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The structure of mimetite, arsenian pyromorphite and hedyphane – A Raman spectroscopic study

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Abstract

The minerals mimetite $Pb_5(AsO_4)_3Cl$, arsenian pyromorphite $Pb_5(PO_4,AsO_4)_3Cl$ and hedyphane $Pb_3Ca_2(AsO_4)_3Cl$ have been studied by Raman spectroscopy complimented with infrared spectroscopy. Mimetite is characterised by a band at 812–3 cm^{-1} attributed to the A_g mode. For the arsenian pyromorphite this band is observed at 818 cm^{-1} and for hedyphane at 819 cm^{-1}. For mimetite and hedyphane bands at 788 and 765 cm^{-1} are attributed to A_u and E_{1u} vibrational modes and are both Raman and infrared active. For the arsenian pyromorphite, Raman bands at 917–1014 cm^{-1} are attributed to phosphate stretching vibrations. Raman spectroscopy clearly identifies bands attributable to isomorphous substitution of arsenate by phosphate. The observation of low intensity bands in the 3200–3550 cm^{-1} region are assigned to adsorbed water and OH units, thus indicating some replacement of chloride ions with hydroxyl ions.

Keywords: Arsenate; Mimetite; Hedyphane; Arsenian pyromorphite; Phosphate; Isomorphous substitution; Raman spectroscopy

1. Introduction

Mimetite lead chloroarsenate $Pb_5(AsO_4)_3Cl$ was named in 1835 from the Greek *mimethes*, meaning "imitator" because of its resemblance to pyromorphite $Pb_5(PO_4)_3Cl$. Mimetite is a secondary mineral of lead formed through mineralisation of the ore bodies. It is formed by the oxidation of galena and arsenopyrite. The mineral consists of small hexagonal crystals with colours ranging from pale yellow to yellowish-brown to orangish-yellow to orangish-red, white and colourless. Studies of the mimetite–pyromorphite series have been undertaken for nearly 100 years [1–3]. Mimetite has an apatite structure and forms solid solutions with pyromorphite and vanadinite [4–6]. Most crystals of mimetite–pyromorphite system are chemically zoned. Recently, the chemical variability in hedyphane was also reported in the journal American Mineralogist [7]. Although the crystal system of mimetite is known as a hexagonal (space group $P63/m$), mimetite has a dimorphic relationship with clinomimetite [8], which is a monoclinic system (space group $P2_1/m$). The phase transition between hexagonal system and monoclinic system shifts O(3) atom position in the crystal structure of mimetite [9,10].

Early investigations of the vibrational spectra of apatites including vanadinite were limited to mid-IR studies. Some early Raman studies of calcium apatites led to some questionable interpretations. Much work has been undertaken on the apatite-type minerals including mimetite, pyromorphite and vanadinite, containing the V group elements, namely As, P and V. In the apatite structure, isomorphous substitution can occur with replacement of F^- by Cl^- and also by OH groups, as in the case for selected mimetites and pyromorphites. The As(V) is replaceable by P(V) or V(V) and the Pb(II) is replaceable by for example Ca(II). Ross reported the infrared and Raman spectra of the free AsO_4^{3-} ion [11]. The v_1 band was observed at 810 cm^{-1}; v_2 at 342 cm^{-1}; v_3 at 810 cm^{-1} and v_4 at 398 cm^{-1}. Ross also reported the v_3 modes of vanadinites at 800 and

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Table 1
Table of the minerals, their origin and formula

Code	Mineral	Formula	Origin
Mime 1	Mimetite	$Pb_5(AsO_4)_3Cl$	Tsumeb, Namibia
Mime 2	Mimetite	$Pb_5(AsO_4)_3Cl$	Geronimo Mine, Yuma Co., Arizona, USA
Mime 3	Mimetite	$Pb_5(AsO_4)_3Cl$	Mount Bonnie Mine, NT
Pyro 8	Arsenian pyromorphite	$Pb_5(PO_4,AsO_4)_3Cl$	Bunker Hill Mine, Kellogg, Idaho, USA
Hedy 1	Hedyphane	$Pb_3Ca_2(AsO_4)_3Cl$	Puttapa Mine, Beltana, SA

736 cm^{-1} and the v_4 modes around 419, 380 and 322 cm^{-1}. In the work mentioned by Ross the position of the v_1 and v_2 vibrations were not reported. Gadsdsen also reported the infrared spectrum of the mimetite [12]. The v_3 mode is reported as lying between 700 to 900 cm^{-1} and the v_4 mode between 300 and 410 cm^{-1}. The v_1 mode, which was not observed in the infrared spectrum as the vibration is inactive, was suggested to be at around 870 cm^{-1}. Griffith reported the Raman spectra of mimetite [13]. Levitt and Condrate reported the infrared and Raman spectra of lead apatite powdered minerals [6]. They reported the v_2 bands for mimetites at 341 and 314 cm^{-1} [6,14–16]. Single crystal Raman spectra of a mimetite at 298 K have been reported [17]. Some arsenates as for sulphates have their symmetry reduced through acting as monodentate and bidentate ligands. In the case of bidentate behaviour both bridging and chelating ligands are known. This reduction in symmetry is observed by the splitting of the v_3 and v_4 in infrared spectra into two components under C_{3v} symmetry and into three components under C_{2v} symmetry. Single crystal spectra of mimetite were reported [18]. In this paper, the v_1 band for mimetite was observed at 816 cm^{-1}, the v_3 at 809 and 787 cm^{-1}, the v_2 at 414, 390 and 335 cm^{-1} and v_4 at 424, 373 and 314 cm^{-1}.

In this work we have obtained Raman and infrared spectra of selected mimetites, arsenian pyromorphite and hedyphane and related the spectra to the structure of the minerals.

2. Experimental

2.1. Minerals

The minerals used in this work, their formula and origin are listed in Table 1. The composition of the minerals was checked by X-ray diffraction and the chemical composition by EDX measurements.

Table 2
EDX analyses of the mimetites

Sample	Spectrum	O*	Al	S	Cl	As	Pb	Mo
Mimetite Pb5(AsO4)3.Cl	*Predicted from formula*	*12.90*			*2.38*	*15.10*	*69.61*	
Wulfenite Pb(MoO4)	*Predicted from formula*	*17.43*					*56.44*	*26.13*
Lead oxide (PbO)	*Predicted from formula*	*7.17*					*92.83*	
Sample 1	Mimetite1	15.36	1.36	0.00	2.32	14.64	66.32	
	Mimetite1b	13.77	0.63	0.00	2.61	14.84	68.14	
	Mimetite1c	12.12	0.96	0.00	2.85	12.78	71.29	
	Average	13.75	0.98	0.00	2.59	14.09	68.58	
	Conversion to At%	0.86	0.04	0.00	0.07	0.19	0.33	
	Divided by At% of Pb	2.60	0.11	0.00	0.22	0.57	1.00	
	Multiply by 5 → Atomic ratios relative to Pb	**12.98**	**0.55**	**0.00**	**1.11**	**2.84**	**5.00**	
Sample 2	Mimetite2	8.74	0.68	1.84	0.00	0.20	67.18	21.36
	Mimetite2b	12.55	0.57	1.16	0.00	0.20	63.81	21.71
	Mimetite2c	12.66	0.56	0.18	0.00	0.48	62.69	23.44
	Average	11.32	0.60	1.06	0.00	0.29	64.56	22.17
	Conversion to At%	0.71	0.02	0.03	0.00	0.004	0.31	0.23
	Divided by At% of Pb	2.27	0.07	0.11	0.00	0.01	1.00	0.74
	Multiply by 5 → Atomic ratios relative to Pb	**11.35**	**0.36**	**0.53**	**0.00**	**0.06**	**5.00**	**3.71**
Sample 3	Mimetite3	6.12	0.68	0.00	2.30	15.20	75.70	0.00
	Mimetite3b	6.27	0.86	0.00	2.53	10.63	79.71	0.00
	Mimetite3black	7.48	10.94	0.00	2.05	10.91	68.62	0.00
	Average	6.62	4.16	0.00	2.29	12.25	74.68	0.00
	Conversion to At%	0.41	0.15	0.00	0.06	0.16	0.36	0.00
	Divided by At% of Pb	1.15	0.43	0.00	0.18	0.45	1.00	0.00
	Multiply by 5 → Atomic ratios relative to Pb	**5.74**	**2.14**	**0.00**	**0.90**	**2.27**	**5.00**	**0.00**

Sample 2 appears to contain some wulfenite and possibly some oxide, very low in mimetite (Arsenic low).
Sample 3 especially mimetite3b may be a mixture of mimetite and oxide (Again arsenic low, and lead higher).
Sample called mimetite3black is unusually high in Al.