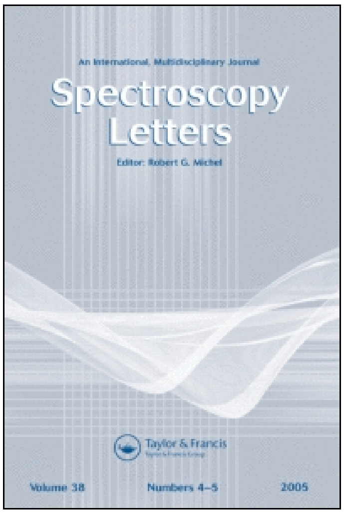

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Infrared Spectra of Three $M^IM^{III}S_2$ Type Synthetic Minerals: (M^I = Ag OR TI, M^{III} = Sb OR As)

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INFRARED SPECTRA OF THREE $M^IM^{III}S_2$ TYPE SYNTHETIC MINERALS

(M^I = Ag OR Tl, M^{III} = Sb OR As)

Keywords: Infrared spectra, synthetic minerals, smithite, lorandite, weissbergite, miargyrite

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ABSTRACT

The infrared spectra of three compounds of the $M^IM^{III}S_2$ type (smithite, $AgAsS_2$; weissbergite, $TlSbS_2$; and miargyrite, $AgSbS_2$) were studied at room temperature (RT) and at the boiling temperature of liquid nitrogen (LNT). The infrared spectrum of smithite was compared with that of the formally analogous mineral lorandite, $TlAsS_2$. Although the mentioned synthetic minerals have crystal structures which differ from each other, the infrared spectra of smithite and lorandite, on the one hand, and of weissbergite and miargyrite on the other, are similar. The anlysis of the spectra indicate that the Tl–S interaction has a more pronounced ionic character than the Ag–S one.

INTRODUCTION

Continuing our work on metal(I) thioarsenate(III) and metal(I) thioantimonates(III) [1-4], we now report the results of our infrared study of three synthetic minerals: smithite, $AgAsS_2$, weissbergite, $TlSbS_2$ and miargyrite, $AgSbS_2$. The infrared spectra of these compounds were compared with the spectrum of lorandite, $TlAsS_2$ [1,4], a mineral which has, at least formally, the same general formula ($M^IM^{III}S_2$).

To the best of our knowledge, the RT infrared spectra of smithite and weissbergite were for the first time mentioned (but not completely analyzed) by Povarennykh and Gerasimenko [5]. In an attempt to determine the symmetric type of the vibrations, the Raman and reflection infrared spectra of weissbergite have also been studied [6, 7].

The crystal structures of all studied compounds have been determined by X-ray diffraction methods. It was found that smithite crystallizes in the monoclinic space group $C2/c$ [8], weissbergite is triclinic, space group $P1$ [9, 10], while miargyrite belongs to the monoclinic system, space group Cc [11]. Lorandite also crystallizes in the monoclinic system, space group $P2_1/a$ [12, 13].

EXPERIMENTAL

The studied compounds were prepared by solid state reactions in sealed quartz tubes [14, 15].

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

CRYSTALLOGRAPHIC DATA

Three crystallographically different As atoms exist in the structure of smithite [8]. They are octahedrally coordinated by six S atoms, with three of the

As-S distances being significantly shorter than the other three contacts (Table 1). Each As atom is situated on the top of a trigonal AsS_3 pyramid, three such pyramids being linked together forming As_3S_6 groups. Three of the S atoms (denoted S_b*) belonging to the As_3S_6 groups are bonded to two As atoms each, forming a six-membered cyclohexane-type ring. The remaining three S atoms are terminal and are correspondingly denoted S_t. The As_3S_6 groups are mutually linked through four crystallographically non-equivalent Ag atoms. The Ag atoms are coordinated by 6 S atoms, forming four groups of four shorter Ag-S distances and four groups of longer Ag-S contacts - two for each crystallographically different silver atom (Table 1). Although the crystal structure of smithite, in general, differs from that of the formally analogous mineral lorandite [12, 13], the AsS_3 pyramids are the building blocks of both structures.

If, among the reported Tl-S distances in lorandite [13], all contacts larger than the sum of the ionic radii (334 pm) are excluded from consideration and an average is calculated from the remaining ones, a value of 311.6 pm is obtained. An analogous estimate leads to an average value of 267 pm for the Ag-S contacts in smithite [8] which is for 20 pm larger than the sum of the atomic radii while the difference between the average Tl-S distance and the sum of the atomic radii of thallium and sulfur is almost twice as large (≈ 39 pm). This indicates that, at least on the average, the Ag-S bonds have less pronounced ionic character than the Tl-S ones. As seen from Table 2, the difference of the electronegativities of sulfur and silver (0.65) is also smaller than the difference between the electronegativities of sulfur and thallium (0.75), this being in line with the already presumed more expressed covalent character of the Ag-S bonds in smithite compared to the Tl-S bonds in lorandite.

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[*] The subscript b stands for bridging.

Table 1. M^{III}-S and M^{I}-S distances (in pm) in the structures of AgAsS$_2$, TlAsS$_2$, TlSbS$_2$ and AgSbS$_2$

	AgAsS$_2$ [8]				TlAsS$_2$ [10]		TlSbS$_2$ [12]		AgSbS$_2$ [13]	
M^{III}-S	As(1)-S	As(2)-S	As(3)-S		As(1)-S	As(2)-S	Sb(1)-S	Sb(2)-S	Sb(1)-S	Sb(2)-S
	221	224	223		208	220	241	243	253	248
	233	228	228		229	230	245	246	258	249
	236	231	232		232	232	260	271	258	254
	306	328	326				296	281	314	326
	309	330	326				369	370	328	329
	333	340	334				261	261	325	334
M^{I}-S	Ag(1)-S	Ag(2)-S	Ag(3)-S	Ag(4)-S	Tl(1)-S	Tl(2)-S	Tl(1)-S	Tl(2)-S	Ag(1)-S	Ag(2)-S
	251	252	267	257	296	297	372	360	244	236
	256	255	267	257	307	301	373	361	250	246
	268	265	282	269	319	319	393	398	258	289
	284	290	282	269	331	323			272	315
	323	332	303	313	336	339			350	353
	337	362	303	313	348	363			355	353
					369	389				

Table 2. The values of the average of the experimentally determined interatomic distances in smithite and lorandite [8, 13], the difference in the electronegativities (Δx) the sum of the atomic radii (Σr_a) [16], and the sum of the effective ionic radii (Σr_i) [17] for Tl and S, Ag and S and As and S [18]

Bond	Average distances/pm		Δx	Σr_a/pm	Σr_i/pm
	$TlAsS_2$	$AgAsS_2$			
Tl-S	312	-	0.75	273	334
Ag-S	-	267	0.65	247	299
As-S	225	228	0.40	223	242

The structure of weissbergite [10] consists of layers formed by two crystallographically non-equivalent SbS_4 trigonal bipyramids. The Sb atoms are situated at the center of the trigonal base of the bipyramid and are bonded to two equatorial (S_e) and two axial S atoms (S_a). The Sb-S_e distances are shorter than the Sb-S_a ones.

The structure of miargyrite [11] is also build up of layers, but this time they are formed by SbS_3 pyramids linked through Ag atoms. The pyramids form pairs bridged by two S atoms. The pyramidal pairs are connected to each other via Ag atoms and diagonally situated chains are thus formed along the unit cell. Both non-equivalent Sb atoms are coordinated to six S atoms, forming three shorter and three longer Sb-S contacts (Table 1).

RESULTS AND DISCUSSION

In the LNT infrared spectrum of smithite (Fig. 1) there are 10 bands in the 500-150 cm^{-1} region. Their frequencies agree well with those presented by Povarennykh and Gerasimenko [5].

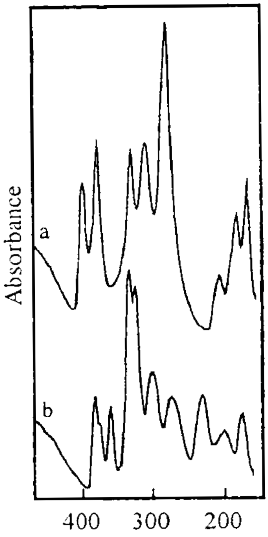

Fig. 1. Infrared spectra of lorandite (a) and smithite (b)

As previously mentioned, smithite and lorandite crystallize in different space groups, but the presence of AsS_3 pyramids in the structures of the two compounds is reflected in the similarity of their infrared spectra (Fig. 1). Naturally, the existing structural differences lead to differences in the spectral appearance as well. Thus, the longer As-S distances in smithite than in lorandite (Table 1 and Table 2) are mirrored in the appearance of two As-S_t stretching bands at lower frequencies (385 and 363 cm^{-1}) than in the lorandite spectrum (403 and 384 cm^{-1}) [1, 4].

The next group of three bands in the smithite spectrum (they appear around 334, 326 and 306 cm^{-1}) corresponds to the similar group in the spectrum of lorandite (336, 316 and 290 cm^{-1}) already attributed to S_b-As-S_b stretchings [4]. Again as in lorandite, the band at 278 cm^{-1} is interpreted as due to one (or more) of the S-As-S bending vibrations.

The ratios between the frequencies of each of the three bands at the lowest frequency region in the smithite spectrum (230, 202 and 175 cm^{-1}) and those of the three similar bands in the spectrum of lorandite (1.08, 1.07 and 1.02 respectively) correspond approximately to the expected value (1.06) for the hypothetical diatomic Ag-S and Tl-S molecules in which the force constants would be of the same magnitude. Taking into account the likelihood of the Ag-S interactions being more covalent in character than the Tl-S ones, it is difficult to assign unequivocally these bands to modes which are mainly M^I-S stretchings in character, despite the fact that their frequencies are similar to those of the bands which, in the spectra of some $M^{I}_{3}M^{III}S_3$ type compounds, were assigned [2] to modes with a noticeable participation of the M^{I}-S stretching coordinates. It is more likely that the modes in the present case are mixed, the observed frequencies being a result of superimposed mass and force-constant effects.

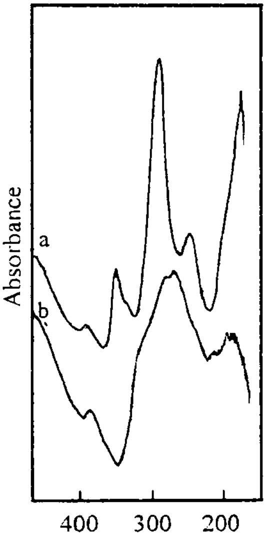

Fig. 2. Infrared spectra of weissbergite (a) and miargyrite (b)

The situation encountered in the case of the lorandite–smithite pair is roughly repeated in the case of weissbergite and miargyrite. These two compounds again crystallize in different space groups [9-11] but, in spite of that, their infrared spectra are rather similar (Fig. 2). However, it should be mentioned that the infrared spectrum of miargyrite is of poor quality (probably because the low crystallinity of this synthetic mineral) and this fact renders impossible the detailed spectral analysis.

In the 500-150 cm^{-1} region of the infrared spectrum of weissbergite there are four bands (at 345, 286, 245 and 170 cm^{-1}) as well as a shoulder (at 332 cm^{-1}). A similar spectral picture has been observed by Povarennykh and Gerasimenko [5], the frequencies in our spectrum being somewhat higher. In the same spectral region of the spectrum of miargyrite (500-150 cm^{-1}) there are two bands at 270 and 185 cm^{-1}, the higher-frequency one being flanked by four shoulders at 385, 320, 280 and 220 cm^{-1}.

The highest frequency band in the spectrum of weissbergite (345 cm^{-1}) and the shoulder at 332 cm^{-1} (Fig. 2) are assigned to the S_e-Sb-S_e vibrations. The relatively small difference between these two frequencies is in agreement with the small differences between the Sb-S_e distances in the two SbS_4 polyhedra (Table 1) [9, 10]. It is also in agreement with the results of the investigation of the reflection infrared spectrum of oriented monocrystals of $TlSbS_2$ reported by Goullet et al. [7].

The strongest band in the spectrum of weissbergite (286 cm^{-1}) is attributed to the S_a-Sb-S_a stretchings. The very high intensity of this band is probably influenced by the existence of a number of similar Sb-S distances.

The band at 245 cm^{-1} in our spectrum of weissbergite can be attributed to the S-Sb-S bending vibration, in line with the assignment of the band at 244 cm^{-1} given by Povarennykh and Gerasimenko [5].

The lowest frequency band (170 cm^{-1}) observed in our spectrum of weissbergite could be attributed to the Tl-S stretching vibration, in line with the assignments found in the literature according to which the bands in the region bellow 170 cm^{-1} in the spectra of thallium containing minerals are treated as due to ν(Tl-S) vibrations [5-7].

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