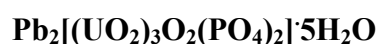




Frost, Ray L. and Cejka, Jiri (2009) *Raman spectroscopic study of the uranyl phosphate mineral dumontite $Pb_2[(UO_2)_3O_2(PO_4)_2] \cdot 5H_2O$* . Journal of Raman Spectroscopy, 40(6). pp. 591-594.

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1 **Raman spectroscopic study of the uranyl phosphate mineral dumontite**



3
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9
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11
12 **Raman spectra of dumontite were measured at 298 and 77 K. Observed**
13 **bands were attributed to the stretching and bending vibrations of**
14 **uranyl and phosphate units and OH stretching vibrations of water**
15 **molecules. U-O bond lengths in uranyls and approximate O-H...O bond**
16 **lengths were calculated. The values of the U-O bond lengths are in**
17 **agreement with the data from the single crystal structure analysis of**
18 **dumontite.**

19
20 **KEYWORDS:** dumontite, dewindtite, uranyl, phosphate, phosphuranylite anion
21 sheet topology, Raman spectroscopy, U-O bond length

22
23 **INTRODUCTION**

24
25 Uranyl phosphates are amongst the most abundant and widespread of uranium
26 mineral species, and together with the structurally corresponding uranyl arsenates,
27 constitute about a third of the described uranium minerals^{1,2}. Dumontite,
28 $\text{Pb}_2[(\text{UO}_2)_3\text{O}_2(\text{PO}_4)_2]\cdot 5\text{H}_2\text{O}$, is a very rare secondary uranyl minerals and together
29 with its structurally corresponding uranyl arsenate hügelite are members of the
30 phosphuranylite group. This group is one of the two major groups of uranyl phosphate

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31 and arsenate minerals and consists of at least sixteen minerals ²⁻⁸. Kobets and
32 Umrieko provided a review of selected uranyl phosphates. ⁹ The structure of
33 dumontite consists of $[(\text{UO}_2)_3\text{O}_2(\text{PO}_4)_2]$ layers, parallel to (100) connected by Pb^{2+}
34 ions bonded to 8 oxygens, three from $(\text{UO}_2)^{2+}$, two from (PO_4) and three from H_2O ,
35 which form distorted antiprism. Each antiprism is bonded to two others by sharing to
36 edges forming a chain parallel to the *b*-axis ^{10,11}. The uranyl anion layers are formed
37 by edge sharing of structurally and symmetrically distinct $(\text{UO}_2)^{2+}$ coordination
38 polyhedra - one UO_2O_6 hexagonal dipyramidal polyhedron and two UO_2O_5
39 pentagonal dipyramidal polyhedra. U-O bond lengths in uranyls are 1.78 and 1.80 Å
40 in UO_2O_6 hexagonal dipyramids and 1.81 and 1.83 Å in UO_2O_5 pentagonal
41 dipyramids ^{10,11}. This corresponds with the phosphuranylite anion-topology ^{1,3,4,12}.
42 The structure of hügelite contains layers that are topologically identical to those in
43 vanmeersscheite and dumontite ³. The unit cell of dumontite is monoclinic with space
44 group $P2_1/m$, $a = 8.118(6)$, $b = 16.819(8)$, $c = 6.983(3)$ Å, $\beta = 109.03(5)^\circ$, $Z = 2$. Two
45 symmetrically distinct U^{6+} cations are present in the crystal structure of dumontite
46 ^{10,11}.

47

48 Raman spectroscopy has proven very useful for the study of minerals. ¹³⁻²¹
49 Indeed Raman spectroscopy has proven most useful for the study of diagenetically
50 related minerals as often occurs with phosphate minerals. ²²⁻³² Some previous studies
51 have been undertaken by the authors using Raman spectroscopy to study complex
52 secondary minerals formed by crystallisation from concentrated solutions. Very few
53 Raman spectroscopic studies of the uranyl phosphate minerals have been forthcoming
54 and what studies that are available are not new. The paper is a part of systematic
55 studies of vibrational spectra of minerals of secondary origin in the oxide supergene
56 zone and their synthetic analogues. In this work we attribute bands at various
57 wavenumbers to vibrational modes of dumontite using Raman spectroscopy at both
58 298 and 77 K and relate the spectra to the structure of the mineral.

59

60 **EXPERIMENTAL**

61 **Minerals**

62

63 The dumontite mineral used in this work was obtained from Museum Victoria.
64 The sample originated from Shinkolowbe, Congo. The samples were phase analysed
65 by X-ray diffraction and for chemical composition by EDX measurements. The
66 chemical composition of this mineral has been published (page 150)³³. The mineral
67 corresponds to the formula $\text{Pb}_2(\text{UO}_2)_3\text{O}_2(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$.

69 *Raman microprobe spectroscopy*

71 The crystals of dumontite were placed and orientated on the stage of an
72 Olympus BHSM microscope, equipped with 10x and 50x objectives and part of a
73 Renishaw 1000 Raman microscope system, which also includes a monochromator, a
74 filter system and a Charge Coupled Device (CCD). Raman spectra were excited by a
75 HeNe laser (632 nm) at a resolution of 2 cm^{-1} in the range between 100 and 4000
76 cm^{-1} . Repeated acquisition using the highest magnification was accumulated to
77 improve the signal to noise ratio. Spectra were calibrated using the 520.6 cm^{-1} line of
78 a silicon wafer. In order to ensure that the correct spectra are obtained, the incident
79 excitation radiation was scrambled. Spectra at liquid nitrogen temperature were
80 obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield,
81 Surrey, England).

83 Spectral manipulation such as baseline adjustment, smoothing and
84 normalisation was performed using the GRAMS® software package (Galactic
85 Industries Corporation, Salem, NH, USA).

87 **RESULTS AND DISCUSSION**

89 **UO Raman vibrations**

91 The Raman spectra of dumontite in the $700\text{ to }900\text{ cm}^{-1}$ region at 298 and 77 K
92 are shown in Fig. 1. Bands at 815, 800 and 780 cm^{-1} (298 K) and 817, 801 and 782
93 (77 K) are attributed to the $\nu_1(\text{UO}_2)^{2+}$ symmetric stretching vibrations. Calculated U-
94 O bond lengths in uranyl (empirical relation $R = 106.5 [\nu_1(\text{UO}_2)^{2+}]^{-2/3} + 0.575\text{ \AA}$ by
95 Bartlett and Cooney, 1989)³⁴ are ($\text{\AA}/\text{cm}^{-1}$) 1.796/815, 1.811/800 and 1.832/780 (298

96 K) and 1.794/817, 1.810/801 and 1.830/782 (77 K) are in agreement with those
97 inferred from the X-ray single crystal structure of dumontite 1.78 and 1.80 Å for
98 UO_2O_6 and 1.81 and 1.83 Å for UO_2O_5 uranyl polyhedra^{10,11}. No bands attributable
99 to the ν_3 antisymmetric stretching vibrations were observed in the Raman spectrum of
100 dumontite.

101

102 Raman spectra in the low wavenumber region are reported in Fig. 2. The
103 spectra may be subdivided into two sections (a) bands in the 400 to 600 cm^{-1} region
104 which may be assigned to phosphate vibrations and (b) bands in the 100 to 300 cm^{-1}
105 region which may be assigned to uranyl vibrations. Bands at 293, 271 and 246 cm^{-1}
106 (298 K) and 292, 274 and 249 cm^{-1} (77K) are assigned to the doubly degenerate ν_2 (δ)
107 $(\text{UO}_2)^{2+}$ bending vibrations and/or ν (U- O_{ligand}) vibrations. Bands at lower
108 wavenumbers may be attributed to PbO and OPbO vibrations.

109

110

111

112 **PO_4 Raman vibrations**

113

114 The Raman spectra of dumontite in the 900 to 1150 cm^{-1} region at 298 and 77
115 K are shown in Fig. 3. Bands observed at 1054 and 1024 cm^{-1} (298 K) and 1062 and
116 1026 cm^{-1} (77 K) are attributed to the triply degenerate ν_3 (PO_4) antisymmetric
117 stretching vibrations and those at 982 and 974 cm^{-1} (298 K) and 985 and 975 cm^{-1} (77
118 K) to the ν_1 (PO_4) symmetric stretching vibrations. The split triply degenerate ν_4
119 (PO_4) bending vibrations and the doubly degenerate ν_2 (PO_4) bending vibrations are
120 observed at 571 and 551 cm^{-1} (298K), 574, 560 and 543 cm^{-1} (77 K), and as well as
121 445 and 440 cm^{-1} (298 K) and 449 and 445 cm^{-1} (77 K), respectively (Fig. 2).

122 **OH Raman vibrations of water molecules**

123 Dumontite contains water molecules in its crystal structure. The Raman
124 spectra of dumontite in the 2800 to 3800 cm^{-1} region at 298 and 77 K are shown in
125 Fig. 4. Bands at 3552, 3475, 3352 and 3189 (298 K) and 3566, 3515, 3467, 3347 and
126 3326 cm^{-1} (77 K) were assigned to the $\nu(\text{OH})$ stretching vibrations of water

127 molecules. There is a hydrogen bonding network in the crystal structure of dumontite.
128 O-H...O bond lengths vary approximately in the range 3.1 – 2.7 Å.

129

130 **CONCLUSIONS**

131

132 Raman spectra of dumontite were studied at 298 and 77 K. Bands related to
133 stretching and bending vibrations of uranyl and phosphate units and stretching
134 vibrations of water molecules were attributed. No band related to the antisymmetric
135 stretching vibration of the uranyl ion was observed. Calculated U-O bond lengths in
136 uranyls agree with the data inferred from the X-ray single crystal structure analysis.
137 Approximate O-H...O bond lengths were given.

138

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140

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146

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198 **List of Figs**

199

200 Fig. 1 Raman spectra of dumontite in the 700 to 900 cm^{-1} region at 298 and 77K.

201

202 Fig. 2 Raman spectra of dumontite in the 100 to 700 cm^{-1} region at 298 and 77K.

203

204 Fig. 3 Raman spectra of dumontite in the 900 to 1150 cm^{-1} region at 298 and 77K.

205

206 Fig. 4 Raman spectra of dumontite in the 2800 to 3800 cm^{-1} region at 298 and 77K.

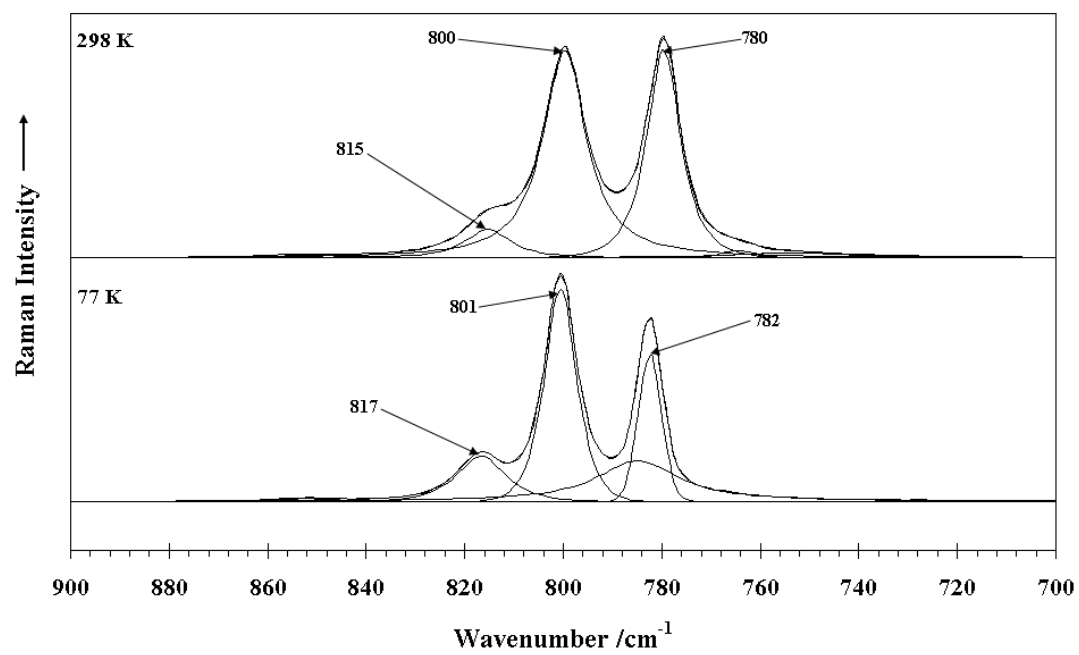
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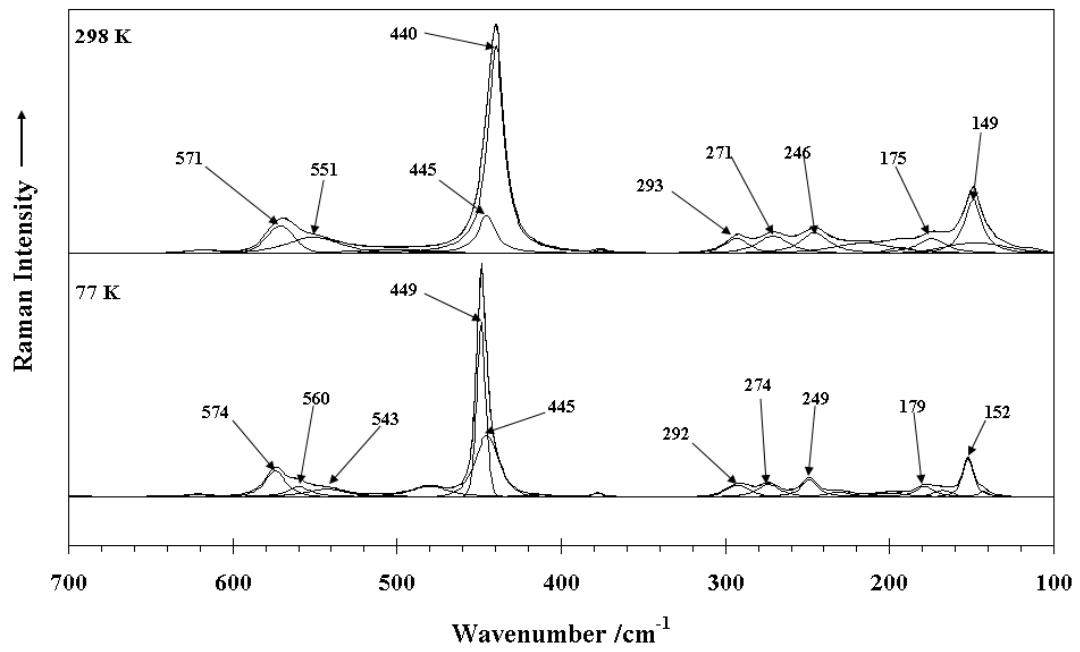


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214 **Fig. 1**

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219 **Fig. 2**

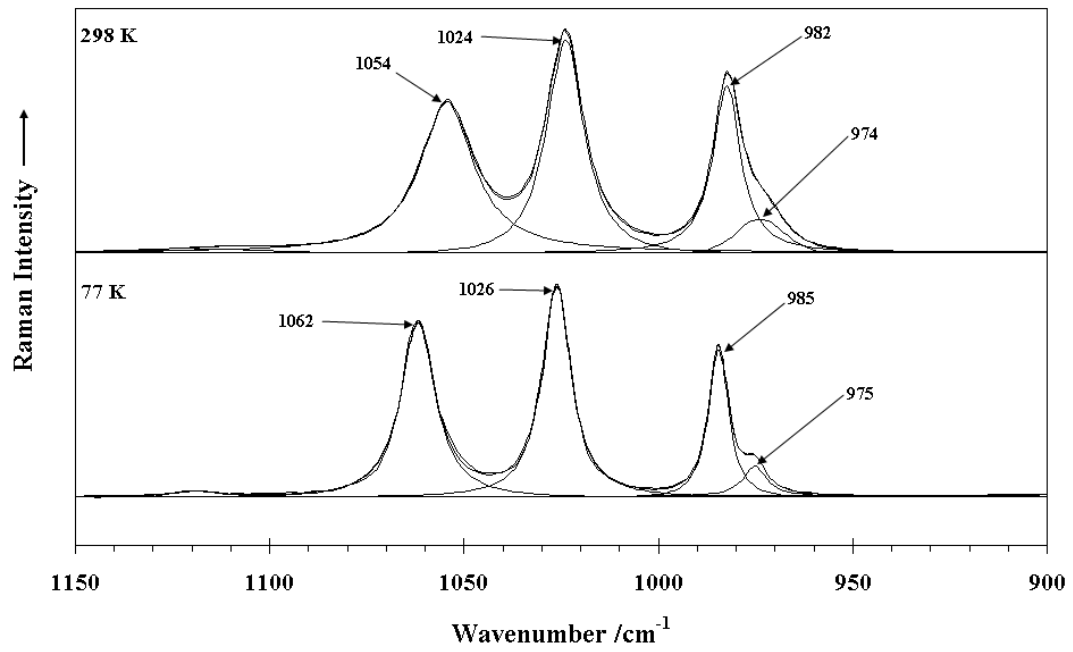
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227 **Fig. 3**

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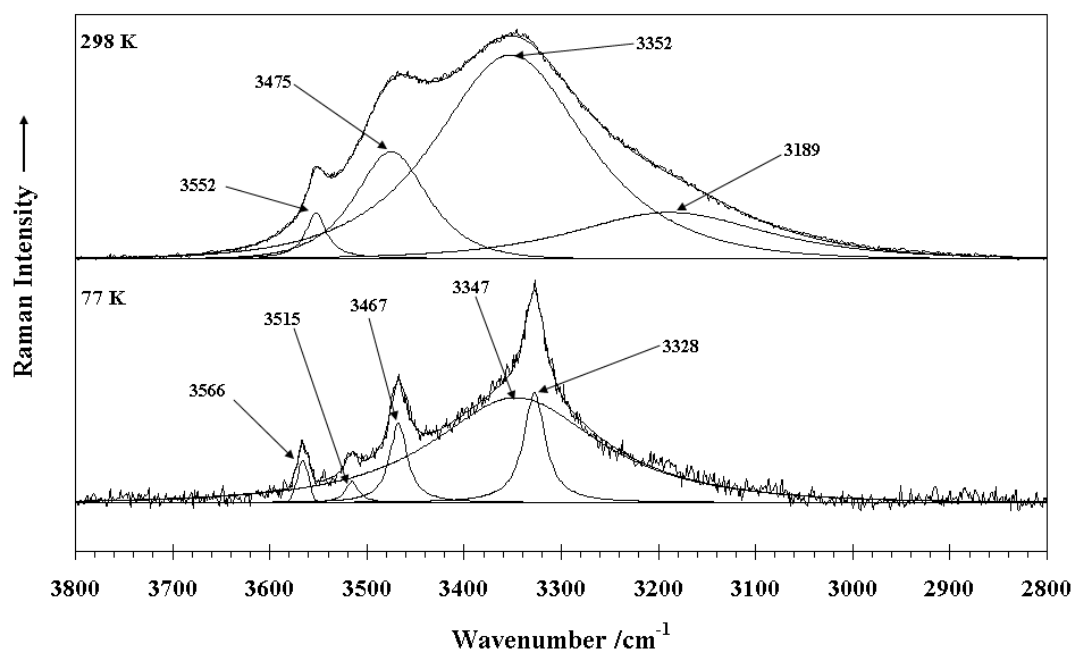
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245 **Fig. 4**