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Preparation of Ytterbium and Europium Oxides in Liquid Ammonia

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Third-law thermodynamic calculations¹ indicated that a lower oxide of ytterbium might be stable if it were prepared at low temperatures. At elevated temperatures YbO is unstable with respect to the disproportionation reaction to the metal and sesquioxide. Reports²⁻⁴ that ytterbium and europium metals dissolve in liquid ammonia to form blue paramagnetic solutions characteristic of the divalent cation and solvated electrons and that alkali or alkaline earth metal-ammonia solutions react with oxygen to yield various oxygen-containing products depending upon the reaction conditions caused us to investigate the reaction of oxygen with ytterbium in liquid ammonia.

Experimental Section

Ytterbium metal (99.9%, Research Chemicals, Inc., Phoenix, Ariz.), europium metal (99.9%, Michigan Chemical Corp., St. Louis, Mich.), anhydrous ammonia (Matheson), argon (Liquid Carbonic), and oxygen (National Cylinder Gas) were used as received. A 0.1-1.0-g lump of metal was added to about 50 ml of liquid ammonia. Oxygen or oxygen diluted with argon was introduced to the solution through a glass bubbler jet. After the characteristic blue color disappeared, the gas flow was maintained, but the test tube was allowed to warm to room temperature and the ammonia was boiled away. Reactions were carried out at -78° (ethylene glycol slush bath), -63.5° (chloroform slush bath), and -33° (normal boiling point of ammonia).

To effect preparation of $\text{Yb}(\text{NH}_3)_2$, powdered platinum or ferric chloride catalyst was added to metal-ammonia solutions. Dry argon (dew point -78°) was bubbled through the mixture.

The oxide products were washed with 0.01 M HCl and then with distilled water prior to being vacuum dried. The acid wash was tested for metal content by adding saturated oxalic acid solution. Washed samples were examined for basic nitrogen by dissolution in 6 M HCl and treatment with Nessler's reagent.⁵ Possible interferences and sensitivity of this test were determined using LaN as a reference.

Samples were annealed in air at 25, 110, 230, and 850° and then subjected to X-ray powder diffraction analysis. Europium samples were examined by using a Debye-Scherrer camera and iron K radiation ($\lambda\bar{\alpha}$ 1.9373 Å). Samples of both metal oxides were examined with a Guinier-Hägg forward focusing camera employing copper K radiation ($\lambda\alpha_1$ 1.5405 Å). Platinum powder ($a = 3.9237 \pm 0.0003$ Å) mixed with samples provided an internal standard. Lattice parameters were obtained using the method of least regression as described by Lindquist and Wengelin.⁶

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Results

The characteristic blue color of metal-ammonia solutions appeared immediately after metal was added to the liquid. The rate of dissolution was greater for europium than for ytterbium. Occasionally the copper-bronze color indicative of concentrated solutions was observed at the bottom of the test tube. Introduction of oxygen resulted in the dispersal of the color and the formation of a flocculent white precipitate. As the blue color dissipated, a greenish yellow color which has been observed for aqueous solutions of Yb(II) or Eu(II) was noted. The color was entirely eliminated within a few hours depending upon the amount of metal initially present and the rate of oxygen flow. If oxygen was added before the metal had dissolved completely, further dissolution was hindered. It should be noted that although the addition of oxygen to the solution proceeded quietly, exposure of very concentrated solutions to air by transferring from one vessel to another resulted in explosive oxidation of the metal.

Attempts to prepare $\text{Yb}(\text{NH}_3)_2$ for a reference were unsuccessful. In the absence of air the blue color remained for more than 24 hr even in the presence of a catalyst. Only very diffuse diffraction lines (perhaps attributable to a metal-ammonia complex) were obtained from the solid remaining after the ammonia was distilled off.

The oxides produced were grayish white. They were extremely finely divided with the entire sample passing readily through a 325-mesh screen. The samples were rapidly soluble in 1 M HCl but the oxalate test on the 0.01 M HCl wash was negative. The tests with Nessler's reagent set an upper limit of 60 ppm for the basic nitrogen content after washing. Gravimetric analyses were not conducted due to the difficulty of bringing samples to constant weight since different annealing temperatures were used.

The X-ray powder diffraction patterns of all samples except those annealed at 850° had diffuse lines. Long exposures (up to 70 hr with iron radiation at 35 kV and 10 mA) were necessary to produce films with good contrast. The diffraction lines for the ytterbium oxide samples before and after the HCl wash are listed in Table I.

Discussion

The diffuseness of the powder patterns makes unequivocal assignment of the various lines difficult. The extremely finely divided state of the sample undoubtedly caused both the poor quality of the X-ray patterns and its high reactivity in 1 M HCl. Although the reaction conditions were not controlled rigorously, no difference was noted in the products for the various reaction temperatures and different oxygen concentrations. The oxygen-hindered dissolution of the metal is probably due to the growth of a protective oxide layer on the surface.

The only identifiable phase in the europium system is EuO with a measured lattice parameter of $a = 5.14 \pm$

TABLE I
COMPARISON OF OBSERVED INTERPLANAR d
SPACINGS WITH THOSE CALCULATED FOR YbO AND A-Yb₂O₃

| $d(\text{obsd}), \text{\AA}$ | | YbO ^a | | A-Yb ₂ O ₃ ^b | |
|------------------------------|---------------|-------------------------------|-------|---|-------|
| Before washing | After washing | $d(\text{calcd}), \text{\AA}$ | hkl | $d(\text{calcd}), \text{\AA}$ | hkl |
| 3.17 | 3.17 | | | 3.19 | 100 |
| 2.94 | 2.94 | | | 2.95 | 002 |
| 2.82 | | 2.82 | 111 | | |
| 2.79 | 2.80 | | | 2.81 | 101 |
| 2.44 | | 2.44 | 200 | | |
| 2.16 | 2.15 | | | 2.16 | 102 |
| 2.10 | 2.10 | | | | |
| 1.91 | 1.91 | | | | |
| 1.82 | 1.82 | | | 1.83 | 110 |
| 1.72 | | 1.72 | 220 | | |
| 1.69 | | | | | |
| 1.67 | 1.67 | | | 1.67 | 103 |
| 1.60 | 1.60 | | | 1.60 | 200 |
| 1.53 | 1.53 | | | 1.53 | 112 |
| 1.47 | 1.47 | 1.47 | 311 | 1.47 | 004 |

^a $a = 4.87 \text{ \AA}$. ^b $a = 3.68 \text{ \AA}$, $c = 5.59 \text{ \AA}$.

0.02 \AA , a value in good agreement with that reported by Rau.⁷ There is insufficient evidence to permit positive identification of any other europium-oxygen phase.

The diffraction patterns of the ytterbium-oxygen products contain reflections assignable to the A form of Yb₂O₃ with lattice constants of $a = 3.68 \pm 0.04 \text{ \AA}$, $c = 5.59 \pm 0.04 \text{ \AA}$, and $c/a = 1.52$. The molar volume of 41.7 cm³ falls on the molar volume vs. ionic radius line plotted by Hoekstra.⁸ Owing to the diffuseness of the patterns, it is difficult to obtain reliable relative intensities. There is no apparent change in the reflections when this phase is annealed at 110° for several weeks, but after a few days at 230° reflections of both the A and C forms of Yb₂O₃ are present. Even after 1 month at 230° the A form is still present. However, when the sample is heated 1 hr at 850°, the pattern is that of well-annealed C form. We have seen no indication for the reverse transition from the C to the A form.

The diffraction patterns of samples which have neither been washed nor heated contain reflections which probably result from a YbO phase isostructural with EuO. The destruction of this phase upon heating or acid washing, while not allowing us to prove that it is not nitrogen stabilized and hence similar to the Sm-O-N system,⁹ is parallel to results obtained for EuO which had been prepared by the reduction of EuOCl with LiH at elevated temperature. From the lattice parameter for this cubic phase ($a = 4.87 \pm 0.01 \text{ \AA}$) and an oxide radius of 1.40 \AA obtained from the EuO lattice parameter and an Eu(II) radius of 1.17 \AA , the calculated Yb(II) radius is 1.03 \AA . Values of the Yb(II) radius calculated from YbSe and YbTe are 1.017 and 1.054 \AA , respectively. The three lines in the pattern which are not assigned to YbO or A-Yb₂O₃ do not permit identification of another ytterbium-oxygen phase.

At least five different forms designated A, B, C, H, and X, the latter two observable only when the tem-

perature is greater than 2000°, are recognized for the various lanthanide sesquioxides. The relative stabilities and the reversibility of the transformations among the A (hexagonal), B (monoclinic), and C (cubic) forms are not clearly resolved as has been described in reviews by Brauer¹⁰ and Foex and Traverse.¹¹ This A-Yb₂O₃ is particularly noteworthy in two respects. First, the A form has not been observed previously for any of the heavy lanthanides, and, second, the A form undergoes a transition to the C form with increasing temperature in contrast with the C to A transitions observed for La₂O₃, Nd₂O₃, Pr₂O₃, and Y₂O₃.^{12,13}

The unsuccessful attempts of Brauer, *et al.*,¹⁴ to prepare YbO by LiH reduction of YbOCl or reaction of Yb with Yb₂O₃ are understandable in view of the low temperature required for its preparation. The form of the Yb₂O₃ produced initially by oxidation of YbO could not be determined.

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Metal-Ammonia Solutions. VII. The Electrolysis of Liquid Ammonia Solutions of Aluminum(III) Iodide and Magnesium(II) Chloride

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Liquid ammonia solutions of alkali and alkaline earth metals as well as of tetraalkylammonium radicals can be prepared by the electrolysis of solutions of the corresponding alkali and alkaline earth metal or tetraalkylammonium halides.¹ Spectroscopic results indicate that these solutions are indistinguishable from solutions containing the solvated electron which arise from, for example, the dissolution of sodium or potassium in liquid ammonia. In the course of these investigations an attempt was made to generate liquid ammonia solutions of both aluminum and magnesium by

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