the case of orpiment and realgar. One of the bands (that with an RT frequency of 283 cm^{-1}), however, is shifted considerably more, the LNT value being 290 cm^{-1} . If the shifts of the bands to higher frequencies are interpreted as mainly due to contractions of the unit cells on lowering the temperature, then it is tempting to assign a particularly temperature-sensitive band (such as the 283 cm^{-1} one) to some mode involving a considerable inter-chain motion, i.e. one in which the Tl-S coordinates play a significant role. The frequency of the above-mentioned band, however, is much higher than those of the bands which in the literature were interpreted as due to Tl-S stretches (their reported frequencies in a series of thallium-containing minerals* are lower than 170 cm^{-1} [11-13]).

If the literature assignments are correct, then the Tl-S stretching bands** are too low to be observed in our infrared spectra and are to be found in the Raman spectrum only. In absence of a reliable criterion other than the comparison with the assignments made in the literature, it is difficult to make a safe choice.

* Lorandite itself is not among them.

** It is highly unlikely that the corresponding modes are pure Tl-S stretches.

As has been discussed previously [2], we are inclined to believe that the bands at highest frequencies (401 and 381 cm^{-1}) are due to motions involving mainly the sulfur atoms which were called terminal, whereas the next group (comprised of three bands, the lowest one being considerably more intense than the other two) is most probably due to stretchings predominantly involving the bridging sulfurs. The reasoning behind such an assignment is simple: the As-S_t distances [6] are *shorter* (especially one of them) than the As-S_b ones (the superscripts t and b standing for terminal and bridging respectively). Although the vibrations are certainly not *localized* As-S_t and As-S_b stretchings, the approximate description given above is probably satisfactory.

The large shift of the lowest of these three bands on going from RT to LNT seems to indicate that the two As atoms bonded *via* the bridging sulfurs come closer together, this leading to an increase of some of the As-S_b force constants.

As in the case of realgar and orpiment, the infrared and the Raman frequencies do not coincide, although their values are rather close - an indication of not very pronounced correlation-field splitting effects.

No attempt was made to interpret the low-frequency part of the Raman spectrum of lorandite where the Tl-S stretchings (and the corresponding bendings), as well as other lattice modes are expected to appear. The reasons for this were mentioned above: we were unable to find a reliable criterion for assigning these bands. Our hopes that the study of isotypic minerals (in which As is replaced by Sb or Tl is replaced by Ag) may help turned out to be ill-founded. Such minerals (and their synthetic analogues) do exist, but they are *not* isostructural with lorandite. The effects of the change in mass are, hence, obscured by the acting of different selection rules, by the differences (probably significant) in the nature of the normal modes etc. Since we were unable to perform polarization measurements on oriented single crystals and the normal coordinate analysis was out of the scope of the present paper, any attempt to attribute the observed Raman bands to particular modes would be purely speculative.

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