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INFRARED ABSORPTION SPECTRA OF SWEDENBORGITE AND QUEITITE

ALEXANDER S. POVARENNYKH
Institute of Geochemistry and Physics of Minerals, Academy of Sciences of the Ukrainian SSR, Palladin Prosp., Kiev–68, USSR

PAUL KELLER
Institut für Mineralogie and Kristallochemie der Universität Stuttgart, Pfaffenwaldring 55, D–7000, Stuttgart, West Germany

ROY KRISTIANSEN
P.O. Box 19, No-1652 Torp, Norway

ABSTRACT

Infrared absorption spectra of swedenborgite $NaBe_4SbO_7$ and queitite $Pb_4Zn_2(SO_4)(SiO_4)(Si_2O_7)$ are reported. Swedenborgite from the Långban deposit, Sweden, has nine absorption bands in its IR spectrum, whereas queitite, from the Tsumeb deposit, Namibia (S.W. Africa), has a more complicated spectrum with fourteen absorption bands.

Keywords: swedenborgite, queitite, infrared spectra, absorption bands, Långban, Tsumeb.

SOMMAIRE

On présente les spectres d'absorption infrarouge de la swédenborgite $NaBe_4SbO_7$ et de la queitite $Pb_4Zn_2(SO_4)(SiO_4)(Si_2O_7)$. La swédenborgite, du gisement de Långban (Suède), montre neuf bandes d'absorption dans l'infrarouge. La queitite, du gisement de Tsumeb (Namibie), possède un spectre plus compliqué, montrant quatorze bandes d'absorption.

(Traduit par la Rédaction)

Mots-clés: swédenborgite, queitite, spectre d'absorption infrarouge, bandes d'absorption, Långban, Tsumeb.

INTRODUCTION

Study of the infrared absorption of minerals has become increasingly popular in recent years; the spectra, which can be obtained quickly at modest cost, provide important data about the chemistry and chemical bonding. Interpretation of IR spectra gives information on acid radicals, atomic co-ordination, valence, mass and other structural features of minerals (Povarennykh 1978). Reference books on IR spectra of minerals (*e.g.*, Farmer 1974) permit the detailed analysis of a large variety of species according to the position and intensity of their infrared absorption bands.

Swedenborgite $NaBe_4SbO_7$ and queitite $Pb_4Zn_2(SO_4)(SiO_4)(Si_2O_7)$ are minerals whose IR spectra are unknown. Swedenborgite has, to date, only been found at the Långban deposit in Sweden (Pauling *et al.* 1935). With space group $P6_3mc$, it has a unique structure in which the Be atoms have four-fold co-ordination and Sb atoms six-fold co-ordination; all tetrahedra and octahedra are connected by vertices only. There are four common vertices for BeO_4 tetrahedra and three common vertices for two BeO_4 tetrahedra and one SbO_6 octahedron. The Na ions, in twelve-fold co-ordination, occur in large cavities between the larger atoms. The interatomic distances Me–O_n correspond to normal medium-size distances characteristic of Be–O_4 and Sb–O_6 bonds (the absorption band of Na–O_{12} is < 400 cm^{-1} and thus beyond the range of measurement).

Queitite was described recently from Tsumeb, Namibia (S.W. Africa) by Keller *et al.* (1979) and the crystal structure determined by Hess & Keller (1980). Queitite, space group $P2_1$, has a compact structure built up from SiO_4 tetrahedra, Si_2O_7 diortho groups and tetrahedra of SO_4 radicals. These polyhedra are bound by ZnO_4 and PbO_{8-9} polyhedra into a compact structure with a sublayer motif parallel to the *ab* plane.

SAMPLES INVESTIGATED AND EXPERIMENTAL

The samples studied came from the personal collections of P. Keller (queitite) and R. Kristiansen (swedenborgite). The identity of both minerals was ascertained by optical methods, and their purity by spectrographic analyses. The latter gave very minor impurities (less than 0.1%) of Al, Cu, Sb, Bi and Ge in queitite and K, Mg and Sn in swedenborgite.

The infrared absorption spectra of these minerals were recorded using the KBr pellet method in which 400 mg KBr was added to 1.5 mg of each mineral. The IR spectrophotometer (type UR–20) has a dispersion of 4000–400 cm^{-1}. The equation for the relative bond-strength $\sigma = k\,(V_k \cdot V_a)/CN \cdot d\sqrt{M}$ was used to determine assignments of the main absorption-bands (V_k and V_a are valences of cation and anion; k is the coefficient of relative bond-strength, which varies from 1 to 2 according to the degree of covalency of the bond; CN is the co-ordination number of cation; d is the interatomic distance cation–anion; M is the reduced mass of cation, equal to the sum of atomic weights of a given cation and of all anions that co-ordinate it (Povarennykh 1978). This equation, together with an additional coefficient A, allows a calculation of the frequency of each valent vibration in the IR spectrum according to the relation $\nu_3 = A\sigma$ cm^{-1} (Povarennykh 1978).

RESULTS

Swedenborgite

Assuming that the accuracy of the 1935 measurements of interatomic distances was relatively poor, we may consider that the BeO_4 and SbO_6 polyhedra are slightly distorted, giving rise to some doubled absorption-bands. Thus, the peaks at 906 and 808 cm^{-1} correspond to the ν_3 vibrations for BeO_4 tetrahedra, and those at 750 and 720 cm^{-1} are characteristic of SbO_6 octahedra (Table 1, Fig. 1). The weaker absorption bands at 638 and 576 cm^{-1} also belong to valent bond vibrations of distorted SbO_6 octahedra, as shown in the IR spectra of complex antimony oxides such as byströmite, tripuhyite, ordonezite and schafarzikite (Povarennykh 1979). The maxima at 470, 434 and 407 cm^{-1} may be assigned to deformational vibrations ν_4 of Be–O bonds as observed in IR spectra of beryllium minerals such as bromellite, chrysoberyl, and taaffeite and of other minerals with Be–oxygen bonds, such as many silicates (bavenite, chkalovite, phenakite, beryl) and phosphates (hurlbutite, beryllonite, moraesite) (Povarennykh 1979).

TABLE 1. ABSORPTION BANDS IN INFRARED SPECTRA OF SWEDENBORGITE AND QUEITITE BETWEEN 4000 AND 400 cm^{-1}

$NaBe_4SbO_7$ cm^{-1}	I*	Tentative assignment**	$Pb_4Zn_2[SO_4][SiO_4][Si_2O_7]$ cm^{-1}	I*	Tentative assignment**
906	m	$\nu_3(Be\text{-}O_4)$	1168	vs	$\nu_3(S\text{-}O_4)$
808	vs				
			1077	vs	$\nu_3(O\text{-}Si\text{-}O)$
750	vs	$\nu_3(Sb\text{-}O_6)$	1062	m	
720	m		1038	vs	
			956	vs	$\nu_3(Si\text{-}O_4)$
638	vw	$\nu_3(Sb\text{-}O_6)$	928	m	
576	vw		874	vs	
			828	m	
470	vw	$\nu_4(Be\text{-}O_4)$	656	m	$\nu_4(S\text{-}O_4)$
434	vw		620	vw	
407	vs		592	s	$\nu_4(O\text{-}Si\text{-}O)$
			512	vs	$\nu_4(Si\text{-}O_4)$
			486	vs	
			446	m	$\nu_3(Zn\text{-}O_4)$

I* relative absorption-band intensity denoted as follows: vs very strong, s strong, m medium, vw very weak.
** ν_3 bond-stretching vibrations, ν_4 bond-bending deformation.

Queitite

The greater accuracy of the 1980 structural work on queitite permits a better interpretation

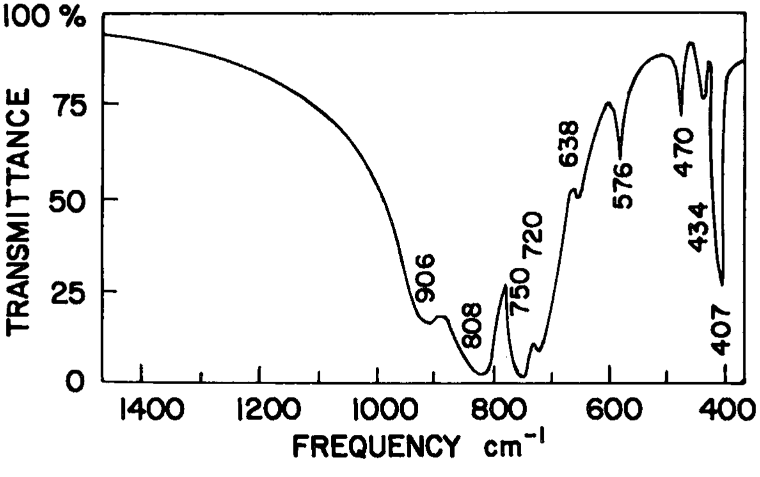

FIG. 1. Infrared absorption spectrum of swedenborgite $NaBe_4SbO_7$.

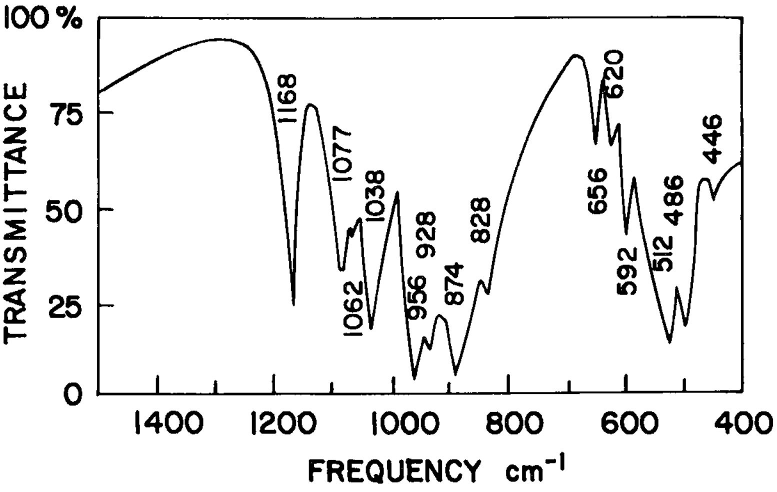

FIG. 2. Infrared absorption spectrum of queitite $Pb_4Zn_2[SO_4][SiO_4][Si_2O_7]$.

of its IR spectrum (Fig. 2). For example, the sharp absorption-peak at 1168 cm^{-1} undoubtedly is due to valent vibrations v_3 of the radical $S–O_4$ bonds, which vary very slightly in their lengths (medium bond-length 1.48 Å). The SiO_4 tetrahedra have outer Si–O bonds in Si_2O_7 diortho groups and stronger bridge O–Si–O bonds in diortho groups. The peaks at 1077, 1062 and 1038 cm^{-1} are assigned to v_3 vibrations for O–Si–O valent bonds and at 956, 928, 874 and 828 cm^{-1} to $Si–O_4$ bond vibrations. Two lower-intensity absorption-bands at 656 and 620 cm^{-1} correspond to deformational vibrations v_4 of $S–O_4$ bonds. An absorption band at 592 cm^{-1} may be due to deformational vibrations of O–Si–O bridge bonds (see Table 1). The peaks at 512 and 486 cm^{-1} represent the strongest absorption-bands owing to deformational vibrations of the large $Si–O_4$ bonds. The valent $Zn–O_4$ vibrations v_3, produced by the weakest bonds in the structure, are represented by the peak at 446 cm^{-1}. The Pb–O bond vibrations, as expected, do not register in the 4000–400 cm^{-1} region owing to the highly co-ordinated Pb atoms (eight- and nine-fold).

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