Hybrid Uranyl-Arsonate Coordination Nanocages

Pius O. Adelani,[1] Ginger E. Sigmon,[1] and Peter C. Burns*[1,2]

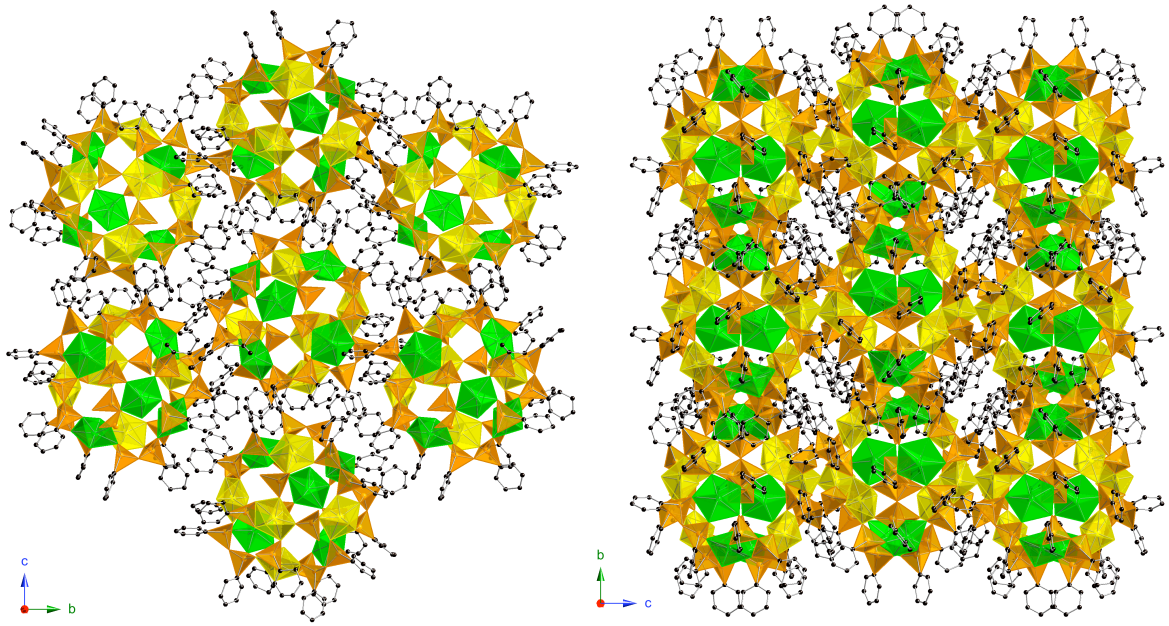
[1]Department of Civil and Environmental Engineering and Earth Sciences and [2]Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556

SUPPORTING INFORMATION

Note 7: 1 and **2**: UO_3 (28.6 mg, 0.1 mmol), phenylarsonic acid (50.5 mg, 0.25 mmol), MeCN (0.5 mL), 2-propanol (0.3 mL), and HF (~10 µl, 0.27 mmol) were loaded into a PTFE-lined Parr 4749 autoclave with a 23 mL internal volume. The autoclave was sealed and heated to 160 ^{o}C in a box furnace for 5 days and was then cooled at an average rate of 9 ^{o}C/hr to 25 ^{o}C. The resulting products were washed with distilled water and methanol and were allowed to air dry at room temperature. Yellow-green tablets of **1** and yellow needle-like crystals of **2** suitable for XRD studies were manually separated from the mixture of crystals and brown powder suspected to be decomposition products of the ligand. The crystals of **2** formed the major product (~50%), and the crystals of **1** formed ~ 30% of the product. In the absence of 2-propanol, only **1** was isolated, along with unreacted ligand. **3**: Yellow plate-like crystals of **3** were synthesized over the temperature range of 110 - 140 ^{o}C following a similar procedure to that described above. When we used other organic solvents such as methanol, ethanol, and 2-propanol, **3** was also produced over the temperature range of 110 - 160 ^{o}C. Powder X-ray diffraction studies reveal that **3** forms along with unreacted ligands as minor impurities (yield: 71% on the basis of uranium). See the Supporting Information for pictures, SEM images, and EDX analysis of compounds **1**-**3**. **1** was further characterized by XRF analysis because of the slight disparity in the ratio of the elemental composition of As:U from the EDX analysis relative to the formula (EDX = 3.05, XRF = 2.36).

Note 10: 1: yellow-green, tablets, crystal dimensions 0.129 x 0.128 x 0.124 mm, orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 18.446(3)$ Å, $b = 32.290(5)$ Å, $c = 35.952(6)$ Å, $V = 21413(6)$ Å^3 ($T = 100$ K), $\mu = 113.0$ cm^{-1}, $R_1 = 0.0585$, $wR2 = 0.1653$. 247991 reflections measured, 48932 independent reflections, all of which were included in the refinement. The data were corrected for Lorentz-polarization effects and for absorption. The structure was solved by direct methods, anisotropic refinement on F^2 by full-matrix least-squares, 940 parameters. SQUEEZE was applied to the data to confirm that a 4330 Å^3 void contains about 1477 electrons. **2**: yellow, needle-like crystals, crystal dimensions 0.215 x 0.053 x 0.052 mm, orthorhombic, *Pbcn*, $Z = 4$, $a = 31.365(3)$ Å, $b = 30.630(3)$ Å, $c = 28.328(3)$ Å, $V = 27215(5)$ Å^3 ($T = 100$ K), $\mu = 109.41$ cm^{-1}, $R_1 = 0.1105$, $wR2 = 0.3718$. 161085 reflections measured, 618 parameters, 31053 independent reflections all of which were included in the refinement. SQUEEZE was applied to the data to confirm that a 4100 Å^3 void contains about 2083 electrons. **3**: yellow platelet, crystal dimensions 0.045 x 0.037 x 0.015 mm, orthorhombic, *Cmma*, $Z = 4$, $a = 7.228(3)$ Å, $b = 18.267(8)$ Å, $c = 17.157(7)$ Å, $V = 2265.2(17)$ Å^3 ($T = 100$ K), $\mu = 172.5$ cm^{-1}, $R_1 = 0.0450$, $wR2 = 0.1555$. 8847 reflections measured, 105 parameters, 1464 independent reflections all of which were included in the refinement. Bruker APEXII Quazar CCD X-ray diffractometer: $\theta_{max} = 27.4°$, MoKα, $\lambda = 0.71073$ Å, 0.5° ω scans.[11] The structural analyses of these compounds were very challenging, a common problem in studies involving large uranyl clusters.[8] The inclusion of organic ligands in these cluster makes refinement even more difficult. This is due to the large scattering contrast between uranium and the lighter elements (hydrogen, carbon, and oxygen), some disorder in the solvent and hydronium molecules, and the presence of relatively large

voids with little electron density as compared to uranium. The outcome of this is weak diffraction at higher angles that limits the resolution of the crystal structure. H atoms cannot be resolved and were assumed in the molecular formula directly. The O/C atoms were refined isotropically and soft constraints were added to the refinement to improve the geometries of the O/C polyhedra.



(1) **(2)**

Figure 1. Packing diagrams for **1** and **2** as viewed along the a-axis.

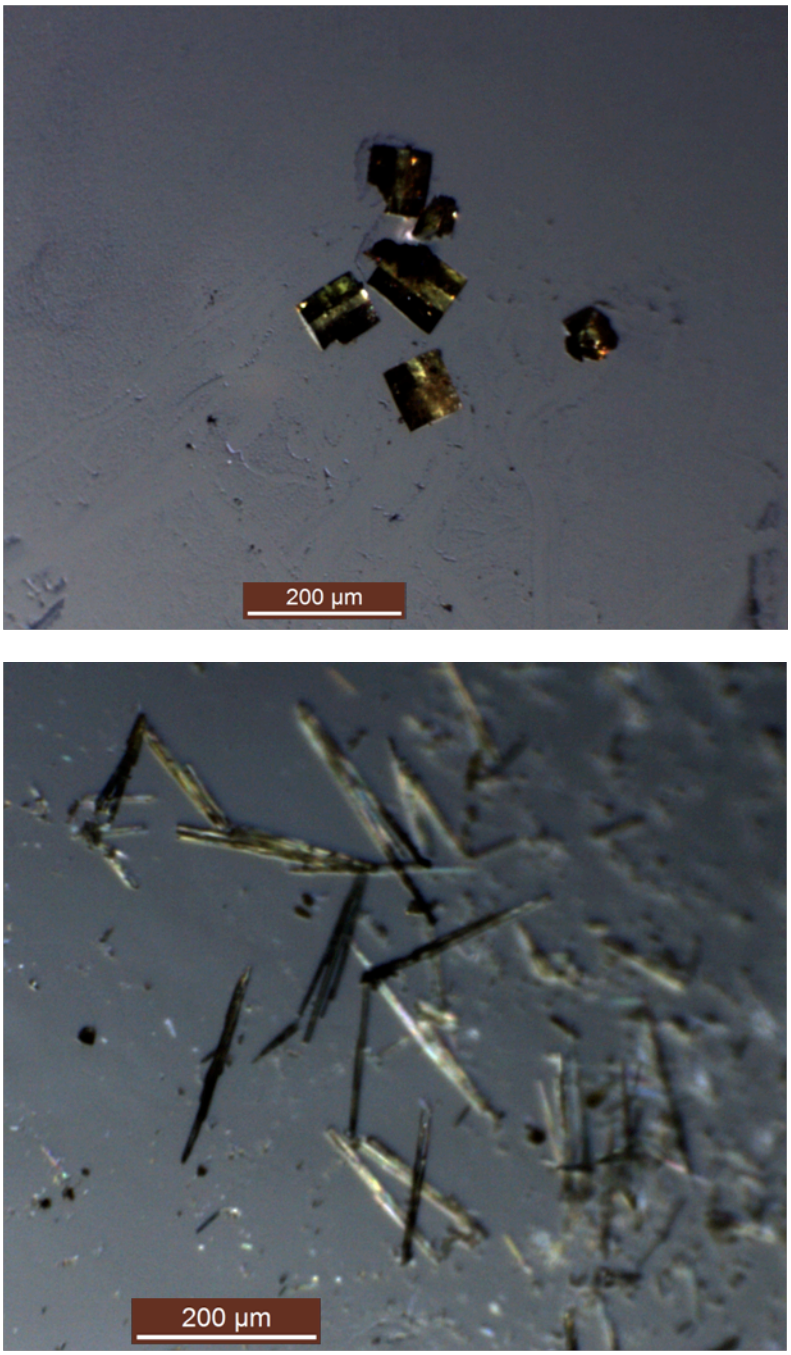


Figure 2. Photos of yellow-green tablets of **1** and weakly diffracting tiny needle-like crystals of **2.**

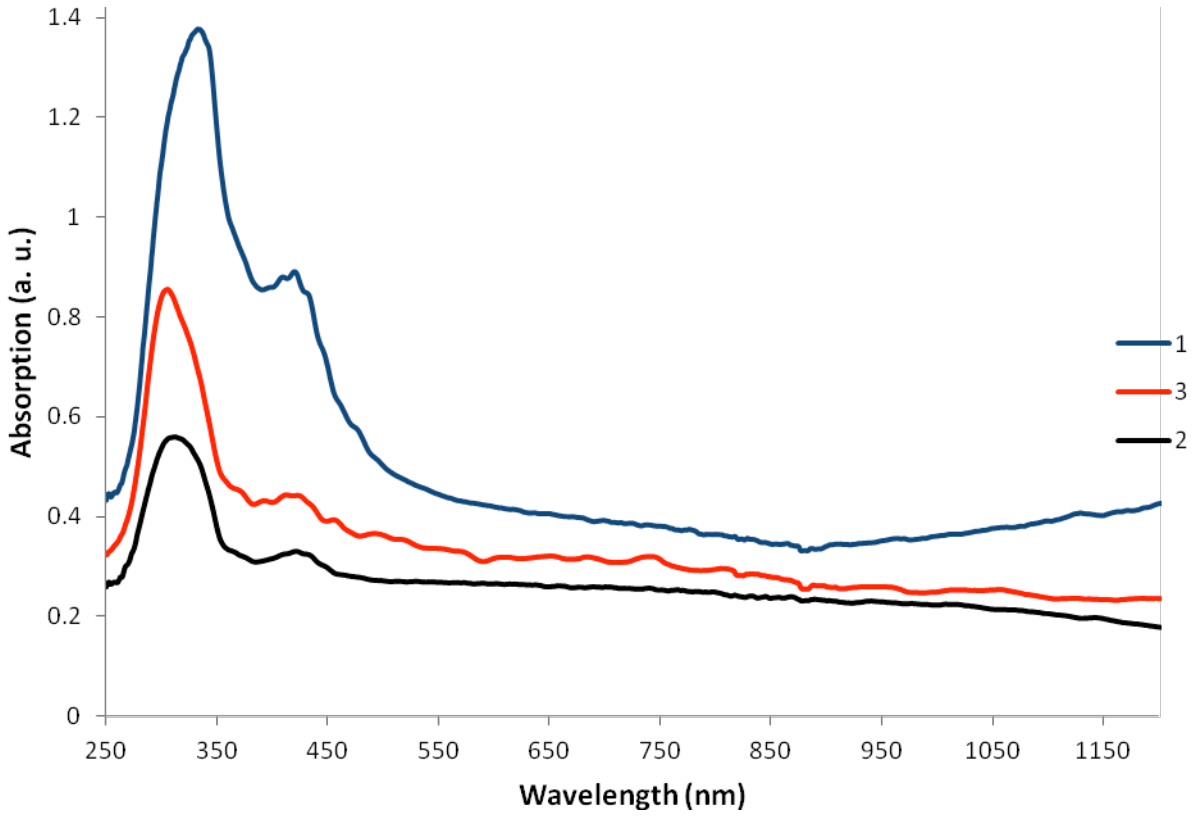


Figure 3. Absorption spectra of **1**, **2**, and **3**

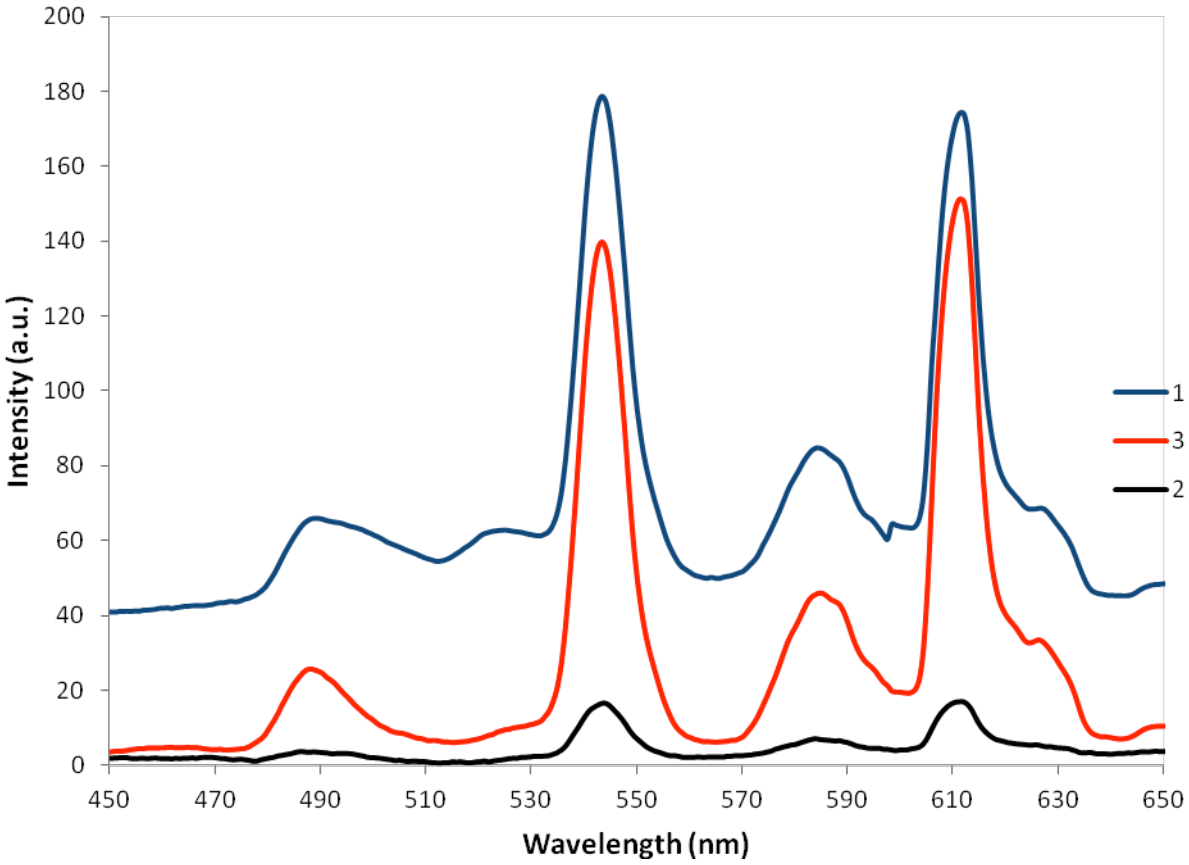


Figure 4. Fluorescence spectra of **1**, **2**, and **3**

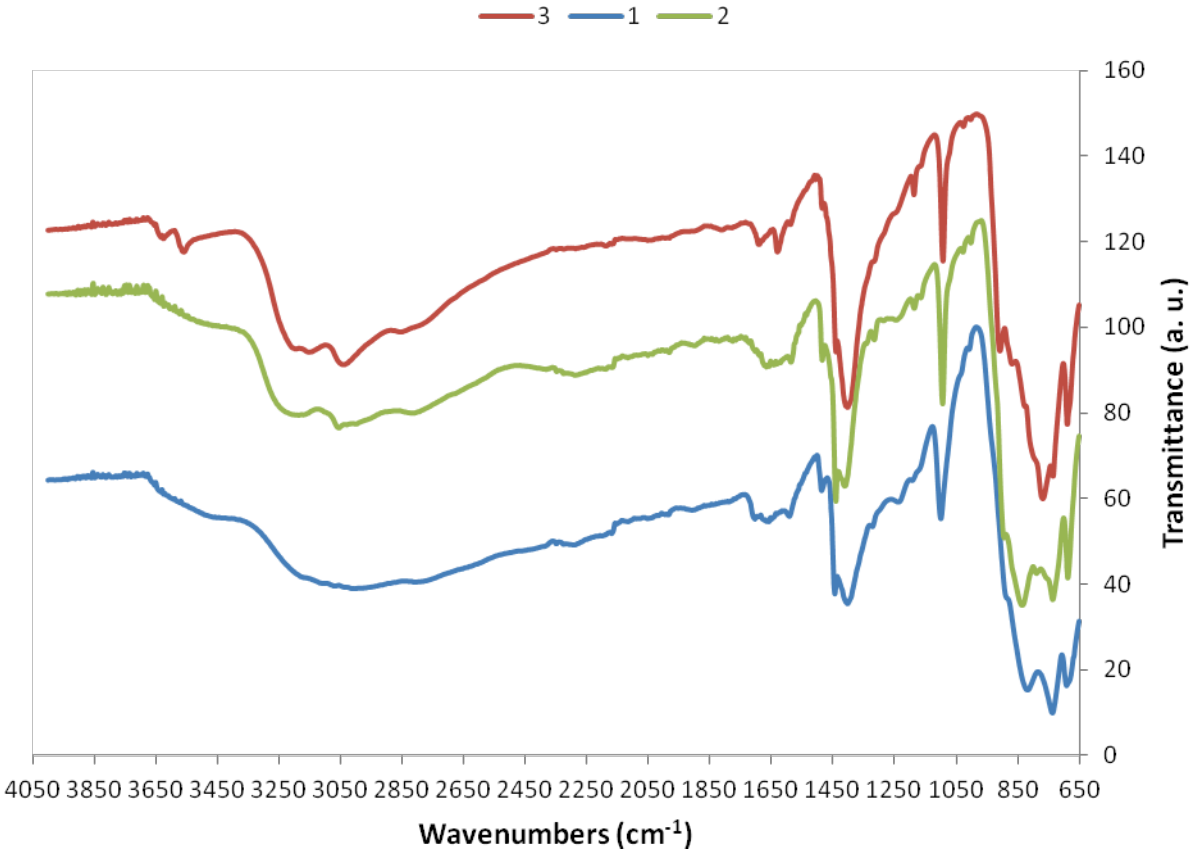


Figure 5. Infrared spectra of **1**, **2**, and **3**

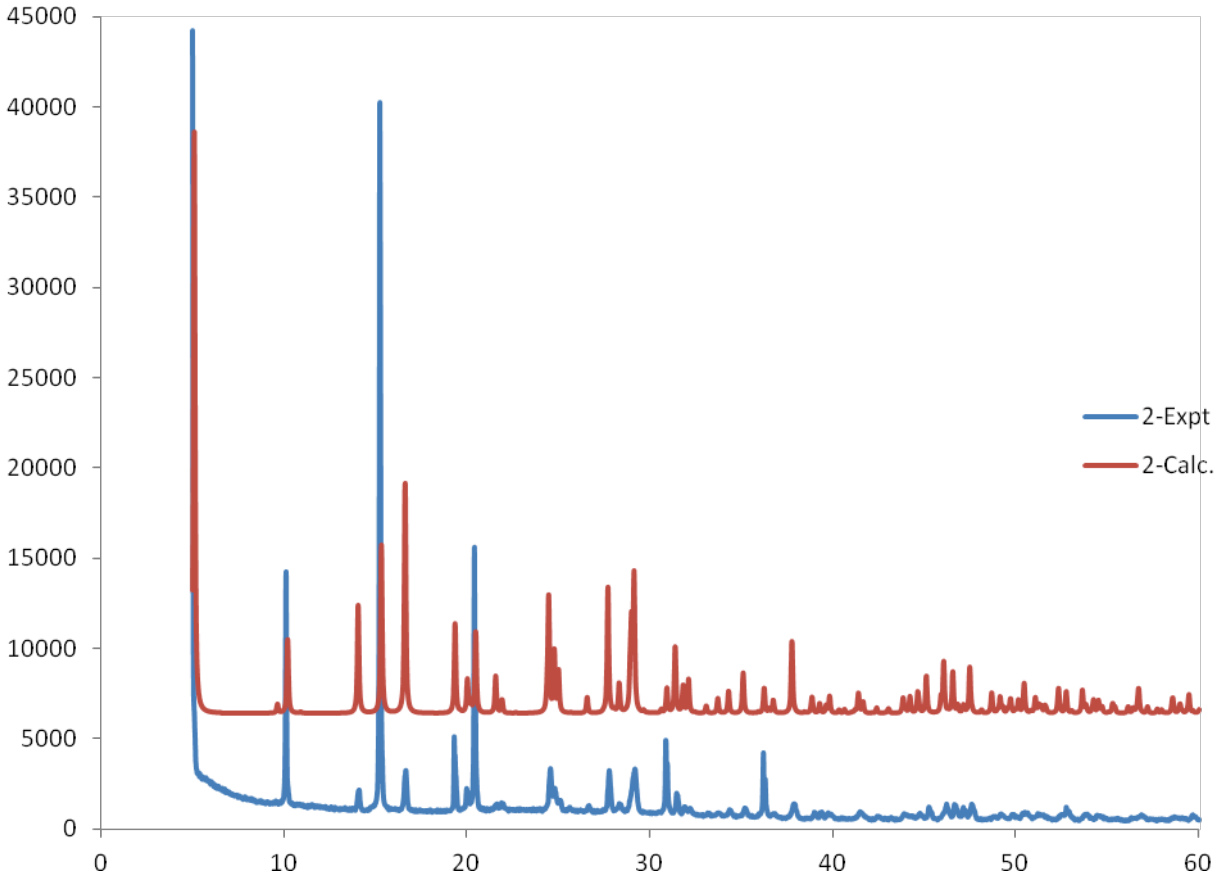
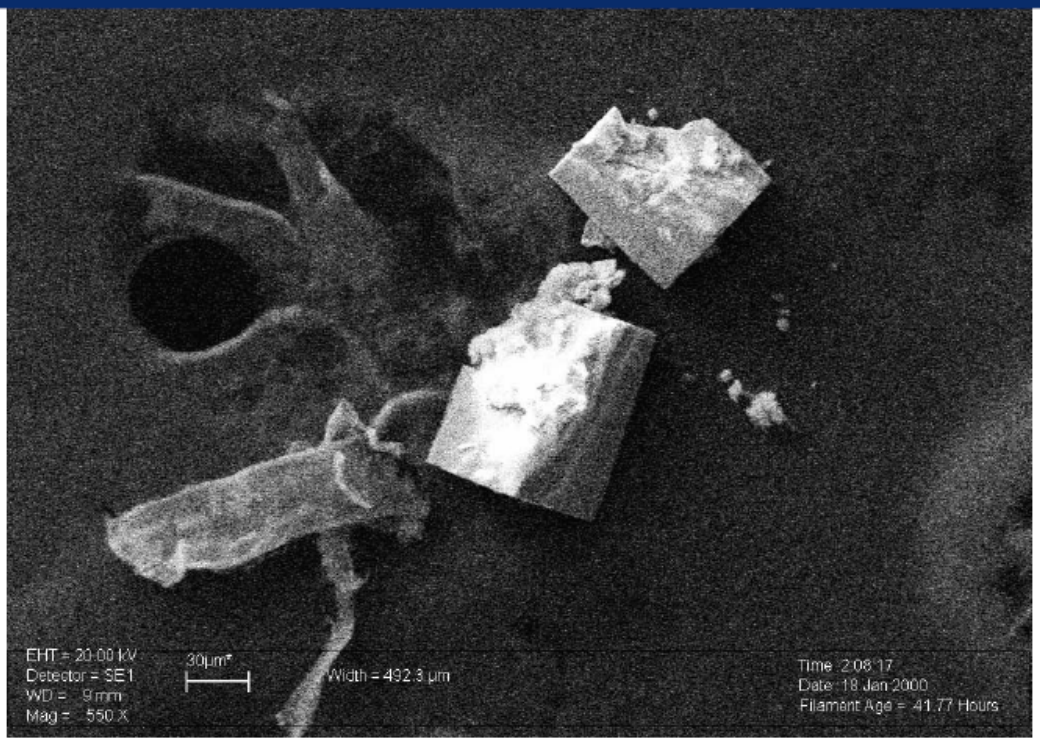


Figure 6. Powder XRD pattern for **3** .

11/30/2012 9:35:17 AM



Spectrum processing :
Peaks possibly omitted : 0.273, 0.526, 1.759 keV

Processing option : All elements analyzed (Normalised)
Number of iterations = 3

Standard :
As InAs 1-Jun-1999 12:00 AM
U U 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
As L	48.98	75.31
U M	51.02	24.69
Totals	100.00	

Comment:

inca

11/30/2012 9:37:09 AM

(2)

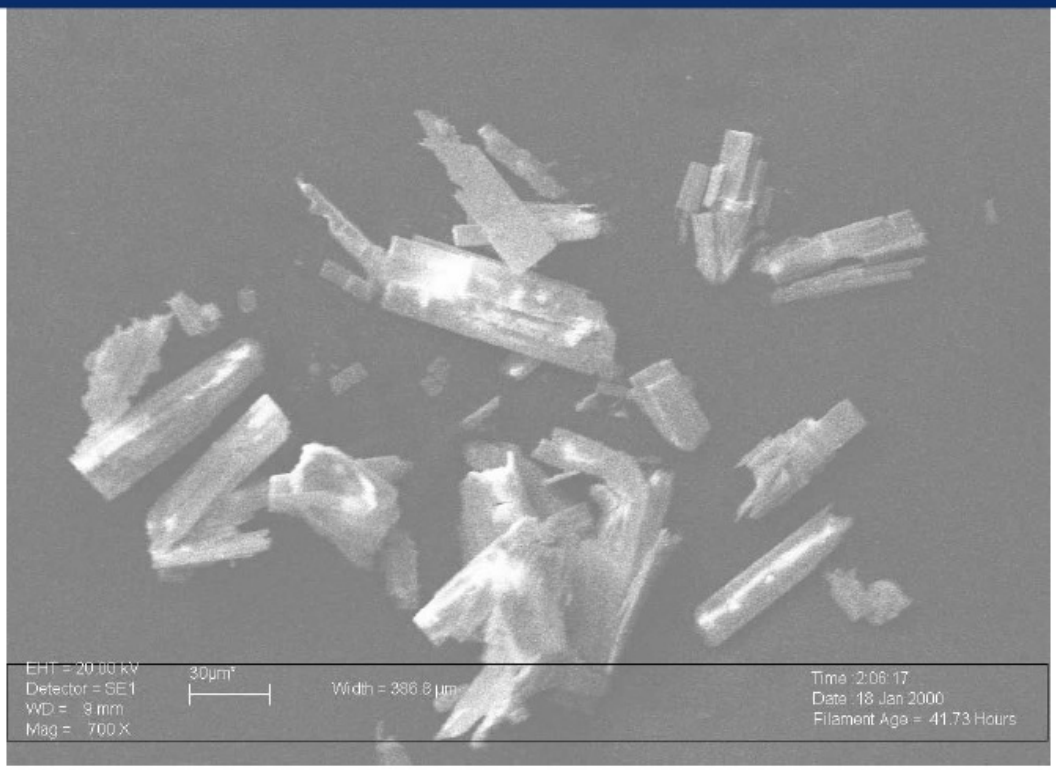
Spectrum processing :
Peaks possibly omitted : 0.272, 0.525, 1.759 keV

Processing option : All elements analyzed (Normalised)
Number of iterations = 3

Standard :
As InAs 1-Jun-1999 12:00 AM
U U 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
As L	44.49	71.80
U M	55.51	28.20
Totals	100.00	

Comment:



Spectrum processing :
Peaks possibly omitted : 0.263, 0.521 keV

Processing option : All elements analyzed (Normalised)
Number of iterations = 3

Standard :
As InAs 1-Jun-1999 12:00 AM
U U 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
As L	23.67	49.63
U M	76.33	50.37
Totals	100.00	

Comment: