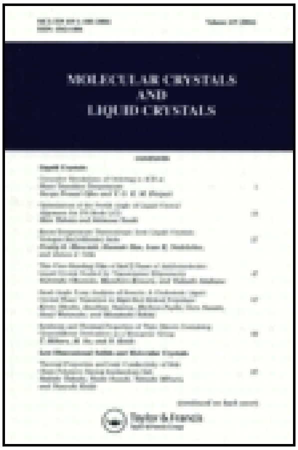

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 23 Oct 2006.

To cite this article: A. Moissette , B. H. Fuzellier , C. J. Dubessy , A. Burneau & M. Lelaurain (1994): Experimental Study of a New Uranyl Sulfate G.I.C., Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 244:1, 53-58

To link to this article: http://dx.doi.org/10.1080/10587259408050082

Mol. Cryst. Liq. Cryst. 1994, Vol. 244, pp. 53–58
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Printed in the United States of America

EXPERIMENTAL STUDY OF A NEW URANYL SULFATE G.I.C.

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Abstract Stability of new graphite uranyl sulfate intercalation compounds has been studied as a function of temperature and concentration. The action of uranyl sulfuric acid aqueous solution on graphite leads to the formation of two mixed phases of intercalation products: the usual sulfate phase (di=800 pm) and a uranyl sulfate phase (di=855 pm).

The structure of uranyl sulfate phase has been characterized by X-ray diffraction. The electronic distribution pattern along the graphite c axis has been established with [00l] reflections while [hk0] reflections has led to the determination of the planar primitive cell.

A complete Raman microspectroscopic study has been done with pure uranyl sulfate graphite compounds from HOPG to stage 1. This technique has also displayed intercalated species.

INTRODUCTION

This chemical study has been initiated by a geochemical problem: the biggest uranium deposit in the world located in Saskatchewan (Canada) are frequently spatially associated with graphite in the unconformity zone [1-3]. Previous studies have shown alteration holes in graphite related to strong corrosion [4]. This graphite alteration is also spatially connected with alteration of pyrite and therefore, with acid sulfate fluids circulation [2]. Then, the aim of this study is to describe the reactivity of uranyl ion in sulfuric acid solutions toward graphite in order to determine the role of graphite for the uranium precipitation.

A previous study carried out with pure sulfuric acid has shown that H_2SO_4 is able to intercalate into graphite layers, spontaneously at temperatures between 190 and 280°C [5]; it is probably the SO_3, being a powerful oxidizing agent, formed by thermal decomposition of the acid which allows the intercalation process at temperatures above 190°C. To connect these results with geological observations and to precise the possible role of uranium in the natural mechanism, uranium trioxide has been added to the sulfuric solution which yields UO_2^{2+} ions. At first, a solution of UO_2^{2+} (0.5 molar) in pure sulfuric acid was used

INTERCALATION OF URANYL IONS

Experiments have shown both the intercalation of sulfate phase alone from 90°C down to room temperature (sulfate phase, di = 800 pm) and the intercalation of two mixed phases above 90°C: the sulfate phase and a new phase where sulfate is associated with uranyl ions (Graphite Uranyl Sulfate phase: GUS phase, di = 855 pm). The addition of UO_3 to sulfuric acid solution increases its oxidizing capacity. Thus, sulfate intercalation becomes possible at room temperature because SO_3 formation is then not necessary to initiate this process.

A qualitative estimation of each phase proportion is given by the [001] reflections ratios of GUS phase to sulfate phase obtained by X-ray diffraction (Figure 1).

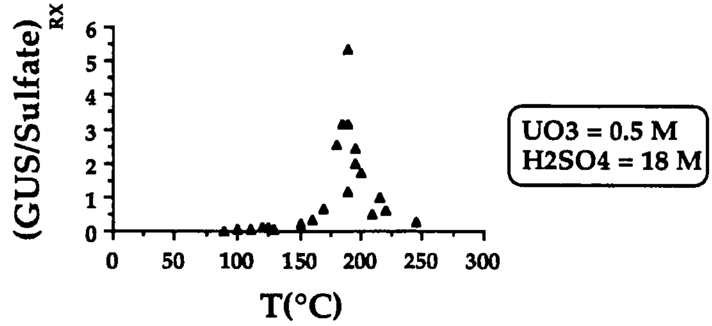

FIGURE 1 Temperature dependance of the proportion of GUS phase relatively to the sulfate phase as obtained by X-ray diffraction.

For temperatures lower than 150°C, the uranyl ions act mainly as oxidizing agent and the proportion of GUS phase is very weak. The GUS phase becomes dominant for temperatures higher than 170°C with a maximum of intercalation around 195°C. Stage 2 compounds of GUS phase are preferentially formed above 150°C whereas stage 1 compounds of GUS phase are formed below this temperature, indicating a thermodynamic stability zone for both stages. Higher stages could not be synthesized by this way.

However, a direct preparation of pure GUS compound is not possible; thus, the synthesis has been carried out using the low thermal stability of the sulfate phase. At first, intercalation of the solution at 195°C produces the two-mixed phase compound; then, the sample is heated in an oven at 200°C in order to expel the sulfate phase. Finally, the sample containing graphite and GUS phase reacts again with the solution at 195°C; this procedure must be repeated several times to obtain a pure stage 2 GUS compound. It is worth noting that the sulfate phase was not able to "reintercalate" itself. The same procedure carried out at 130°C has led to the formation of pure stage 1 GUS compounds.

INFLUENCE OF CONCENTRATION

The minimum concentrations of sulfuric acid and of uranyl ions to form sulfate and GUS graphite intercalation compounds have been determined. With pure sulfuric acid (18 molar) at 195°C and 1 bar, the intercalation of uranyl, to form the GUS phase, requires, at least, a 0.08 molar minimum concentration of uranyl ion in the aqueous solution. Below this concentration, only the pure sulfate phase is formed from stage 2 to stage 9 depending on the uranyl concentration. At 95°C, 1 bar and constant UO_2^{2+} concentration (0.5 molar), the GUS phase is formed, from stage 1 to stage 6, for H_2SO_4 concentrations above 5.4 molar and the sulfate phase above 11.5 molar H_2SO_4. Experiments performed at 195°C and 1000 bar indicate the same trend as in the previous results, demonstrating the small effect of pressure.

STRUCTURE OF THE GRAPHITE URANYL PHASE

The structure of the uranyl sulfate phase has been characterized by X-ray diffraction. Using the Fourier transform of the structure factors of [00l] reflections, an electronic distribution pattern along the graphite c axis has been established. This model applies to stages 1, 2, 3 and 4 with very good agreement: the Fourier transform reliability factor for a stage 2 compound is 5.4%, the composition of which is $C_{13.8}$ (SO_4) $(UO_2)_{0.167}$ (Figure 2).

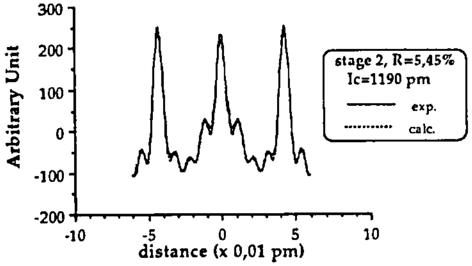

FIGURE 2 Electronic distribution pattern along the graphite c axis for a stage 2 GUS compound.

In this model, the uranyl ions are perpendicular to the graphite layers with a central uranium placed in the median plane between two graphitic layers around intercalated species and two oxygen atoms at ± 170 pm. The sulfate tetrahedrons remain nearly regular but are slightly displaced towards the carbon atoms: the sulfur atoms are placed at 26 pm from the median plane and the oxygen atom levels are 64 and 116 pm.

The [hk0] diffraction pattern obtained with the Laue monochromatic technique shows many spots. These can be indexed in an oblique incommensurate plane structure, the parameters of which are $\underline{A} = \underline{B} = 1520$ pm and $\Gamma = 95°$ (Figure 3).

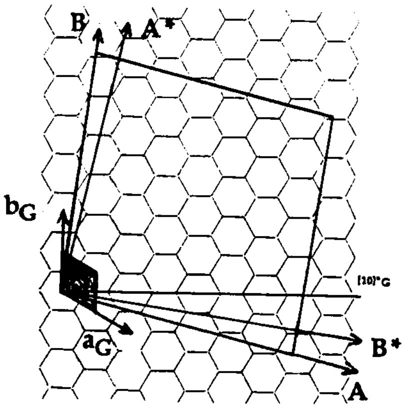

FIGURE 3 Planar primitive cell of a stage 1 GUS compound and corresponding directions of the reciprocal lattice with respect to graphite planes; the cell origin is arbitrary chosen.

The primitive cell parameters are rotated by ± 17° with respect to $\underline{a}_G$. The planar primitive cell of GUS phase contains approximatly 83 carbon atoms, 12 SO_4^{2-} and 2 UO_2^{2+} but their organization is still unknown.

The study of some [hkl] reflections of first stage GUS phase confirmed the existence of three dimensional order and proves that $\underline{C}$ = 2 Ic = 1710 pm (Figure 4).

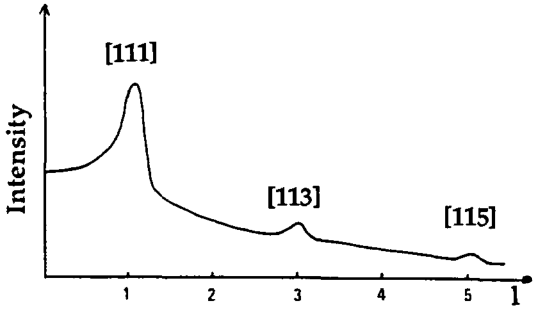

FIGURE 4 Intensity distribution along [111] line of a stage 1 GUS compound.

MICRO RAMAN CHARACTERIZATION

In order to complete the GUS phase study, all the stages have been characterized by Raman microspectroscopy (Figure 5). The Raman frequency of $E_{2g(2)}$ active mode is 1580 cm^{-1} for pristine graphite (HOPG). Intercalation of a compound in graphite results in two frequencies assigned to two type of graphite layers as shown by Solin [6]: a bounding layer adjoining the intercalate layer ($E_{2g(2)^\wedge}$) and an interior layer ($E_{2g(2)^\circ}$).

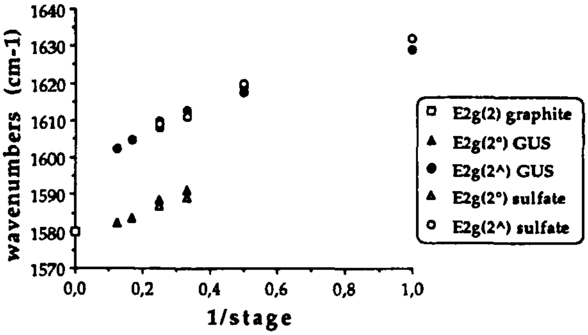

FIGURE 5 Wavenumber shift as a function of the reciprocal stage for graphite-sulfate and GUS compounds.

Raman spectra of GUS compounds are similar to those obtained with pure sulfate GICs: they exhibit the same wavenumber shift with intercalation. However, the homogeneity of GUS compounds is strongly higher than that of the sulfate compounds.

Although only graphitic intralayer mode is highly resonant enhanced, vibrations of intercalated species which have not this advantage have been observed: HSO_4^- at 1038 cm^{-1}, SO_4^{2-} at 988 cm^{-1} and UO_2^{2+} at 858, 865, 882 cm^{-1} (Figure 6). The different frequencies obtained for the uranyl ion make impossible to know exactly the structure of intercalated uranyl as free ion or complex uranyl-sulfate.

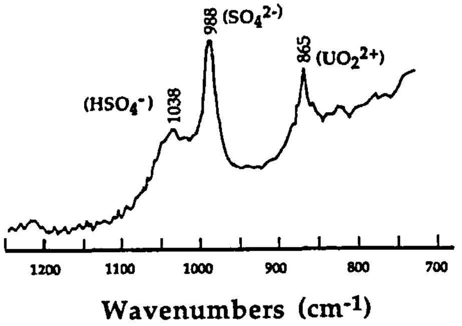

FIGURE 6 Raman spectrum of GUS phase intercalated species.

REFERENCES

1. Hoeve J., Sibbald T.I.I., Econ. Geol., 1978, 73, 1450
2. Hoeve J., Quirt D., Bull. Min., 110, 157 (1987)
3. Pagel M. C.R. Acad Sc. Paris D, 280, 2301 (1975)
4. Wang A., Dhamelincourt P., Dubessy J., Guérard D., Landais P. and Lelaurain M., Carbon, 27, 209 (1989)
5. Moissette A., Fuzellier H., Burneau A., Dubessy J., Guérard D. and Lelaurain M., Mat. Sci. Forum, 91-93, 95 (1992)
6. Solin S.A., 1990, Graphite intercalation compounds I (Zabel and Solin, Springer Verlag, 1990), 157.