

Microwave techniques for the synthesis and deuteration of minerals, with particular reference to scorodite, $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$

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Abstract

Microwave dielectric heating methods for the preparation of a number of arsenate, phosphate, vanadate, molybdate and carbonate minerals and their deuterated analogues are reported; rapid and efficient syntheses of these have been achieved. The application of this to the study of vibrational spectroscopy of minerals is discussed, with particular reference to scorodite.

KEYWORDS: microwave techniques, synthesis, deuteration, scorodite.

Introduction

As part of our continuing interest in the vibrational spectra of minerals (Coleyshaw and Griffith, 1994; Griffith, 1969, 1970a, 1970b, 1974, 1975, 1987) we have sought to deuterate a number of arsenate, phosphate, molybdate and carbonate minerals containing water or hydroxyl groups in order to help in their vibrational assignment. However, obtaining deuterated minerals, most of which are insoluble in water, is not an easy matter since they have to be synthesised from deuterated reactants. In many cases there are either no published methods for preparations of the parent minerals, ill-defined procedures or inconvenient hydrothermal methods involving sealed tube reactions at high temperatures, e.g. for scorodite (Dutrillac and Jambor, 1988), phosphosiderite (Tarte and Pâques-Ledent, 1968) and hydrocerussite (Borgeois, 1886). We report here simple and convenient syntheses of a number of arsenate, phosphate, vanadate, molybdate and carbonate minerals using microwave dielectric heating and the deuteration of a number of these. Relatively little work has been reported in the area of mineral synthesis by microwave methods (Mingos and Baghurst, 1991); a number of zeolites have been made in this way, e.g. ferrierite, heulandite, faujasite and gmelinite (Vartuli *et al.*, 1988; Mingos and Baghurst, 1991) and we have recently reported an

efficient microwave synthesis of scorodite (Baghurst *et al.*, 1995).

Deuteration studies of minerals are of value in a number of ways. In materials containing aqua or hydroxy groups the preparation of the corresponding partially or completely deuterated materials is very helpful in assigning fundamental modes of vibration. Examples for which deuteration has been essential in such spectroscopic studies of minerals include gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Siedl *et al.*, 1969), kainite, $\text{KMgCl}(\text{SO}_4) \cdot 3\text{H}_2\text{O}$ (Mathew and Nayer, 1989), malachite, $\text{Cu}_2(\text{OH})_2\text{CO}_3$ and brochantite, $\text{Cu}_4(\text{OH})_6(\text{SO}_4)$ (Schmidt and Lutz, 1993), monetite $\text{Ca}(\text{PO}_3(\text{OH}))$ (Petrov *et al.*, 1967) and duttonite, $\text{VO}(\text{OH})_2$ (Ferrer and Baran, 1994). By using partial deuteration (the so-called isotopic dilution technique (Flörke, 1967; Falk and Knop, 1973)) the equivalence or non-equivalence of water molecules within a crystal lattice can be demonstrated even if there is crystallographic disorder; gypsum (Seidl *et al.*, 1969) and mitscherite $\text{K}_2[\text{CuCl}_4] \cdot 2\text{H}_2\text{O}$ (Thomas *et al.*, 1974) are classic cases demonstrating use of the technique. Deuteration can also help in assessing the importance of hydrogen-bonding in a material (e.g. in gypsum (Seidl *et al.*, 1969) or hydroxylapatite (Elliot, 1994; Fowler, 1974)). It can also be used in an analytical context: the presence of hydroxyl or aqua groups can be distinguished, and the presence of 'isolated' hydroxy groups (e.g. in hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) can be distinguished from hydroxy groups which are covalently bound to another atom, e.g. in monetite, $\text{Ca}(\text{PO}_3(\text{OH}))$ (Petrov *et al.*, 1967).

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TABLE 1. Microwave preparation of synthetic minerals

Mineral	Formula	Conditions of microwave experiment				Yield (%)	Colour	JCPDS Data
		Temp. (°C)	Pressure (bar)	Time (min)				
<i>Arsenates:</i>								
Scorodite	FeAsO ₄ ·2H ₂ O	145	9	40	70.3	pale green	37-0468	
Scorodite-d	FeAsO ₄ ·2 ² H ₂ O	150	9	40	56.0	pale green		
Mansfieldite	AlAsO ₄ ·2H ₂ O	170	9	40	67.6	white	23-0123	
Mansfieldite-d	AlAsO ₄ ·2 ² H ₂ O	170	9	60	21.8	white		
Köttigite	Zn ₃ (AsO ₄) ₂ ·8H ₂ O	170	9	60	15.9	white	1-0744	
Köttigite-d	Zn ₃ (AsO ₄) ₂ ·8 ² H ₂ O	170	9	60	9.7	white		
Olivenite	Cu ₂ AsO ₄ OH	170	9	100	25.0	pale green	42-1353	
Olivenite-d	Cu ₂ AsO ₄ O ² H	170	9	100	45.6	green		
Mimetite	Pb ₅ (AsO ₄) ₃ Cl	120	9	100	16.1	off-white	19-0683	
<i>Phosphates:</i>								
Berlinite (tridymite form)	AlPO ₄	170	9	60	7.3	white	20-0044	
Phosphosiderite	FePO ₄ ·2H ₂ O	150	9	160	26.5	pale pink	33-0666	
Phosphosiderite-d	FePO ₄ ·2 ² H ₂ O	150	9	160	22.3	pale pink		
Hopeite	Zn ₃ (PO ₄) ₂ ·4H ₂ O	170	9	60	12.1	white	37-0465	
Hopeite-d	Zn ₃ (PO ₄) ₂ ·4 ² H ₂ O	170	9	100	9.8	white		
Libethenite	Cu ₂ PO ₄ OH	170	9	100	83.6	olive green	36-0404	
Libethenite-d	Cu ₂ PO ₄ O ² H	170	9	160	52.1	dark green		
Pyromorphite	Pb ₅ (PO ₄) ₃ Cl	120	9	100	26.3	off-white	19-0701	
Hydroxyapatite	Ca ₅ (PO ₄) ₃ (OH)	120	9	60	8.9	white	9-0432	
Iron phosphate hydroxide	Fe ₄ (PO ₄) ₃ (OH) ₃	170	9	40	44.4	dark green	42-0429	
<i>Vanadates:</i>								
Vanadinite	Pb ₅ (VO ₄) ₃ Cl	120	9	100	12.6	off-white	19-0684	
<i>Molybdate:</i>								
Lindgrenite	Cu ₃ (MoO ₄) ₂ (OH) ₂	170	9	100	17.4	bright green	36-0405	
Lindgrenite-d	Cu ₃ (MoO ₄) ₂ (O ² H) ₂	170	9	100	32.3	bright green		
<i>Carbonates:</i>								
Hydrocerussite	Pb ₃ (CO ₃) ₂ (OH) ₂	170	9	160	14.2	white	13-0131	
Deuteroicerussite	Pb ₃ (CO ₃) ₂ (O ² H) ₂	170	9	160	8.8	white		
Plumbonacrite	Pb ₁₀ O(CO ₃) ₆ (OH) ₆	170	9	160	10.3	white	19-0680	
Sodium lead carbonate hydroxide	NaPb ₂ (CO ₃) ₂ OH	170	9	160	89.8	white	37-0501	

Experimental

Chemicals were purchased from Aldrich and used without further purification.

Microwave conditions. These are listed in Table 1. Microwave syntheses were carried out in a sealed Teflon autoclave (capacity 100 cm³) using a CEM MDS 2000 Microwave Cavity, with maximum power, temperatures and pressures of 1.1 kW,

200°C and 17 bar respectively. During exposure the temperatures of the solutions were maintained constant at preset values for the times stated in Table 1 and the associated pressures were monitored via a Teflon tube to a transducer outside the oven.

Preparation of minerals and their deuterates. The quantities and conditions for the starting solutions before microwave heating are given below. All the mixtures used for microwave heating were homo-

geneous unless otherwise indicated. All deuteration were prepared under a dry dinitrogen atmosphere to minimise $\text{H}_2\text{O} - {}^2\text{H}_2\text{O}$ exchange. The products were fine microcrystalline powders.

Vibrational spectra. Infrared spectra were recorded on a Perkin Elmer FTIR 1720 spectrometer and ATI Matson Research Series FT IR in the region 4000 to 220 cm^{-1} with a resolution of 2 cm^{-1} . All minerals were finely ground and their spectra recorded as KBr pellets. Raman spectra were recorded on a Perkin Elmer Fourier Transform Raman 1700 \times spectrometer with a Spectron Nd : YAG laser with 1064 nm excitation. Mineral samples were placed as powders in glass capillary tubes. The spectral resolution was 2 cm^{-1} ; in most cases 50 scans were taken with laser powers up to 1 W.

XRD data. These were measured on a Siemens D-500 instrument using $\text{Cu-K}\alpha$ radiation and matched with data from the JCPDS powder diffraction file. The numbers given in the right hand column of Table 1 are those to XRD patterns of materials from the file; original references are also given where appropriate. In all cases the XRD patterns of the deuterated minerals were very similar to those of the parent materials.

Arsenates

Scorodite, $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$, was prepared from anhydrous FeCl_3 (0.162 g., 1.0 mmol.) in 10 cm^3 of water and $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (0.312 g., 1.0 mmol.) in 10 cm^3 of water with the pH adjusted to 1 with HCl. The deuterate $\text{FeAsO}_4 \cdot 2{}^2\text{H}_2\text{O}$ was prepared in analogous fashion but using half-quantities, ${}^2\text{H}_2\text{O}$ replacing water. $\text{Na}_2{}^2\text{HAsO}_4$ was made from Na_2HAsO_4 (0.312 g., 1.0 mmol.) by one recrystallization from ${}^2\text{H}_2\text{O}$ (5 cm^3). The pH control was effected with ${}^2\text{HCl}$. For the 10% deuterated sample no recrystallization of the starting materials was necessary; 3 cm^3 ${}^2\text{H}_2\text{O}$ was added to a total of 20 cm^3 H_2O and normal reagents used as above.

Mansfieldite, $\text{AlAsO}_4 \cdot 2\text{H}_2\text{O}$, was made from $\text{Al}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ (0.342 g., 1.0 mmol.) in 10 cm^3 of water with $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (0.642 g., 2.0 mmol.) in 10 cm^3 water or ${}^2\text{H}_2\text{O}$ and the pH adjusted to 2 with $2\text{M H}_2\text{SO}_4$. For the deuterate, half-quantities were used and the hydrated starting materials were first recrystallized from ${}^2\text{H}_2\text{O}$. It was noted that higher temperatures and pressures were needed for preparation of mansfieldite than of scorodite and similarly for the deuterates.

Köttigite, $\text{Zn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$, was made from $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.595 g., 1.0 mmol.) in 20 cm^3 of water mixed with $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (0.312 g., 1.0 mmol.) in 10 cm^3 of water. For the deuterated mineral half quantities were used, and hydrated starting materials were first recrystallized from ${}^2\text{H}_2\text{O}$.

Olivenite, $\text{Cu}_2(\text{AsO}_4)(\text{OH})$, was made from $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.483 g., 1.0 mmol.) in 20 cm^3 of water mixed with $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (0.312 g., 1.0 mmol.) in 10 cm^3 of water. The deuterate was made similarly by a single recrystallization of $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ from 5 cm^3 of ${}^2\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in 10 cm^3 of ${}^2\text{H}_2\text{O}$ and the solutions mixed.

Mimetite, $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$, was prepared by a modification for microwave synthesis based on the preparative procedure of Baker (1966). A stock solution of PbCl_2 (7.108 g., 25.5 mmol.) was prepared with 250 cm^3 of H_2O and 10 cm^3 of this solution was mixed with a similar quantity of a solution of $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (0.2 g., 0.64 mmol.).

Phosphates

Berlinite (tridymite form), AlPO_4 , was prepared by modification of the hydrothermal method of Morales and Clemente (1990). Solutions of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.75 g., 2.0 mmol.) and KH_2PO_4 (0.27 g., 2.0 mmol.) both in 10 cm^3 water were mixed.

Phosphosiderite (metastrengite), $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$, was prepared by an adaptation of the hydrothermal procedure of Tarte and Pâques-Ledent (1968). Anhydrous FeCl_3 (3.0 g., 18.5 mmol.) in 4 cm^3 of 4M HCl , 1 cm^3 of $15\text{M H}_3\text{PO}_4$ and 12.5 cm^3 H_2O were mixed. The deuterate was made similarly in ${}^2\text{H}_2\text{O}$ using ${}^2\text{HCl}$ and ${}^2\text{H}_3\text{PO}_4$ acids diluted with ${}^2\text{H}_2\text{O}$.

Hopetite, $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, was prepared by mixing solutions of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (0.358 g., 1.0 mmol.) in 10 cm^3 of water with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.595 g., 1.0 mmol.) in 20 cm^3 of water. The deuterate was similarly prepared after recrystallization of both starting materials from 5 cm^3 portions of ${}^2\text{H}_2\text{O}$.

Libethenite, $\text{Cu}_2(\text{PO}_4)(\text{OH})$, was prepared by a method based on the room temperature procedure of Toman (1978) by mixing $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (3.58 g., 10 mmol.) in 10 cm^3 of water with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (3.75 g., 15.0 mmol.) in 10 cm^3 of water. The deuterate was made similarly in ${}^2\text{H}_2\text{O}$ using half quantities, with starting materials recrystallized twice from ${}^2\text{H}_2\text{O}$.

Hydroxylapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, was prepared by an adaptation for microwave synthesis of the preparation of Bett *et al.* (1967). A solution of $\text{Ca}(\text{OH})_2$ (0.287 g., 3.87 mmol.) was made up with 184 cm^3 of water and stirred for 30 minutes under dinitrogen. To this 3 cm^3 of 0.769 M H_3PO_4 was added dropwise and the solution stirred for a further 30 minutes. 35 cm^3 of the resulting solution was subjected to microwave heating.

Pyromorphite, $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$, was prepared as for mimetite: 10 cm^3 of the PbCl_2 stock solution used for the mimetite preparation was mixed with 10 cm^3 of a solution of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (0.2 g., 0.56 mmol.).

Iron phosphate hydroxide, $\text{Fe}_4(\text{PO}_4)_3(\text{OH})_3$, was obtained as a result of an attempt to prepare strengite, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$. A solution of $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ (0.49 g., 1.0 mmol.) in 10 cm^3 water was added to Na_2HPO_4 (0.28 g., 1.97 mmol.) in 10 cm^3 water, the mixture adjusted to pH 2.7 with 2M H_2SO_4 . At this pH the starting solution contained a gel-like precipitate.

Vanadate

Vanadinite, $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$, was prepared by mixing 10 cm^3 of the PbCl_2 stock solution used for the preparation of mimetite mixed with a solution of $\text{Na}_3[\text{VO}_4] \cdot 14\text{H}_2\text{O}$ (0.2 g, 0.46 mmol.) in 10 cm^3 of water.

Molybdate

Lindgrenite, $\text{Cu}_3(\text{MoO}_4)_2(\text{OH})_2$, was prepared by dissolving $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.483 g., 1.0 mmol.) in 20 cm^3 of water; this was mixed with $\text{K}_2[\text{MoO}_4]$ (0.238 g., 1.0 mmol.) in 10 cm^3 of water. The deuterate was similarly prepared by dissolving half quantities of both starting materials in $^2\text{H}_2\text{O}$.

Carbonates

Hydrocerussite, $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$, was made by a method based on that used for room temperature by Taylor and Lopata (1984). A suspension of cerussite, PbCO_3 (0.213 g., 0.80 mmol.) (previously prepared by passing carbon dioxide through a solution of $\text{Pb}(\text{OAc})_2$ in 20 cm^3 of water was adjusted to pH 11 with $1 \times 10^{-3} \text{ M}$ NaOH . The mixture was then subjected to microwave heating. The deuterated form was similarly made by using NaO^2H and $^2\text{H}_2\text{O}$.

Plumbonacrite, $\text{Pb}_{10}\text{O}(\text{CO}_3)_6(\text{OH})_6$, was made from hydrocerussite made as above (0.5 g., 0.64 mmol.) suspended in an aqueous solution of 0.23 molar K_2CO_3 and 0.09 molar aqueous KOH (20 cm^3) and the mixture subjected to microwave heating.

Sodium lead carbonate hydroxide, $\text{NaPb}_2(\text{CO}_3)_2\text{OH}$, was obtained when NaOH was used in place of KOH during the preparation of plumbonacrite above.

Results and discussion

Preparation of deuterated minerals and related species

The synthetic minerals prepared as part of this study are listed in Table 1 together with the microwave conditions used. In all cases the products were characterised by their XRD patterns; where published data were available the products were also characterised by their infrared and Raman spectra.

It is clear that microwave dielectric heating methodology described in this paper could be of real value to the geologist or mineralogist: the method is relatively simple and the equipment not unduly costly. In this study we have prepared minerals from the variscite, apatite, vivianite and pyromorphite groups, and is likely that many other members of these and of other mineral groups could be made by microwave methods. Nevertheless, at this preliminary stage, it is clear that microwave procedures for mineral preparations require more careful study and control of conditions, starting materials etc. In some cases phosphates can be prepared in similar fashion to the corresponding arsenates: thus the preparations of pyromorphite and vanadinite were achieved by a straightforward adaptation of the procedure developed for mimetite. However, we are so far unable to obtain strengite by an adaptation of the microwave procedure successfully used for the preparation of scorodite (a basic phosphate, $\text{Fe}_4(\text{PO}_4)_3(\text{OH})_3$, was obtained instead and identified by its XRD pattern): the reasons for this are not clear. Similarly, while hydrocerussite could easily be made and deuterated by an adaptation of the literature method (Taylor and Lopata, 1984), difficulties were encountered in the preparation of plumbonacrite because sodium from sodium hydroxide used in the preparation became incorporated into the product and the basic carbonate $\text{NaPb}_2(\text{CO}_3)_2\text{OH}$ was formed instead. Our microwave procedure designed for the preparation of tarbuttite, $\text{Zn}_2\text{PO}_4\text{OH}$, unexpectedly gave hopeite, $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, while that designed for adamite, $\text{Zn}_2\text{AsO}_4\text{OH}$, gave köttigite, $\text{Zn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$. Scorodite was prepared in a manner similar to that described by us earlier (Baghurst *et al.*, 1995) but with modifications; FeCl_3 , $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ and ^2HCl were used since the $^2\text{H}_2\text{SO}_4$ supplied appeared to contain substantial amounts of H_2SO_4 .

In the course of this work we prepared (and have included in Table 1) some minerals which do not contain protons, and also some basic phosphates and basic carbonates for which confirmatory XRD data are available, allowing their unambiguous identification, but for which there are no known natural occurrences.

Vibrational spectra of normal and deuterated minerals

In Table 2 our Raman and infrared data for the normal and deuterated minerals prepared by microwave methods are summarized. Only those bands attributable to ν_{OH} and to $\nu_{\text{O}^2\text{H}}$, the O—H or O— ^2H stretches of the aqua or hydroxyl groups in the material and to δ_{HOH} and $\delta_{\text{HO}^2\text{H}}$, the bending modes in those minerals containing water have been cited. It can be seen that the absence of a bending mode near 1600 cm^{-1} indicates that the mineral is hydroxy- rather than

TABLE 2. Spectroscopic data for aqua and hydroxy groups in synthetic and deuterated minerals

Mineral	Formula	VOH	VOH	δ_{HOH}	δ_{HOH} (cm^{-1})	Other Refs.
Scorodite	$\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$	IR	3511 s, sh, 2927 br, s	1587m,r		Pâques-Ledent and Tarte, 1969†
Scorodite-d	$\text{FeAsO}_4 \cdot 2^2\text{H}_2\text{O}$	IR		2605 s, sh, 2236 s	1154 m	
Mansfeldite	$\text{AlAsO}_4 \cdot 2\text{H}_2\text{O}$	R	3541 s, sh, 3104 s, 2890 s	1622 m, 1561 m		
Mansfeldite-d	$\text{AlAsO}_4 \cdot 2^2\text{H}_2\text{O}$	R		2623 s, sh, 2555 m, 2360 m	1158, 1126 m, br	
Köttigite	$\text{Zn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$	IR	3403, 3127, 2980 m, br	1622, 1582 m, br		Moenke, 1962, 1966*
Köttigite-d	$\text{Zn}_3(\text{AsO}_4)_2 \cdot 8^2\text{H}_2\text{O}$	R	3416, 3228, 3172 (2)	160vw		
Olivinite	$\text{Cu}_2\text{AsO}_4\text{OH}$	R	3419 sh	2612, 2527, 2425, 2359, 2243 sh, m	1107 m, br	
Olivinite-d	$\text{Cu}_2\text{AsO}_4\text{O}^2\text{H}$	R	3255 vw	2677 (2), 2615 (6)	1105 w	Braithwaite, 1983†
Phosphosiderite	$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$	R	3377, 3084, 2928, 2828 m, br	2532 sh, m		
Phosphosiderite-d	$\text{FePO}_4 \cdot 2^2\text{H}_2\text{O}$	R	3382, 3144 vw	2538 w		
Hopelite	$\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	R	3532 sh, 3402 br	2577w, 2490m, 2360, 2338 s, sh	1206 m, sh	Eshchenko <i>et al.</i> , 1973*
Hopelite-d	$\text{Zn}_3(\text{PO}_4)_2 \cdot 4^2\text{H}_2\text{O}$	R	3386 (1), 3252 (2)	2485 (1), 2390 w, 2311 w	1200 (3)	
Libethenite	$\text{Cu}_2\text{PO}_4\text{OH}$	R	3446 sh, m	2529, 2453 s, sh	observed	Hill and Jones, 1976*
Libethenite-d	$\text{Cu}_2\text{PO}_4\text{O}^2\text{H}$	R	3470 (1)	2517 (3), 2454 (4)		Braithwaite, 1983†
Lindgrenite	$\text{Cu}_3(\text{MoO}_4)_2(\text{OH})_2$	R	3437, 3339 m, sh	2561 m, sh		
Lindgrenite-d	$\text{Cu}_3(\text{MoO}_4)_2(\text{O}^2\text{H})_2$	R	3074, 3082 w	2875 w		
Hydrocerussite (Na)	$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$	R	3530 sh, m, 3446 br, w	2548, 2488 m, sh		Brooker <i>et al.</i> , 1983*
Deuteriocerussite	$\text{Pb}_3(\text{CO}_3)_2(\text{O}^2\text{H})_2$	R		2550, 2495 w		
		R		2622 sh, w,		
		R		2620 (3)		

* The literature reference is to the undeuterated mineral.

† The literature reference is to the normal and deuterated mineral.

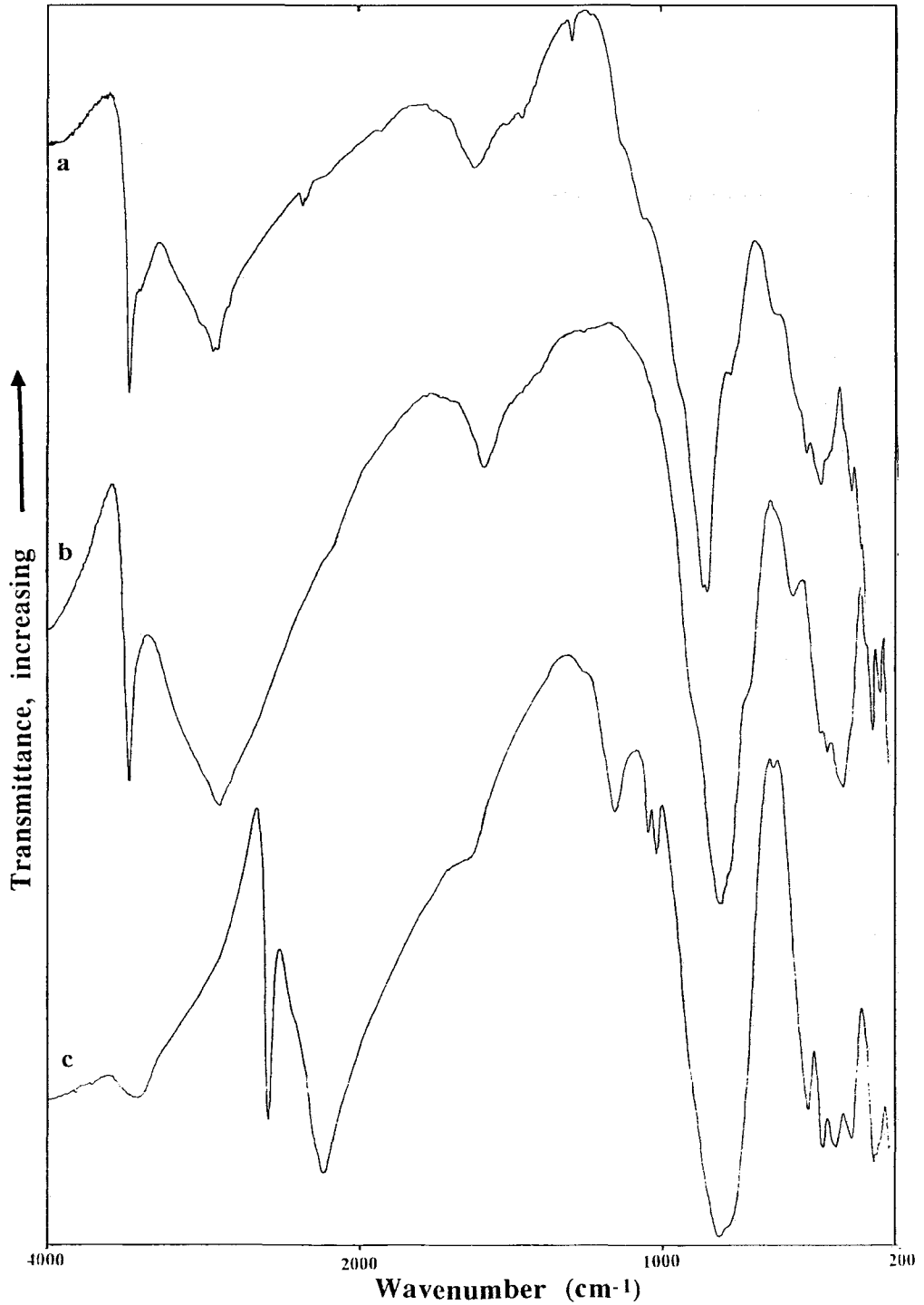


FIG. 1. Infrared spectra of scorodite (a) natural mineral (Hemerdon Mine, Plympton, Devon); (b) synthetic material made by the microwave method; (c) deuterated material made by the microwave method.

water-containing. We have also given references in Table 2 to the infrared spectra of those minerals for which published data are available.

With the exception of scorodite, few of these minerals listed here have been deuterated before. For scorodite, the deuterated material had been previously prepared by high temperature sealed tube hydrothermal methods. In Fig. 1 we show the infrared spectra of natural scorodite (*a*) from Hemerdon Mine, Plympton, Devon; synthetic scorodite (*b*) and the deuterated sample (*c*) prepared by microwave methods. It is clear that in (*c*) approximately 95% deuteration has occurred; the spectrum is in close agreement with that reported by Pâques-Ledent and Tarte (1969). Although these authors suggest that scorodite is better formulated as $\text{FeAsO}_4 \cdot (\text{OH}^-)(\text{H}_3\text{O}^+)$ rather than as $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$, two crystal structure studies have since shown that the dihydrated formulation is correct (Kitahama *et al.*, 1975; Hawthorne, 1976). The spectrum of natural scorodite (*a*) differs in some minor details from that of the synthetic material (*b*), but is similar to that reported by Cech *et al.* (1976). The spectrum of the synthetic material (*b*) is similar to those of two samples from Cligga Head, Perranporth, Cornwall (Braithwaite, priv. comm., 1996)¹. The XRD patterns of both the natural and synthetic samples closely match the database pattern (Table 1), although that of the natural material also has peaks attributable to a minor quartz impurity.

An example of the value of partial deuteration is given by a preliminary study which we report here on scorodite. The X-ray crystal structures for scorodite of Kitahama *et al.* (1975) and Hawthorne (1976) suggest that the two water molecules are in different crystallographic environments and the latter paper showed that within each of the two water molecules, the O-H bond lengths are different. We present here a preliminary study of the infrared spectrum of partially deuterated scorodite which illustrates this.

In the partial deuteration technique (Falk and Knop, 1971; Schiffer and Hornig, 1969; Lutz *et al.*, 1978) the hydrated sample is deuterated to ca. 5–10% and the infrared and/or Raman spectra are recorded at low temperatures to give maximum resolution of peaks. After H_2O the only other H-containing species present will be HO^2H : because the degree of deuteration is so small the amount of $^2\text{HO}^2\text{H}$ is negligible. Under these circumstances the HO^2H molecules will exhibit no significant inter- or intramolecular coupling with the HOH molecules, and the OH and O^2H frequencies of the HO^2H then give direct information on the environment of the hydrate molecules in the lattice.

For scorodite enriched in 10% $^2\text{H}_2\text{O}$ (prepared by using the microwave technique already described) we observe bands in the O^2H stretching region at 2580, 2352, 2285 and 2254 cm^{-1} (the spectra were recorded at -100°C). The presence of four bands suggests that there are indeed four different O^2H (and therefore four different O-H) distances in scorodite. A similar situation arises in $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, which also exhibits four O^2H stretches in a similarly partially deuterated sample (Lutz *et al.*, 1978).

Conclusions

This preliminary study has shown that microwave dielectric heating is a viable procedure for the preparation of a number of minerals, and in particular is well adapted to the preparation of fully or partially deuterated samples.

Acknowledgements

We thank the EPSRC for a grant to one of us (EEC), and the University of London Intercollegiate Research Service for the Raman spectrometer. We are grateful to Dr Fred Armitage, Kings College, London for a sample of scorodite; we thank Ben Halstead for his assistance with the microwave syntheses, Dr Stefan Menzer for assistance with the XRD and John Tucker for the use of the low temperature IR. We also thank Dr Jamie Wilkinson and Dr Vladimir Petrusevski, Skopje, for their helpful comments and suggestions. BP plc is thanked for endowing DMPM's chair.

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¹ We are grateful to a referee for pointing out the spectral differences between (*a*) and (*b*).

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[Manuscript received 3 November 1995;
revised 6 March 1996]