

Infrared spectra of lorandite and some other minerals from Allchar

By

Bojan Šoptrajanov, Magdalena Trajkovska, Gligor Jovanovski and
Trajče Stafilov, Skopje

With 4 figures and 2 tables in the text

ŠOPTRAJANOV, B., TRAJKOVSKA, M., JOVANOVSKI, G. & STAFILOV, T.: Infrared spectra of lorandite and some other minerals from Allchar. – N. Jb. Miner. Abh. 167: 329–337; Stuttgart 1994.

Abstract: The infrared spectra of the mineral lorandite, TiAsS_2 from the Allchar deposit (Crven Dol locality) near Kavadarci, Macedonia, as well as those of some accompanying minerals such as realgar, AsS are recorded and discussed.

Key words: Infrared spectra, minerals, lorandite, realgar, orpiment, Allchar mine.

Introduction

In the Crven Dol locality of the Allchar deposit near Kavadarci in FYR Macedonia the mineral lorandite, TiAsS_2 (seems to be the best possible mineral detector for solar neutrinos) is found. Lorandite is almost always accompanied by other sulfide minerals of which realgar, AsS and orpiment, As_2S_3 are most common. Other sulfide minerals (such as marcasite, FeS_2 and stibnite, Sb_2S_3) are also present in the Allchar deposit.

The crystal structures of lorandite (ZEMANN & ZEMANN 1959, FLEET 1973), as well as those of realgar and orpiment (MULLEN & NOWACKI 1972) have been determined and satisfactorily refined. Some spectral data on relevant sulfide minerals are also available (POVARENNIKH & GERASIMENKO 1981, BUES et al. 1983, MORI et al. 1984) but the spectra are of varying quality and were recorded mainly from synthetic minerals. To the best of our knowledge, however, the vibrational spectra of either lorandite itself or of its synthetic analogue have not been studied.

In order to elucidate the vibrational properties of lorandite and those of other sulfide minerals from Allchar, the infrared spectra of hand-picked crystals of lorandite, realgar and orpiment have been recorded and studied. Understandably, our attention will be focussed on the spectrum of lorandite.

As shown later, our spectra of the minerals containing As–S bonds (lorandite, realgar and orpiment) are of good quality so that comparisons can be

made (internally and with the published spectra of various sulfide minerals). The low-frequency limit of our spectra (150 cm^{-1}) is lower than that of the published spectra of realgar (Bues et al. 1983) and orpiment (MORI et al. 1984).

Using the data on related systems as a guide, an assignment of the observed bands was attempted and the spectral data were correlated with the crystallographic ones.

The well-known difficulties in detecting the presence of lorandite crystals in the realgar matrix on the one hand, and the existence, in the spectrum of lorandite, of a band well above those in the spectra of either realgar or orpiment, on the other, opened a possibility to use infrared spectra to detect small quantities of lorandite in, for example, realgar.

Experimental

All studied minerals originate from the Allchar deposit. They were carefully hand-picked from the ore samples in which they were found.

Artificial mixtures of lorandite and realgar were prepared by simply mixing appropriate amounts of pure minerals.

The infrared spectra were recorded from KBr pellets on a Perkin-Elmer 580 spectrophotometer and from CsI pellets on a Bruker IFS 113V Fourier-transform instrument.

Results and discussion

The infrared spectrum of lorandite in the $450\text{--}250\text{ cm}^{-1}$ region recorded on the Perkin-Elmer instrument is shown in Fig. 1 and that obtained in the $450\text{--}150\text{ cm}^{-1}$ region (using the FTIR instrument) is given in Fig. 2. As can be seen from Table 1, the agreement between the frequencies of the observed bands in the overlapping region is rather good so that the obtained values could be considered as reliable to within 2 cm^{-1} .

The FTIR spectra of realgar and orpiment are shown in Fig. 3.

Table 1. Frequencies (in cm^{-1}) of the main observed infrared bands in the spectra of lorandite.

Perkin-Elmer 580	FTIR	Tentative assignment
402	401	As-S _t stretching
383	381	As-S _t stretching
333	332	
311	310	S _b -As-S _b stretching
283	283	
	213	S-As-S bending
	195 sh	
	188	S-As-S bending
	172	

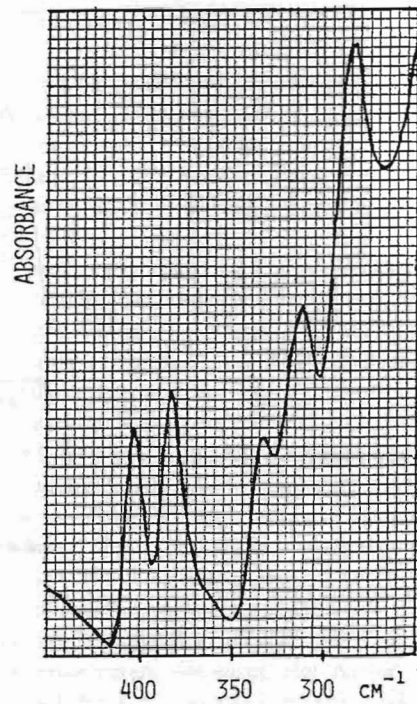


Fig. 1. The infrared spectrum of lorandite recorded on the Perkin-Elmer 580 instrument.

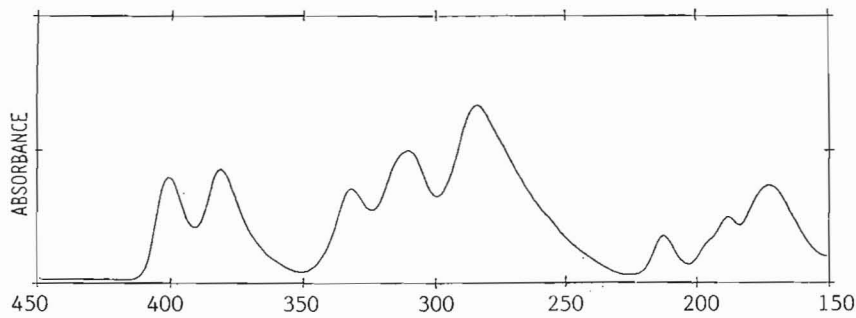


Fig. 2. The infrared spectrum of lorandite recorded on the FTIR instrument.

Crystal structure of lorandite

Lorandite crystallizes in the space group $P2_1/a$ with four $TlAsS_2$ formula units in the unit cell (FLEET 1973).

Its crystal structure consists (ZEMANN & ZEMANN 1959, FLEET 1973) of spiral chains composed of two crystallographically non-equivalent types of AsS_3 pyramids linked by Tl atoms. In each AsS_3 group, two sulfur atoms act as bridges

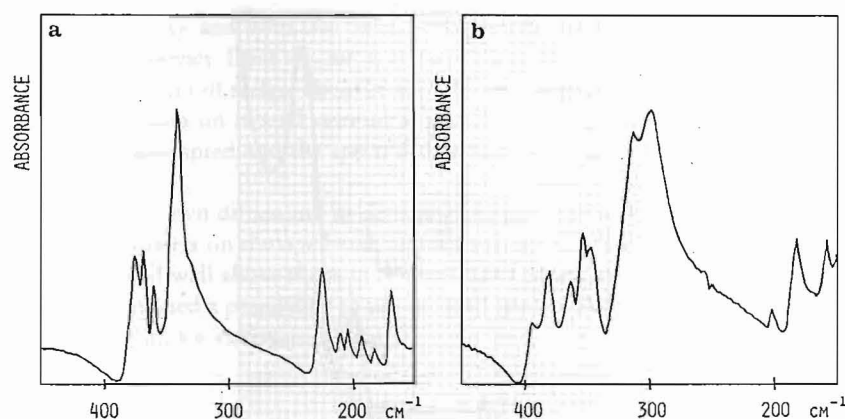


Fig. 3. FTIR spectra of realgar (a) and orpiment (b).

Table 2. Selected distances (in pm) and angles (in °) in the crystal structure of lorandite (FLEET 1973).

Distances		Angles	
As(1)–S(1)	208	S(1)–As(1)–S(3)	100.2
As(1)–S(3)	229	S(1)–As(1)–S(4)	100.5
As(1)–S(4)	232	S(3)–As(1)–S(4)	95.9
As(2)–S(2)	220	S(2)–As(2)–S(3)	102.9
As(2)–S(3)	230	S(2)–As(2)–S(4)	100.5
As(2)–S(4)	232	S(3)–As(2)–S(4)	91.5

between non-equivalent As atoms, whereas the third sulfur atom is a terminal one i.e. it does not participate in the chain formation*. In agreement with this, two of the As–S distances are considerably shorter than the rest (Table 2).

The Tl–S distances (FLEET 1973) range from 296 to 393 pm. There are various opinions, however, which of these could be ascribed to Tl–S bonds. Thus, FLEET (1973) describes the coordination polyhedron around Tl as a flattened square pyramid with fivefold coordination with sulfur. NOWACKI et al. (1982), on the other hand, think that the coordination number of Tl in lorandite is 2, whereas BALIĆ-ŽUNIĆ & ŠČAVNIČAR (1988) and GRŽETIĆ (1988) speak of sevenfold coordination. As discussed later, we are unable to see the bands originating from motions in which the thallium atoms take significant part so that the details of the structure related to the Tl environment are hardly of any significance for our present purposes.

More details about the crystal structure are to be found in FLEET (1973).

* These sulfure atoms participate in the Tl–S bonding, however.

Infrared spectra of lorandite

As seen in Figs. 1 and 2, three groups of bands can be separated in the studied infrared region. First of all, there is a doublet of bands whose frequencies are 401 and 381 cm^{-1} , respectively. Then there is a triplet with well-developed maxima at 332, 310 and 283 cm^{-1} and, finally, a complex feature at lower frequencies consisting of at least three bands and a clearly visible shoulder around 195 cm^{-1} .

In order to facilitate the treatment, the AsS_3 groups will be considered as the simplest vibrational units. This, of course, is a gross oversimplification, especially because of the possibility of covalent Tl-S bonding. Having in view the data contained in Table 2, the local symmetry of each AsS_3 pyramid can be taken as close to C_3 (the symmetry of an ideal ZXY_2 molecule).

With six As-S distances present in the structure (two AsS_3 pyramids), six vibrational modes which could be described as As-S stretches should appear. In addition, six vibrations which would be mainly S-As-S bendings are expected. Of these, the *stretching* modes should have frequencies which are *higher* than those of the *bending* vibrations.

The stretching modes could be approximately described as As-S_t stretches (the subscript *t* meaning *terminal*) and symmetric $\text{S}_b\text{-As-S}_b$ and antisymmetric $\text{S}_b\text{-As-S}_b$ stretches (*b* standing for *bridging*) of each AsS_3 pyramid. Corresponding to the shorter As-S_t distances, the As-S_t stretching frequencies would be higher than those of the modes involving mainly the bridging sulfur atoms.

The description of the bending modes as S-As-S deformations is somewhat arbitrary since some of them (those in which the bridging sulfur atoms are involved) could equally well be described as As-S-As deformations. The simple model is certainly not ideal but it will be used as a guide.

There is little doubt that the bands at 401 and 381 cm^{-1} in the spectrum of lorandite are due to modes which are mainly As-S_t stretchings. Although the chances to have As-S stretchings *strictly* localized in the As-S_t bonds are perhaps slight, the above assignment is reasonable. Namely, the existence in the structure of lorandite (FLEET 1973), of two rather short As-S distances should certainly increase the values of the respective As-S force constants and this would then lead to frequencies higher than those of the modes involving mainly the bridging sulfur atoms and, for that matter, higher than in related systems. It should be noted, for example, that in the spectrum of Tl_3AsS_3 the highest-frequency band assigned to As-S stretching is found at 358 cm^{-1} (POVARENNIKH & GERASIMENKO 1981) and no bands around 400 cm^{-1} are present in the spectra of realgar and orpiment; cf. our Fig. 3 and Refs. (BUES et al. 1983, MORI et al. 1984).

The assignment of the bands forming the complex feature at lower frequencies is somewhat more complicated. Of the six vibrational modes which could be described as As-S stretches, namely, *four* remain to be identified (those

which can be approximately described as S_b-As-S_b stretches) but only *three* candidates (the bands around 332, 310 and 283 cm^{-1}) exist for the expected *four* such modes. It should be noted, however, that the intensity of the band centered at approximately 283 cm^{-1} is undoubtedly at least double that of the band at 332 cm^{-1} . It is thus safe to assume that the above-mentioned bands are indeed due to the four expected S_b-As-S_b stretches.

As pointed out above, *six* additional bands due to vibrations of the AsS_3 groups originating from the $S-As-S$ bendings should be found. The band at 213 cm^{-1} is a clear candidate – a value of 206 cm^{-1} is reported (POVARENNIKH & GERASIMENKO 1981) for such a mode in the spectrum of Tl_3AsS_3 and frequencies between 222 and 166 cm^{-1} are given for the $As-S-As$ bending vibrations in realgar by BUES et al. (1983). Whether all the remaining modes of this type give rise to bands located at lower frequencies (below 200 cm^{-1}) or some of them are responsible for the broadening of the low-frequency side of the 283 cm^{-1} band is perhaps open to discussion. Presently we believe that in the spectrum of lorandite 213 cm^{-1} is the upper frequency limit for the bending $S-As-S$ modes. If this is true, then for the expected six $S-As-S$ bendings we only have the bands at 213, 188 and 172 cm^{-1} visible in our infrared spectrum. In addition to that, a shoulder at around 195 cm^{-1} is also visible. As in the case of the bands assigned to $As-S$ stretchings, the intensity of the band appearing at lowest frequency (the 172 cm^{-1} one) exceeds considerably that of the bands at higher frequency. The assignment of the $S-As-S$ modes, consequently, appears to be satisfactory.

It is unlikely that bands due to $Tl-S$ stretchings appear in our spectra (in Ref. of POVARENNIKH & GERASIMENKO 1981, for example, band with frequencies *lower than* 160 cm^{-1} are assigned to such modes).

The assignment is summarized in Table 1.

Infrared spectra of the other investigated minerals

As mentioned in the introduction, the infrared spectra of natural realgar and of synthetic orpiment have already been studied (BUES et al. 1983, MORI et al. 1984).

Our spectra of *realgar* (Fig. 3 a) agree well with those reported by BUES et al. (1983) except that most of our frequencies are *somewhat lower* and an additional band (at 359 cm^{-1}) has been resolved.

The agreement between the frequencies in our spectra of *orpiment* (Fig. 3 b) and those given by MORI et al. (1984) is satisfactory but worse than in the previous case. In addition to the already reported bands, at least three new ones (at 202, 182 and 158 cm^{-1}) are present in our spectra.

It should be emphasized once again that in the spectra of realgar and orpiment the highest-frequency band in each of the spectra is found *below* 400 cm^{-1} , i.e. at lower frequencies than that of the 401 cm^{-1} band in the spectrum of lorandite. This, as will be shown, is very convenient for the analytical applica-

tions of the infrared spectra. The presence of the newly-resolved 359 cm^{-1} band in the spectrum of realgar is important because of similar reasons.

Analytical application of the spectra

As already mentioned in the introductory section, the appearance in the spectrum of lorandite of a band at 401 cm^{-1} (well above the bands appearing in the spectrum of realgar) led us to attempt to apply the infrared spectra for detecting the presence of small quantities of lorandite in realgar. Synthetic mixtures of the two minerals with different realgar:lorandite ratios were prepared

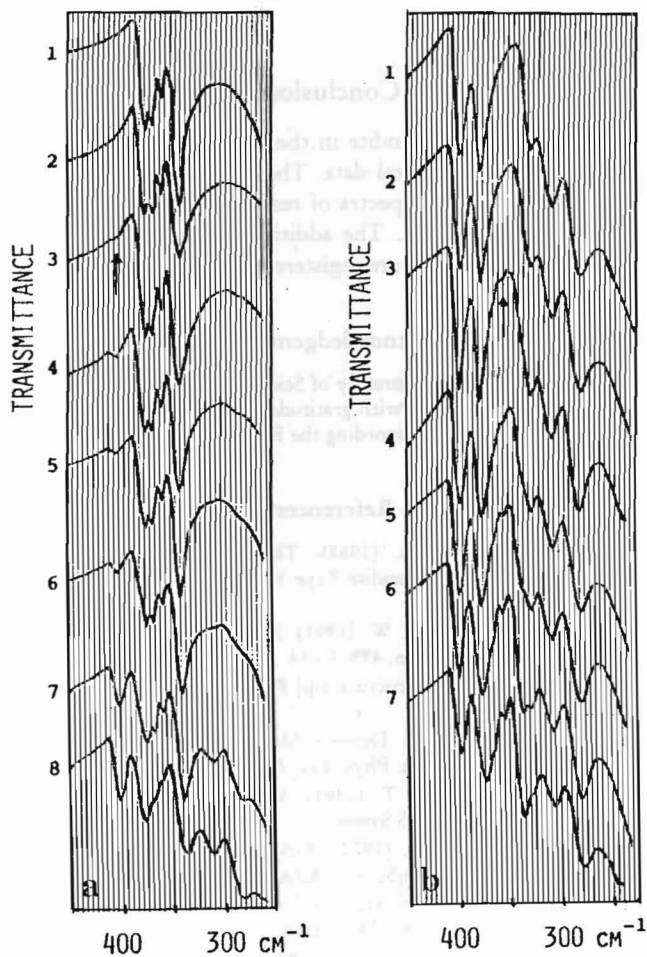


Fig. 4. Infrared spectra of pure realgar and of mixtures containing 1, 2, 3, 5, 10, 30 and 50% lorandite (a) and of lorandite and mixture with 5, 10, 15, 20, 30 and 40% realgar.

and their infrared spectra recorded. As seen in Fig. 4 a, the existence of a maximum around 400 cm^{-1} is clearly visible even when the lorandite content is as low as 2%.

More interesting would be of course, the opposite of what has been done – detecting impurities in the separated lorandite minerals. Unfortunately, this is much more difficult since most of the bands in the spectra of the potential impurities fall in the same spectral regions as in the spectrum of lorandite itself. It is true that in the spectrum of realgar for example there is a band outside the regions masked by lorandite bands (its frequency is around 360 cm^{-1}) but the intensity of this band is rather low and only when the realgar content exceeds 10%, the band begins to appear in the wing of the much more intense lorandite one (cf. Fig. 4 b).

Conclusion

The infrared spectrum of lorandite in the $450\text{--}150\text{ cm}^{-1}$ region is assigned and correlated with the structural data. The satisfactory agreement between the frequencies of our infrared spectra of realgar and orpiment and those presented in the literature is found. The additional bands in the low frequency spectral region of those minerals are registered.

Acknowledgements

The financial support of the Community of Scientific Interests of Macedonia is gratefully acknowledged. Acknowledged with gratitude is the aid of our colleagues from the Bulgarian Academy of Sciences for recording the Fourier-transform spectra.

References

- BALIĆ-ŽUNIĆ, T. & ŠČAVNIČAR, S. (1988): The Crystallochemical Behaviour of Thallium and Lead in the Lorandite-Type Sulfosalts. – *Nucl. Instr. Meth. Phys. Res. A* **271**: 304–307.
- BUES, W., SOMER, M. & BROCKNER, W. (1983): Schwingungsspektren von As_4S_4 und As_4Se_4 . – *Z. Anorg. Allg. Chem.* **499**: 7–14.
- FLEET, M. E. (1973): The Crystal Structure and Bonding of Lorandite, $\text{Tl}_2\text{As}_2\text{S}_4$. – *Z. Kristallogr.* **138**: 147–160.
- GRŽETIĆ, I. (1988): Local Electron Density Models for Tl to Pb Conversion in Lorandite. – *Nucl. Instr. Meth. Phys. Res. A* **271**: 308–313.
- MORI, T., MATSUISHI, K. & ARAI, T. (1984): Vibrational Properties and Network Topology of Amorphous As–S Systems. – *J. Non-Cryst. Solids* **65**: 269–283.
- MULLEN, D. J. E. & NOWACKI, W. (1972): Refinement of the Crystal Structure of Realgar, AsS and Orpiment, As_2S_3 . – *Z. Kristallogr.* **136**: 48–65.
- NOWACKI, W., EDENHARTER, A., ENGEL, P., GOSTOJIĆ, M. & NAGL, A. (1982): In: AMSTUTZ, G. C., EL GORESY, A., FRENZEL, G., KLUTH, C. & MOH, G. (eds.): *Ore Genesis – The State of the Art.* – Berlin, Springer, p. 689.
- POVARENNIKH, A. S. & GERASIMENKO, V. S. (1981): Long-wave IR Spectra of Synthetic Analogs of Some Natural Sulfides. – *Miner. Zh.* **3**: 16–28.

ZEMANN, A. & ZEMANN, J. (1959): Zur Kenntnis der Kristallstruktur von Lorandit. -
Acta Crystallogr. 12: 1002-1006.

Manuscript received by the editor February 8, 1994.

Addresses of the authors:

BOJAN ŠOPTRAJANOV, GLIGOR JOVANOVSKI and TRAJČE STAFILOV, Institut za hemija,
PMF, Univerzitet "Sv. Kiril i Metodij", POB 162, 91001 Skopje, Macedonia.

MAGDALENA TRAJKOVSKA, Rudarski Institut, 91000 Skopje, Macedonia.