

Infrared spectra of $M^I_3M^{III}S_3$ type synthetic minerals ($M^I = Tl$ or Ag , $M^{III} = As$ or Sb)

By

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With 1 figure and 2 tables in the text

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Abstract: The infrared spectra of four compounds of the $M^I_3M^{III}S_3$ type with $M^I = Tl$ or Ag , and $M^{III} = As$ or Sb were studied at room temperature (RT) and at the boiling temperature, respectively, of liquid nitrogen (LNT). The contribution of the $Ag-S$ coordinates to the vibrational modes producing the infrared bands in the spectra of the silver compounds is more pronounced than that of the $Tl-S$ coordinates in the corresponding thallium compounds. This conclusion is in line with the more pronounced covalent character of the $Ag-S$ bonds as compared with the $Tl-S$ ones.

Key words: Infrared spectra, synthetic minerals, ellisite, stibioellisite, proustite, pyrargyrite.

Introduction

In continuation of our studies on thallium-containing minerals (mainly lorandite, $Tl_2As_2S_4$), among other minerals from Alšar, Macedonia (TRAJKOVSKA et al. 1990, 1992), we now report the results of our infrared investigation of two synthetic minerals of thallium: ellisite, Tl_3AsS_3 , and stibioellisite, Tl_3SbS_3 . To facilitate the interpretation, the corresponding silver compounds proustite, Ag_3AsS_3 , and pyrargyrite, Ag_3SbS_3 , were similarly studied.

Whereas only ellisite has been studied by infrared spectroscopy (POVAREN-NYKH & GERASIMENKO 1981), the crystal structures of all four compounds have been determined by X-ray diffraction methods (ENGEL & NOWACKI 1966; GOSTOJIĆ 1980; REY et al. 1984). The two thallium compounds crystallize in the rhombohedral space group $R\bar{3}m-C_{3v}^5$ with one molecule per unit cell.

The silver-containing compounds are also rhombohedral, but crystallize in the space group $R\bar{3}c-C_{3v}^6$. Thus, the four compounds are grouped into two isomorphous pairs. Although the thallium compounds are not strictly isomorphous with the silver ones, there is a sufficient structural similarity as to warrant a parallel investigation of their spectra. Some of the relevant crystallographic data will be given below.

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In view of the known structural similarity of the four studied compounds it appeared to be advantageous to examine in detail their infrared spectra, making spectral comparisons of the two trithioarsenates(III) and of the two trithioantimonates(III) or, alternatively, comparing the spectra of the two thallium or of the two silver compounds. It was, namely, believed that (if the spectra turned out to be sufficiently alike), the frequency similarities (or differences) within a given pair would not only clear the assignments but would also shed some light on the structural peculiarities in these compounds.

Experimental

The four studied compounds were prepared by solid-state reactions in sealed quartz glass tubes (MOH & TAYLOR 1971; GRŽETIĆ 1990).

The infrared spectra were recorded, from CsI pellets, on a Perkin-Elmer 580 instrument. The spectra at the boiling temperature of liquid nitrogen (LNT, for short) were recorded using a VLT-2 variable-temperature cell (RIIC - London) provided with polyethylene windows.

Results

The infrared spectra of Tl_3AsS_3 , Tl_3SbS_3 , Ag_3AsS_3 and Ag_3SbS_3 in the $500-180\text{ cm}^{-1}$ region are shown in Fig. 1, and their respective band frequencies in Table 1.

As seen, they all consist of two stronger and one much weaker band, some additional features being, perhaps, visible below 250 cm^{-1} in the spectra of the two silver compounds. The broad feature around 400 cm^{-1} originates from the polyethylene windows of the low-temperature cell.

Crystallographic data

As mentioned above, the two thallium compounds crystallize in the space group $R3m-C_{3v}^5$, whereas their silver counterparts crystallize in the space group $R3c-C_{3v}^6$.

Around each M^{III} atom there are three sulfur atoms as nearest neighbours, at distances which are close to the sum of the atomic radii (HUHEEY 1983) of the M^{III} and sulfur atoms (cf. Table 2). A regular pyramid with the M^{III} atom at its apex is thus formed. Three additional sulfur atoms are found in the vicinity of the M^{III} atoms but at considerably longer distances.

Five or six sulfur atoms are located around each M^{I} atom. Three of them are situated closer to the Tl (or Ag) atom than the remaining ones. There is a significant difference in the coordination of Tl and Ag. The coordination around Tl, namely, can be described as *trigonal* pyramidal, whereas Ag is essentially *two-coordinated*, with a gap between the two shorter Ag-S distances and the next longer one of $\approx 40\text{ pm}$, another sulfur atom being found at $\approx 30\text{ pm}$ further away (cf. Table 2).

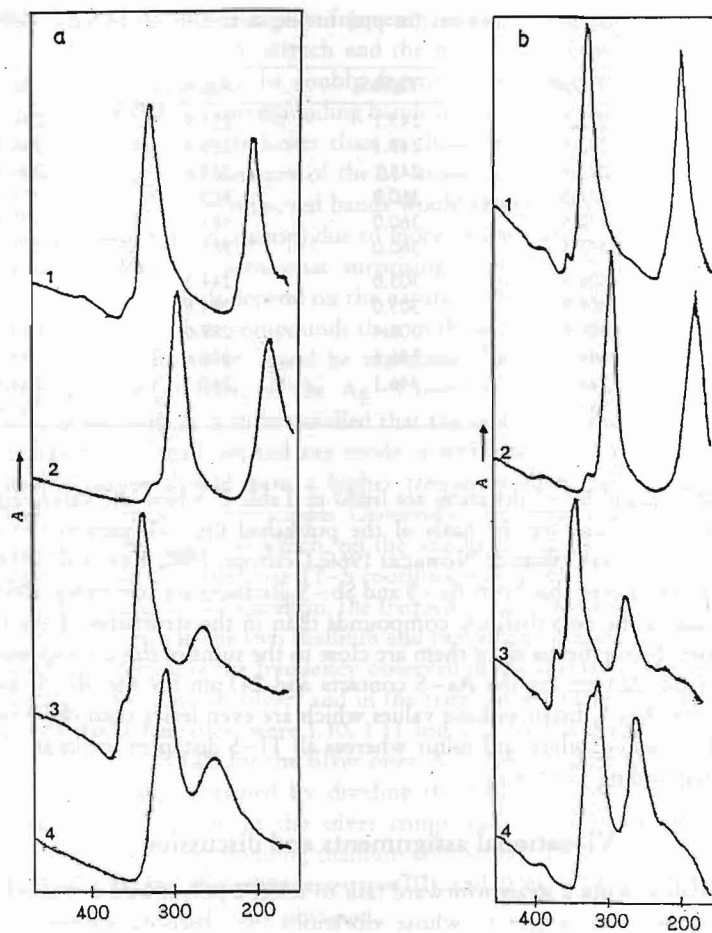


Fig. 1. RT (a) and LNT (b) infrared spectra of Tl_3AsS_3 (1), Tl_3SbS_3 (2), Ag_3AsS_3 (3) and Ag_3SbS_3 (4).

Table 1. Frequencies (in cm^{-1}) of the bands in the infrared spectra of Tl_3AsS_3 , Tl_3SbS_3 , Ag_3AsS_3 and Ag_3SbS_3 *.

Tl_3AsS_3		Tl_3SbS_3		Ag_3AsS_3		Ag_3SbS_3	
RT	LNT	RT	LNT	RT	LNT	RT	LNT
355 sh	357 w	324 sh	326 w	361 sh	364 w	?	322 sh
327 vs	330 vs	295 vs	296 vs	337 vs	340 vs	308 vs	312 vs
202 vs	204 vs	185 vs	185 vs	265 vs	274 vs	252 s	261 s

* Abbreviations: RT - room temperature; LNT - liquid-nitrogen temperature; w - weak; s - strong; sh - shoulder; v = very

Table 2. $M^{\text{III}}-\text{S}$ and $M^{\text{I}}-\text{S}$ distances (in pm) in the structures of Tl_3AsS_3 , Tl_3SbS_3 , Ag_3AsS_3 and Ag_3SbS_3 .

	Tl_3AsS_3	Tl_3SbS_3	Ag_3AsS_3	Ag_3SbS_3
$M^{\text{III}}-\text{S}$	222.5	243.1	225.4	246.3
	222.5	243.1	225.4	246.3
	222.5	243.1	225.4	246.3
	377.5	360.0	383.1	375.9
	377.5	360.0	383.1	375.9
	377.5	360.0	383.1	375.9
$M^{\text{I}}-\text{S}$	304.9	303.0	244.3	243.3
	304.9	303.0	244.8	245.0
	309.8	308.4	288.6	288.4
	344.3	346.1	318.4	314.6
	344.3	346.1	342.1	354.8
	389.5			366.8

The $M^{\text{III}}-\text{S}$ and $M^{\text{I}}-\text{S}$ distances are listed in Table 2, where the values given are newly calculated on the basis of the published unit-cell parameters and atomic coordinates (ENGEL & NOWACKI 1966; GOSTOJIĆ 1980; REY et al. 1984).

It should be noted that both As-S and Sb-S distances are somewhat shorter in the case of the two thallium compounds than in the structures of the two silver ones. Nevertheless all of them are close to the sums of the corresponding atomic radii (223 pm for the As-S contacts and 243 pm for the Sb-S ones). Two of the Ag-S distances have values which are even lesser than the sum of the atomic radii of silver and sulfur whereas all Tl-S distances are larger than the corresponding Tl-S sum.

Vibrational assignments and discussion

Although it is not a straightforward task to select a polyatomic group which could be treated as a unit to whose vibrations the observed infrared bands could be attributed, it seems that the most serious candidates for such units are the $M^{\text{III}}\text{S}_3$ pyramids. This appears to be an obvious choice especially in the case of the two thallium compounds where the length of the Tl-S contacts suggests that the corresponding bonds are intermediate between covalent and ionic and, consequently, *weaker* than the $M^{\text{III}}-\text{S}$ ones. Tentatively, the $M^{\text{III}}\text{S}_3$ groups can be selected as the basic vibrational unit in the case of the silver compounds as well. In the latter case, however, the contribution of the Ag-S vibrational coordinates to some of the high-frequency modes could not be ruled out *a priori*.

For a pyramidal XY_3 group with a C_{3v} symmetry, two stretchings (one non-degenerate and one doubly degenerate) and two bendings (again one non-degenerate and one doubly degenerate) are expected.

The stretching bands are expected to appear at higher frequency and to be less mixed than the bending ones. It would, therefore, be reasonable to at-

tribute the weak band at highest frequency in each of the four studied spectra to the symmetric $M^{III}-S_3$ stretch and the much more intense band at somewhat lower frequency to the doubly degenerate $M^{III}-S_3$ stretch. The fact that the frequencies of the corresponding bands in the spectra of the trithioantimonates(III) are significantly lower than in those of the trithioarsenates(III) but are less sensitive to the nature of the M^I atoms is in line with such an assignment. The third of the observed bands would then be (within the framework of the accepted approximation) due to more or less pure $S-As-S$ or $S-Sb-S$ bending modes. It is somewhat surprising, however, to find that the frequencies of these bands depend on the nature of the M^I atom and are higher in the spectra of the silver compounds than in those of their thallium analogues.

This finding, however, could be explained if a contribution of the M^I-S coordinates (or, at least, of the $Ag-S$ ones) to the corresponding normal modes is assumed. It is to be recalled that the relative atomic mass of silver is less than that of thallium and any mode in which silver atoms move to a considerable degree should have a higher frequency than the similar mode in which thallium atoms participate. Obviously, the effect would be even more pronounced for modes in which, on the one hand, $Ag-S$ coordinates do participate and, on the other, the $Tl-S$ coordinates do not.

In order to clarify the situation, the frequency ratios were calculated for each of the three bands in the two thallium and two silver compounds. These ratios (obtained by dividing the frequency observed in the spectra of the trithioarsenate(III) of thallium (or silver) and in the trithioantimonate(III) spectrum and denoted As/Sb hereafter) were 1.10, 1.11 and 1.10 for the thallium compounds and 1.13, 1.09 and 1.05 for the silver ones. Another set of frequency ratios (denoted Ag/Tl) was obtained by dividing the frequency of each of the three bands in the spectrum of the silver compounds by those observed in the spectrum of the corresponding thallium compound. This time values of 1.02, 1.03 and 1.34 for the trithioarsenates(III) and 0.99, 1.04 and 1.41 for the trithioantimonates(III) were obtained.

Taken together these values suggest that the contribution of the $Tl-S$ coordinates to the normal modes giving rise to the observed bands is negligible (the As/Sb ratios for the three bands are practically constant in the case of the two thallium compounds), whereas the $Ag-S$ coordinates contribute to the normal modes in the case of the silver compounds. This contribution must increase as the frequencies of the bands decrease and be especially pronounced for the case of the modes giving rise to the bands found around 250 cm^{-1} or slightly higher (the Ag/Tl ratios are by far the largest for these bands).

These conclusions correlate well with the crystallographic data. As pointed out above, the $Ag-S$ bonds must have a substantial degree of covalence whereas the $Tl-S$ ones have a much higher degree of ionic character. Thus the approximation that we can treat the $M^{III}S_3$ groups as the units giving rise to the observed bands would be closer to the real situation in the case of the thallium compounds than in the case of the silver ones.

In fact, judging from the differences in the electronegativities of the end atoms, the order of the covalent character of the relevant bonds would be $\text{Tl-S} < \text{Ag-S} < \text{Sb-S} < \text{As-S}$. Thus the higher frequency of the bands in the spectra of the trithioarsenates(III) than in those of the trithioantimonates(III) may not be entirely due to the effect of the mass of the M^{III} atoms but partly to the smaller values of the Sb-S force constants as compared to those of the As-S ones.

Conclusions

The parallel analysis of the infrared spectra of the four compounds with the same general formula ($\text{M}^{\text{I}}_3\text{M}^{\text{III}}\text{S}_3$, where $\text{M}^{\text{I}} = \text{Tl}$ or Ag , and $\text{M}^{\text{III}} = \text{As}$ or Sb) made it possible to conclude that the Ag-S coordinates contribute to the normal modes giving rise to bands appearing in the $400-200\text{ cm}^{-1}$ region, especially to those to which the bands found around 250 cm^{-1} are due. On the other hand, the contribution of the Tl-S coordinates to the corresponding modes in the case of trithallium trithioarsenate(III) and trithallium trithioantimonate(III) must be much lesser and, perhaps, negligible.

Such conclusions are in line with the more pronounced covalent character of the Ag-S bonds as compared with the Tl-S ones. That the Ag-S bonds do have a more pronounced covalent character than the Tl-S ones can be deduced from the difference of the electronegativities of the end atoms and from the comparison of the observed Ag-S or Tl-S distances, on the one hand, and the sums of the atomic or ionic radii of the end atoms, on the other. The fact that the As-S or Sb-S distances are shorter in the case of the thallium compounds than in those of silver lends additional support to such a conclusion. If namely, the Ag-S bonds have a more covalent character than the Tl-S ones, the redistribution of the electron densities would make the As-S (or Sb-S) bonds weaker (and, thus, longer) in the silver than in the corresponding thallium compounds.

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