

SHORT COMMUNICATIONS

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The infrared absorption spectra of the three polymorphs of $\text{PbSO}_4(\text{CO}_3)_2(\text{OH})_2$ (leadhillite, susannite, and macphersonite)

MROSE AND CHRISTIAN (1969) reported an investigation, including infrared (IR) spectroscopy, of leadhillite and its high-temperature dimorph susannite, but no spectral details have appeared in

the literature. This omission, and the recent discovery of a third polymorph—macphersonite (Livingstone and Sarp, 1984)—has prompted this communication, the main purpose of which is to

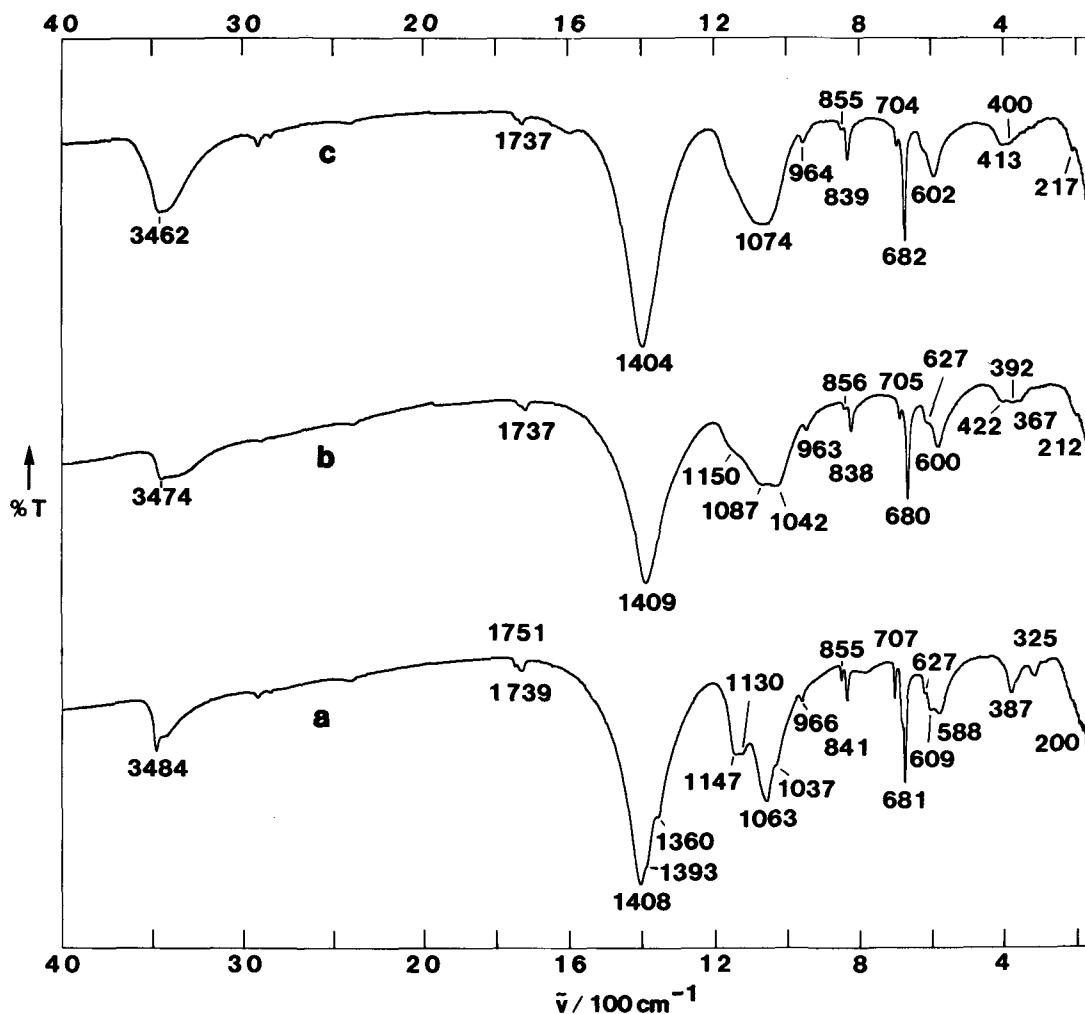


FIG. 1. Infrared spectra of $\text{Pb}_4\text{SO}_4(\text{CO}_3)_2(\text{OH})_2$ polymorphs: a, macphersonite; b, leadhillite; c, susannite. 0.8 mg in 13 mm CsI pressed disks recorded on Perkin Elmer 580B spectrometer.

show, first, that the three polymorphs can be distinguished by their IR spectra, and, secondly, that the spectra can be interpreted to give some information on the environment of the carbonate, sulphate, and hydroxide anions in the three structures.

The IR spectra of the polymorphs, all of which originate in Leadhills, Scotland, are very similar (fig. 1) as would be expected from their identical compositions. However, the sharpness and complexity of absorption bands decrease in the order macphersonite > leadhillite > susannite, an observation which reflects the decreasing symmetry of their respective space groups, D_{2h}^{15} , C_{2h}^5 , C_{3i}^2 , and crystal systems, orthorhombic, monoclinic, and trigonal.

Several specimens designated susannite were examined by IR during the investigation. It was found that those which were green coloured, uniaxial and therefore susannite, gave the spectrum shown in fig. 1c, whereas those which were white to pale yellow in colour and biaxial gave the spectrum of leadhillite (fig. 1b). Electron probe microanalysis failed to reveal any additional ionic species in the green susannite which might explain its colour. Although the structures of the three polymorphs are not yet known, certain information about the environments of the three anions can be deduced from the spectra.

Hydroxyl groups. The steadily increasing frequency of the hydroxyl stretching band which appears at 3462 cm^{-1} in susannite, 3474 cm^{-1} in leadhillite, and 3484 cm^{-1} in macphersonite, and also a corresponding increase in sharpness of these bands, indicate an increase in $\text{OH} \dots \text{O}$ distances from about 2.87 to 2.90 Å using the relationship between stretching frequencies and O–O distances in hydrogen bonds described by Nakamoto *et al.* (1955). Pressed disks of the three polymorphs contain only small amounts of adsorbed water and consequently spectra in the OH stretching region show little change after heating the disks for several hours at 100°C . Broad absorption remaining in the range $3450\text{--}3250\text{ cm}^{-1}$ is strongest in susannite (fig. 1c) and weakest in macphersonite (fig. 1a) indicating that more of the OH groups in susannite are involved in a larger range of OH \dots O distances.

Carbonate ions. Absorption bands arising from vibrations of the carbonate ion do not vary significantly from susannite to leadhillite (fig. 1b, c), but in macphersonite they exhibit well-resolved fine structure on the ν_3 vibration in the 1400 cm^{-1} region, and also on the ν_4 vibration near 680 cm^{-1} ; under higher resolution and slower scan speeds, this latter band shows a closely spaced weak doublet at 691 and 687 cm^{-1} (fig. 2a), features not resolved in spectra of the other two polymorphs

(fig. 2b, c). This enhanced multiplicity of carbonate bands suggests more crystalline regularity of the carbonate sites in macphersonite.

Sulphate ions. Sulphate vibrations show the same trend as carbonate vibrations, ν_3 near 1070 cm^{-1} and ν_4 near 600 cm^{-1} exhibiting the most clearly resolved splitting in macphersonite; these bands are essentially broad and unresolved in susannite, and only partially resolved in leadhillite. The marked splitting in macphersonite particularly of the ν_3 sulphate band, which is an F_2 stretching mode, is again indicative of the greater crystallinity of this polymorph.

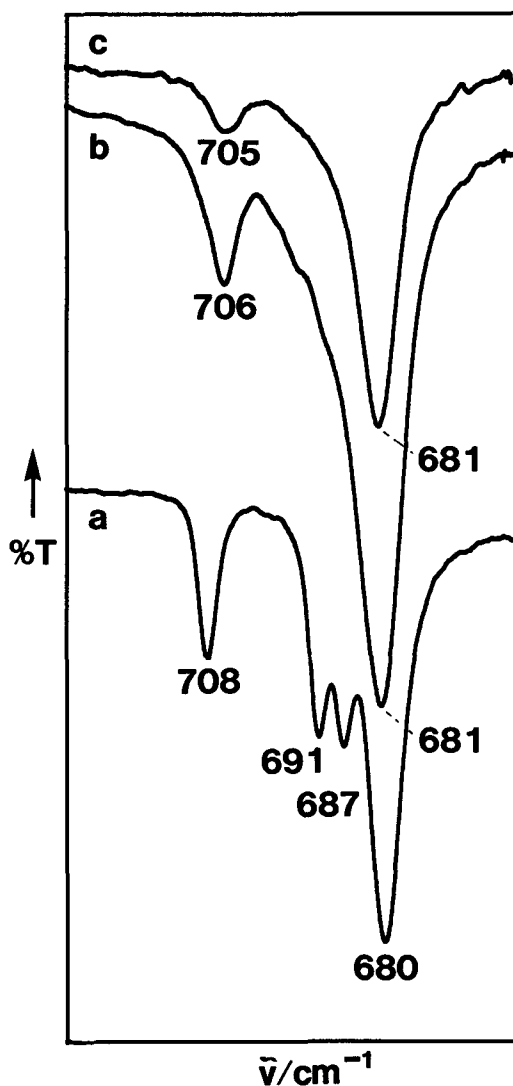


FIG. 2. As fig. 1, but recorded with higher resolution.

All three polymorphs exhibit a single broad asymmetric band at 140 cm^{-1} (not shown), the assignment of which is not known.

Conclusions. The variation in spectra described here for the three polymorphs differs from that described previously for various specimens of leadhillite (*sensu strictu*) by Russell *et al.* (1983) who showed that the relative intensity of OH, CO_3 , and SO_4 absorption bands varied, and proposed that mutual substitution of these ions occurs within the leadhillite structure.

The X-ray powder pattern of macphersonite is distinctly different from those of susannite and leadhillite (Livingstone and Sarp, 1984), which themselves, as reported by Mrose and Christian (1969), are virtually indistinguishable. It is shown here, however, that all three polymorphs are readily distinguished by their IR spectra. Moreover, the

appearance in a high resolution IR spectrum of the closely spaced $691, 687\text{ cm}^{-1}$ doublet may be diagnostic for macphersonite.

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Discovery of volkonskoite

STANDARD texts (Ross and Hendricks, 1945; Hey, 1955; Strunz, 1966; Nemeč, 1981) all attribute the first description of the mineral volkonskoite to Kämmerer (1831). However, in his account (taken from the letter, dated 10 April 1831, he sent from 'Petersburg' to von Leonhard) Kämmerer merely states:

'Im vorigen Sommer wurde im Ochansky'schen Kreise des Gouvernements Perm ein neues Mineral entdeckt; das zu Ehren des Herrn Ministers des Kaiserlichen Hofes, Fürsten Wolchonskoy, Wolchonskoit, benannt worden ist . . .'

and then goes on to give a description: nowhere does he claim to have found or named the mineral. Moreover, in his paper (which seems to have been largely neglected) giving the first analysis of volkonskoite, Berthier (1833) states that 'la découverte de cette substance a été annoncée dans le *Journal des mines russes* [my italics], l'année dernière'.

As this could not refer to Kämmerer's account, published in a German journal, a search was

instituted of *Gornyi Zhurnal* for the period between Summer 1830 and the appearance of Berthier's paper. This resulted in the discovery, in the issue published on 26 November 1830, of a paper (Anon. 1830) in Russian entitled, 'Description of the occurrence of a green-coloured mineral discovered on a certain estate in the Province of Perm and named in honour of Mr Minister of the IMPERIAL Court *Volkonskoite*'—an article that gives information on the stratigraphy of 'Mount Efimyata' (presumably near the village of Efimyata—Pustovalov, 1928), on which the mineral was found in July 1830, together with a detailed description of the mineral and its mode of occurrence. Unfortunately, it is anonymous and consequently the author (who clearly had first-hand information) cannot now be traced, although he might have been one of the editors of the journal or, perhaps, the 'apothecary Helm' who first detected the presence of chromium. As this was done in Ekaterinburg (now Sverdlovsk), the reference is most probably to F. Gustav Helm who described various mines and smelters in that