largely exceed a surface process and can be ascribed to a hydroxycarbonate phase. In addition, curve (i) of Fig. 2 shows the XPS spectra of Yb_2O_3 aged for 4 years in air. As can be observed, the ratio of hydroxyl signal intensity to the one of the oxide clearly shows that most of the oxygens within the photoelectron escape depth are in the form of OH^- group.

Although the mechanistic aspects of the slow hydration and carbonation of the heavier Ln_2O_3 are out of the scope of this article, the poisoning effect of CO_2 can be easily understood: CO_2 competes with H_2O for the basic centres necessary for dissociative adsorption. This fact, together with the strongly basic properties of the carbonate and bicarbonate surface species formed on CO_2 adsorption, can hinder the proton mobility.

1 R. Alvero, S. Bernal, J. A. Odriozola and J. M. Trillo; *J. Chem. Soc. Dalton*, in press.
2 R. Alvero, S. Bernal, I. Carrizosa, J. A. Odriozola and J. M. Trillo, *J. Less Comm. Met.*, in press.
3 D. Touret and F. Queyroux, *Rev. Chim. Miner.*, **9**, 883 (1972).
4 M. A. Rosynek and D. T. Magnuson, *J. Catal.*, **46**, 402 (1977).
5 S. Bernal, R. Garcia and J. M. Trillo, *React. Kinet. Catal. Lett.*, **10**, 125 (1979).
6 S. Bernal, R. Garcia, J. M. Lopez and J. M. Rodriguez-Izquierdo, *Collect. Czech. Chem. Comm.*, in press.
7 B. P. Padalia, J. K. Gimzewski, S. Affrossman, W. C. Lang, L. M. Watson and D. J. Fabian, *Surf. Sci.*, **61**, 468 (1976).

D14

Preparation of Actinide Thin Film Deposits for Nuclear Physics and Solid State Physics Researches

J. KWINTA*, PH. BROSSARD, J. J. MICHEL and J. THOREUX

Commissariat à l'Energie Atomique, Centre d'Etudes de Bruyères-le-Chatel, B.P. 561, 92542 Montrouge Cédex, France

Actinide targets used in nuclear physics as well as some samples studied in solid state physics must, generally, meet very precise specifications which determine the quality of the results. This is particularly true for thin film deposits for which the usual characteristics are the following:

Elements: Th, Pa, U, Np, Pu, Am, Cm, Cf...
Chemical state: metal, oxide or salt
Deposit area: $1-10$ cm^2
Thickness: $10-100$ μg cm^{-2}
Homogeneity: better than 10%
Amount of material used: a few milligrams or less

One has also to take into account the radioactivity of the actinides (especially the short half life ones) and the fact that some isotopes are scarce.

These restrictions impose to set up special equipments in glove boxes for the deposition and the control. The examples of electrospraying and focused ion beam sputtering are presented. Although the electrodeposition in aqueous or organic media and the classical vacuum deposition are widely used, these techniques will not be discussed in this paper.

Electrospraying. The principles of electrospraying were first stated by Zeleny in 1917 [1]. However the technique only became efficient after the work of Verdingh and Lauer at the CBNM (GEEl, Belgium) [2]. A solution containing the element to be deposited flows through a capillary. A positive potential with respect to the substrate is applied to a wire lodged into the capillary. At its exit, due to the electrical forces, the drop becomes unstable and explodes forming a spray which sprinkles the substrate. Usually the solvent evaporates before the microdroplets reach the backing. Moreover the electrical field accelerates the formed particles improving their adhesion on the foil. For example, in the case of actinide acetates dissolved in methanol and with usual experimental conditions, the number of such droplets is about 4×10^{11} per cubic centimeter. A special mechanism allows the substrates to move in x and y directions in order to improve the film uniformity. The deposits can be heated at 450 °C to get the oxides. The whole system can easily be mounted in a glove box with exterior monitoring. We have realized in our laboratory targets or samples of the following isotopes: ^{230,232}Th, ^{231}Pa, ^{237}Np, ^{233,235,238}U, ^{239,241}Pu, ^{241,243}Am, ^{244}Cm, ^{252}Cf as acetates or oxides.

Focused Ion Beam Sputtering

One drawback of electrospraying is that only a limited number of chemical species can be deposited i.e. mainly acetates and eventually oxides. Thus focused ion beam sputtering was developed in our laboratory for actinide target preparations as this technique allows the use of only milligrams of starting material. Moreover practically all the chemical forms of actinide compounds, including the metals, can be sputtered. The principle is the following: ions (generally from rare gas) produced by an ion source (duoplasmatron-type or cold cathode-type) are accelerated and then focused by mean of einzel lens on the source material. The sputtered atoms are then collected on the substrates suitably disposed around the beam-stop.

The typical running parameters are the following:
— ion current: $1-2$ mA
— extraction voltage: 10 kV
— focus voltage: $1-2$ kV

Since actinide compounds and particularly the oxides have low sputtering yields, deposits in the $10-100$ μg cm^{-2} thickness range require deposition times ranging from several minutes to a few hours. The glove box adaptation is made by disconnecting the control unit from the deposition chamber and the pumping unit. The glove box is divided in two compartments: one containing the deposition chamber and the other the pumping group. When metallic samples are handled, the glove box is flushed with pure argon or nitrogen.

Deposits of the following isotopes have been prepared: ^{230,232}Th, ^{231}Pa, ^{233,235,238}U, ^{237}Np, ^{239,241}Pu, ^{241,243}Am, ^{244}Cm as oxides and ^{232}Th, ^{235}U, ^{238}U, ^{239}Pu, ^{241}Am as metals.

Generally actinide thin film deposition starting from metals leads to oxide deposits. The realization of metallic layers requires special care towards the glove box atmosphere purity, particularly in the case of Pu and trans Pu isotopes.

The characterization of the oxidation state can be achieved using ESCA and the deposition rate is monitored either by integrating the ionic current or by a quartz oscillating monitor.

Electrospraying and focused ion beam appear as complementary techniques for thin film depositions of actinide compounds and particularly the scarce isotopes when classical methods such as vacuum evaporation or electrodeposition are ineffective.

1 J. Zeleny, *J. Phys. Rev., 1*, 1917.
2 K. F. Lauer and V. Verdingh, *Nucl. Inst. and Meth., 21*, 161 (1963).

D15

Oxysulfide Glasses in the La$_2$S$_3$–La$_2$O$_3$–Ga$_2$S$_3$–Ga$_2$O$_3$ System

M. GUITTARD, A. M. LOIREAU-LOZAC'H, F. BERGUER and J. FLAHAUT*

Laboratoire de Chimie Minérale Structurale associé au CNRS, Faculté de Pharmacie, 4, avenue de l'Observatoire, F-75270 Paris Cédex 06, France

Glasses were previously described in the La$_2$S$_3$–Ga$_2$S$_3$ and La$_2$O$_2$S–Ga$_2$S$_3$ systems. Actually, a very large glass former region exists in the La–Ga oxyde-sulfide system, in the neighbouring of Ga$_2$S$_3$ (which alone does not form glass by quenching). In order to explain the formation of glasses, a tentative phase diagram is proposed from DTA and X-rays diffraction studies. A large concentration of ternary invariants is present in the glass former region. Some new quaternary compounds have been identified, and

their structures were solved. The La$_{10/3}$Ga$_6$S$_{12}$O$_2$ compound is only formed from glasses by convenient heat treatment. Its structure is supposed to be closely related to the structure of the glasses. Glasses are generally obtained by quenching the melt products at $1100-1200$ °C. Along two eutectic valleys, glasses can be obtained after slow cooling. The thermal properties of the glasses (T_g, T_c, T_m) are described. Glasses have yellow brown colour. They are transparent in large regions of the visible and I.R. spectra.

Some informations have been obtained with Nd-doped glasses: a large nephelauxetic effect is observed in the absorption spectra, in relation with strong covalent character of the rare earth–non metal bonds. Moreover the Raman spectra of the glasses are not exactly the envelope of the Raman spectra of the crystalline products: the stronger Raman band at 230 cm^{-1} which is characteristic of a stretching mode of Ga–S$_4$ tetrahedra is not observed with the glasses.

D16

Magnetic Properties of Es$_2$O$_3$ and EsF$_3$

PAUL G. HURAY*, S. E. NAVE, R. G. HAIRE and J. R. MOORE

Physics Department, The University of Tennessee, Knoxville, Tenn. 37996-1320, U.S.A., and Transuranium Research Laboratory, Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830, U.S.A.

The first quantitative measurements of the magnetic properties of einsteinium have been made on Es$_2$O$_3$ and EsF$_3$. The data were collected at temperature between 4.2 and 180 K while maintaining the samples in various applied magnetic fields. The paramagnetic moment per einsteinium atom was 10.4 ± 0.3 μ_B for the Es$_2$O$_3$ sample and 11.4 ± 0.3 μ_B for the EsF$_3$ sample. These values may be compared to a theoretical value of 10.6 μ_B for a $5f^{10}$(Es^{3+}) free ion calculated by using Hund's Rule and L–S coupling.

Sample Preparation. The einsteinium used in the study was purified by ion exchange chromograph techniques and 30 μg of a ^{253}Es–^{254}Es isotope mixture were obtained as a chloride solution. A micro-precipitation technique using teflon molds [1] was employed to precipitate the einsteinium as an oxalate, and this material was then calcined up to 1000 °C in air to form an off-white, Es$_2$O$_3$ product. A similar approach was used to prepare EsF$_3$. Electrolytic grade HF was added to the purified chloride solution of trivalent einsteinium to produce a micro-precipitate. The resulting washed precipitate