

6×10^{-5} mol kg^{-1} CrO_4^{2-} , 4×10^{-5} mol kg^{-1} AgCrO_4^- , and 2×10^{-5} mol kg^{-1} Ag_2CrO_4 . The absorbance contribution from only AgCrO_4^- and Ag_2CrO_4 can therefore be deduced by subtraction of $0.50A_1$ from $A_2 - A_3$. The result is represented by the dotted spectrum of Figure 7: a broad field of absorption in the 360–440-nm region with an indication of two maxima around 385 and 400 nm.

The dotted spectrum could of course be tentatively regarded as consisting of two partially overlapping bands with individual maxima at about 380 and 400 nm due to AgCrO_4^- and Ag_2CrO_4 , respectively. At the present state such an assignment would be of a too speculative nature, but the matter certainly deserves a more quantitative and exhaustive experimental study than this preliminary one. Qualitatively, however, the shift toward lower energies upon Ag^+ association is rather interesting. A significant cation–oxygen σ bonding, utilizing the oxygen lone-pair electrons, should rather be expected to change the absorption band toward higher energies. Such spectral changes have been observed upon, e.g., protonation of CrO_4^{2-} to HCrO_4^- with λ_{max} shifted from 370 to 351 nm.^{27,28} Therefore it seems probable that the change toward lower energies for the Ag-coordinated CrO_4^{2-} ion in nitrate melts is a result of an additional d– π back-donation of electrons from silver to chromate. The spectral observations discussed here thus furnish strong evidence for the existence of complexes with a chemical interaction between Ag(I) and CrO_4^{2-} which is fundamentally different from the alkali metal– CrO_4^{2-} interactions in the nitrate melts.

The quasi-lattice theory²⁹ has been used by Sacchetto and co-workers⁶ in an attempt to rationalize data for Ag(I) association with CrO_4^{2-} in nitrate melts. Our results, however, clearly demonstrate the inapplicability of the quasi-lattice

formalism for systems of this kind, containing polyvalent polyatomic ions. The apparent pair association energy ΔA_1 of the model tends to be strongly temperature dependent. A coordination number of 5 yields $d\Delta A_1/dT = -9 \pm 2$ J mol^{-1} K^{-1} , which—for reasons discussed in a previous paper on iodate complexation²—is incompatible with both internal entropy and mixed-solvent effects.⁶

Our analysis of the thermodynamics for the formation of AgCrO_4^- , schematically described by process 1, shows that the association reaction is favored to approximately the same extent by its exothermic character and by the gain in entropy at 553 K. This pattern is somewhat different from that of the $\text{Ag}^+ - \text{IO}_3^-$ association in the same solvent, which is driven by a large entropy gain only.² The minute ΔH°_1 for the IO_3^- association was found to be about the expected one if contributions from changes in electrostatic interactions between hard-sphere model ions were considered only. An analogous model calculation for the CrO_4^{2-} association should probably consider the uncomplexed CrO_4^{2-} as selectively Na^+ -solvated. A hard-sphere interchange with Ag^+ would then yield a positive contribution to ΔH°_1 . The absolute magnitude of such an electrostatic contribution is very much depending on the choice of effective radius for CrO_4^{2-} , but one is inclined to believe that the covalent character of the $\text{Ag}^+ - \text{CrO}_4^{2-}$ bonding—as evidenced by the spectral changes—most probably causes a larger energy gain than -6 kJ mol^{-1} , which is the overall enthalpy change.

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Registry No. Ag_2CrO_4 , 7784-01-2; Na_2CrO_4 , 7775-11-3; KNO_3 , 7757-79-1; NaNO_3 , 7631-99-4; Ag , 7440-22-4.

Supplementary Material Available: Tables IV and V, giving all experimental data from solubility and emf measurements (8 pages). Ordering information is given on any current masthead page.

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Synthesis of Neodymium and Samarium Monoxides under High Pressure

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Under high pressure the neodymium and samarium sesquioxides react with the pure metals, which is not the case at ordinary pressure. The new compounds, recovered at normal pressure probably in a metastable state, have a face centered cubic structure and their cell parameters are respectively 4.994 and 4.943 Å. Chemical analyses do not show major contamination by hydrogen, carbon, or nitrogen. The lattice constant of the neodymium compound is equal to the value calculated for the monoxide on the assumption that the metal is in the trivalent state; for samarium it is slightly larger. Samarium appears to be in a valence state slightly lower than 3. No reaction is observed for thulium although a large range of pressures and temperatures were investigated (10–80 kbar, 500–1200 °C).

Introduction

Until recently bulk preparations of the rare earth monoxides, except for europium monoxide, could not be obtained despite numerous attempts using various techniques (oxidation of the metal, reduction of the sesquioxide by different agents, reactions in open or closed systems). It is now well established^{1,2} that the compounds^{3–5} made with the EuO structure (NaCl

type) were in fact compounds containing large quantities of hydrogen, carbon, or nitrogen. Reported preparations of SmO thin films⁶ with the unlikely zinc blende structure have been demonstrated to be hydride phases.⁷ However, recently Léger et al.⁸ showed that application of high pressures allowed the synthesis of ytterbium monoxide. Whereas the calculated

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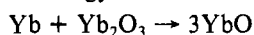
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change of the Gibbs energy ΔG for the reaction



is positive, but small (+8 or 13 kcal/mol),⁹ indicating that under normal conditions the reaction is impossible, the term $P(\Delta V)$ in ΔG is no longer negligible at high pressures; it is negative and large enough to offset the initial value of ΔG , thus making the reaction possible (an estimation⁸ gives $P(\Delta V) = 15$ kcal/mol at 40 kbar). After reaction at 40 kbar and 1000 °C a face centered cubic compound was retained metastably at normal pressure with a cell parameter $a = 4.877 \pm 0.005$ Å. While ytterbium monoxide should be diamagnetic, on the assumption that ytterbium is in the 2+ state, magnetic susceptibility measurements showed that this compound was weakly paramagnetic; this was attributed to the presence of impurities, as confirmed by chemical analysis. Treatment of the reactants at the same pressure but at higher temperature (40 kbar, 1200 °C) yielded a compound with an orthorhombic structure as found for Eu_3O_4 and CaYb_2O_4 ; the cell parameters were similar to those of the latter compound; thus it was inferred that this new compound was Yb_3O_4 .⁸

In the case of divalent samarium monoxide, the $P(\Delta V)$ term is too small to counterweigh the initial ΔG value. However it has been claimed¹⁰ that SmO would not be a semiconductor but would have metallic properties. In effect the width of the d band in the chalcogenides increases as the cell parameter decreases with the radius of the anion and would overlap the f level for this monoxide. This state would then be unstable and would contract toward a state of higher valence and smaller volume. Under these conditions pressure could favor the reaction. The formation of samarium monoxide as well as neodymium monoxide is reported in this paper.

Experimental Section

Pressure experiments were conducted in a compressible gasket apparatus of the belt type calibrated at room temperature by using the polymorphic transitions of bismuth (25.4 and 77 kbar) and barium (55 kbar). Samples (100 mg) were made of mixed powders. The metal was obtained by filing an ingot (nominal purity 99.9%) under argon; the sesquioxide (nominal purity greater than 99.95%) was calcined above 1000 °C in order to remove nonmetallic impurities. An excess of metal was generally added. The powders so obtained were compacted in a tungsten carbide or steel cylinder before introduction into the high-pressure cell. The reaction crucible was made of boron nitride, and a tantalum tube acted as a heater. Pressure was first set to the desired value and then the temperature was slowly raised; it was usually maintained for 4 h. After being unloaded, the samples were crushed, and the products formed during the experiment were identified from an X-ray diffractogram. Chemical analyses of the starting and final reaction products were also performed.

Results

Reaction of Sm + Sm₂O₃. For pressures above 50 kbar and temperatures around 1000 °C a reaction occurred; a golden yellow compound with a metallic luster was obtained. Its structure was face centered cubic with a cell parameter of 4.943 ± 0.005 Å. No foreign line was observed in the diffractogram, but when the reduction of the sesquioxide by the metal was performed at lower pressures, additional lines due to the sesquioxide were clearly seen, although the same temperature conditions were used.

Reaction of Nd + Nd₂O₃. For pressures around 50 kbar and temperatures around 1000 °C the reaction yielded a golden yellow compound with a metallic luster. Its structure was face

Table I. Lattice Parameters of Reported Samarium or Neodymium Monoxides, Nitrides, Hydrides, and Carbides

compd	lattice parameter, Å	ref	compd	lattice parameter, Å	ref
"SmO"	4.988	3			
"SmO"	5.015-5.050	4			
"SmO"	5.15	6	"NdO"	5.068	5
SmN	5.048	11	NdN	5.126	12
SmH ₂	5.37	12	NdH ₂	5.43	12
SmC _{0.33}	5.172	11	Nd ₃ O ₃ C	5.141	13
SmO	4.943 ± 0.005	a	NdO	4.994 ± 0.005	a

^a This work.

centered cubic and the cell parameter was 4.994 ± 0.005 Å. The relative intensities of the lines were similar to those of the compound obtained from the samarium reaction, and no foreign line could be observed. In the open atmosphere it decomposed slowly into hexagonal Nd(OH)₃.

Reaction of Tm + Tm₂O₃. Despite the large variety of pressure and temperature conditions investigated (10–80 kbar, 500–1200 °C), it has not been possible to obtain any new compound, even by quenching of the samples under high pressure. The sesquioxide was always recovered in its monoclinic high-pressure modification, and the metal was not oxidized. We conclude that either no compound was formed in the temperature–pressure field explored or the compound formed decomposed during the decompression into metal and sesquioxide at a pressure where the monoclinic phase of this latter compound was still stable.

Discussion

The two compounds obtained from the samarium and neodymium reactions performed under high pressures have not been previously reported. Their cell parameters are much smaller than any found for the monoxides which, in fact, were oxynitrides or hydrides as it was shown later; they are (see Table I) the smallest ones of all the known face centered cubic compounds of these rare earths with hydrogen, oxygen, carbon, and nitrogen, the elements which may be present in the samples due to a possible contamination by the various parts of the high-pressure cells. The small values of the lattice parameters definitely show that the rare earths are not in the divalent state in the compounds obtained here.

The impurity contents of the reaction products have been determined for carbon, nitrogen, and hydrogen. Several analyses gave nearly identical results; typical values were C \approx 1000 ppm, N \approx 200 ppm, and H < 200 ppm. It was concluded that the major impurity was hydrogen (less than 3 atom %), followed by carbon (1 atom %) and nitrogen (0.2 atom %). It must be noted that these values are not very different from those found for the starting products as measured just prior to introduction into the high-pressure cell, so that use of purer starting materials could increase the final purity of the compounds formed. These analyses clearly reveal that two new rare earth oxides have been made in these experiments: reaction of the sesquioxide with the pure metal proceeds under high pressure for samarium and neodymium; this is not the case at normal pressure. The stoichiometry of these oxides has been determined from the weight gain in oxygen atmosphere at 1000 °C. These measurements showed that monoxides with oxygen vacancies less than 9% were obtained.

The cell parameters of samarium and neodymium monoxides can be estimated by extrapolating the lattice constants of the corresponding monochalcogenides as a function of the anionic radius. In effect it is not possible to use a simple sum of ionic radii as these compounds are metallic when the rare earth is not in the divalent state.

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Table II. Lattice Parameters of Trivalent Neodymium Chalcogenides (from the ASTM File) and Hypothetical Trivalent Samarium Chalcogenides Obtained by Interpolation

X	lattice parameters (Å)	
	Nd ³⁺ X	Sm ³⁺ X
Te	6.278	6.208
Se	5.900	5.836
S	5.692	5.620
O	4.987 ^a	4.917 ^a

^a Extrapolated value.

In chalcogenides, neodymium is always trivalent and all the compounds are metallic. The extrapolated value for Nd³⁺O is 4.987 Å (Table II), in excellent agreement with the value (4.994 Å) found for the compound made under high pressure. It is thus inferred that neodymium monoxide was obtained with the rare earth in the trivalent state. The low resistivity of the sample confirms that this monoxide exhibits metallic properties as all the chalcogenides of the trivalent rare earths (their formula Ln³⁺X should be better read as Ln³⁺(e⁻)X²⁻).

In the same way the cell parameter of Sm³⁺O is determined by extrapolating those of hypothetical trivalent samarium chalcogenides obtained by interpolation between neodymium and terbium compounds. This yields a parameter of 4.917 Å (see Table II). The lattice constant of the ionic monoxide Sm²⁺O is expected to be 5.15 Å, just slightly larger than the cell parameter of europium monoxide (5.142 Å).

It is then clear from Table II that the samarium compound obtained has a cell parameter which definitely lies between the values so calculated for Sm²⁺O and Sm³⁺O. The difference of the lattice constants does not seem to be accounted for by a variation of the stoichiometry which usually produces a very small decrease¹⁴ of the cell parameter; we observe here the opposite effect, a significant increase. This is too large to be explained by the formation of a ternary compound; it would

imply more than 10 atom % of hydrogen and still higher percentages of carbon or nitrogen, which is much larger than found by chemical analysis. Another reason for rejecting the formation of such compounds is that we did not observe any reaction during the thulium experiments where similar conditions of environment, pressure, and temperature were applied, although compounds of thulium with nitrogen or hydrogen are also known. The hypothesis of samarium not being in a pure valence state is thus the most likely. Such a situation is already known to occur for SmS above 7 kbar where this compound shows the same golden yellow aspect. In addition the resistivity of our sample appears to be low as in the high-pressure phase of SmS which is then metallic. The intermediate valence state of samarium in SmO can be deduced from the cell parameters given in Table II by assuming a linear relationship between valence and lattice constant. A value of 2.92 is then obtained which is quite comparable to the valence state found for SmS under high pressure (2.8–2.9).¹⁵

These reported syntheses raise to four the number of now existing rare earth monoxides, three of them (YbO, SmO, NdO) being obtained only through the use of high-pressure techniques. Europium and ytterbium monoxides are insulators or semiconductors, and samarium monoxide is metallic, but samarium appears to be in an intermediate valence state, close to 3; neodymium monoxide is also metallic but neodymium is in a pure trivalent state. Although thulium monoxide cannot be obtained by using these techniques, it appears that pressure favors the formation of trivalent rare earth monoxides, and therefore the existence of other metallic monoxides seems possible. On the contrary, as stated previously, no other divalent rare earth monoxide, apart from YbO and EuO, could now be obtained by this high-pressure technique.

Registry No. SmO, 12035-88-0; NdO, 12035-20-0; Sm₂O₃, 12060-58-1; Nd₂O₃, 1313-97-9; Sm, 7440-19-9; Nd, 7440-00-8.

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