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Electron Beam Impact: a New Route to Unusual Stoichiometry and Rare Earth Intermediate Oxides*

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The RO_x (R = Ce, Pr and Tb; $1.5 \leqslant x \leqslant 2$) phases are observed in 'metallic' thin films as a result of heat treatment with the electron beam in the residual atmosphere of the electron microscope. The production of these phases is abnormal with respect to the thermodynamic conditions supposed to be relevant under the experimental conditions [1–5].

Recent experiments have suggested a dependence of the results on the absorbed impurities throughout the films and/or on the composition of the microscope residual atmosphere. The thin films are especially difficult to 'crystallize' as definite oxide phases [6] when the atmosphere outside the microscope is very dry. This fact led us to suspect a possible interference in the oxidation and recrystallization processes of the films with the water molecule or the OH radical group. Palatnik *et al.* [7] already suspected, from infrared spectra taken on europium thin films, the inclusion of OH groups in the vacant sites of the anionic sublattice of the C-type sesquioxide. Also, Norby and Kofstad [8] have shown the important influence of water vapor on the electrical resistivity of Y_2O_3 as a powder. As a consequence we undertook a study of the influence of water and carbon dioxide on the behavior of thin films and fine powders.

Experimental

Thin Films

Cerium, praseodymium and terbium metallic thin films (90–120 nm thick) were obtained by evaporation of the metal from a tungsten boat under a vacuum of some 6×10^{-5} Pa. The NaCl crystal substrates were introduced into sealed ampoules. One part of the films was studied as in the previous experiments [2, 3]. The other part was deliberately submitted to water vapor, in air, for 2 or 3 h. Some samples were observed either at once, or after a delay of one or two days inside the vacuum of the electron microscope, or, after that, were put back to ambient atmosphere for several days. All of them were studied by electron microscopy and heating from room temperature up to more than 2000 K, by means of the electron beam [2, 3, 6].

Very Fine Powders

The materials were prepared by total or partial action of CO_2 on Pr_6O_{11} and for comparison on La_2O_3 compounds. The dispersion of the commercial oxides in water in which CO_2 gas was bubbled took place at ambient temperature under the CO_2 flow for 72 h. The X-ray diffraction patterns showed the coexistence of $Pr_2(CO_3)_3 \cdot 8H_2O$ and of PrO_2, with some quantity of $Pr_2(CO_3)_3 \cdot 2\text{–}3H_2O$, whereas Pr_6O_{11} had disappeared. After heating the mixture at 473 K the X-ray patterns showed the decomposition towards intermediate compounds such as A-$PrOHCO_3$ in coexistence with the PrO_2 oxide. For lanthanum, the $La_2(CO_3)_3 \cdot 8H_2O$ compound was predominant at room temperature [9].

Results and Discussion

Thin Films

Cerium

Imaging and electron diffraction patterns of the water-treated thin films show the surprising formation of 'large' CeO_2 crystals (several μ^2 in surface), overlaid by a fine amorphous carbon-like film. These crystals are very brittle. They are broken into polycrystalline material following the impact of the slightly focused electron beam. Then, at higher temperature, they recrystallize yielding the CeO_x phases. A strange diffraction pattern of a $Ce_{12}O_{22}$ member of the Ce_nO_{2n-2} family, showing an f.c.c. (or a b.c.c.) structure is observed instead of the classical monoclinic or triclinic one. During heating at a moderate temperature the surface aspect and the structure of the crystals change continuously [10, 11].

Terbium

In comparison with untreated films few differences are observed. After heating of the B- or C-phase starting material the TbO_x phases appear. The $TbO_{1.806}$ (n = 10.333) oxide is often observed. At high temperature large TbO_2 crystals grow. But, as a function of the annealing temperature the B- or C-Tb_2O_3 and the TbO_2 phases can coexist [12]. On moderate heating the aspects of the classical pole figures and extinction contours change. They become blurred and can finally disappear entirely [11].

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Praseodymium

Praseodymium thin films treated by water vapor are a mixture of mainly PrO_2 crystals with some amounts of $Pr(OH)_3$. During heating there is formation of the A-, B- and C-Pr_2O_3 and of the PrO_x oxides. One of these PrO_x phases has been identified as a $Pr_{12}O_{22}$ compound in intergrowth with the classical A-Pr_2O_3 or PrO_2 structures (Fig. 1). The corresponding lattice of this $Pr_{12}O_{22}$ oxide cannot be indexed on the classical monoclinic cell [3] but can be according to a hexagonal one ($a = 1.34$ nm and $c = 1.885$ nm). By comparison of the calculated inter-reticular distances, one should notice that among the first 50 values of the hexagonal cell 39 of them are equal to those of the monoclinic one. Also different modes of annealing, or of cooling, with the electron beam show that it is possible to observe the A- to C-Pr_2O_3 transformation and to obtain the B-Pr_2O_3 as a stabilized phase. The electron diffraction patterns show either the A-/B-Pr_2O_3 or the PrO_2/B-Pr_2O_3 epitaxy (Fig. 2) [12].

Fine Particles

The final product of the CO_2 action, as observed by electron microscope for the smaller particles, shows the formation of single crystals as parallelepipedic platelets and needles (Fig. 3). Some elec-

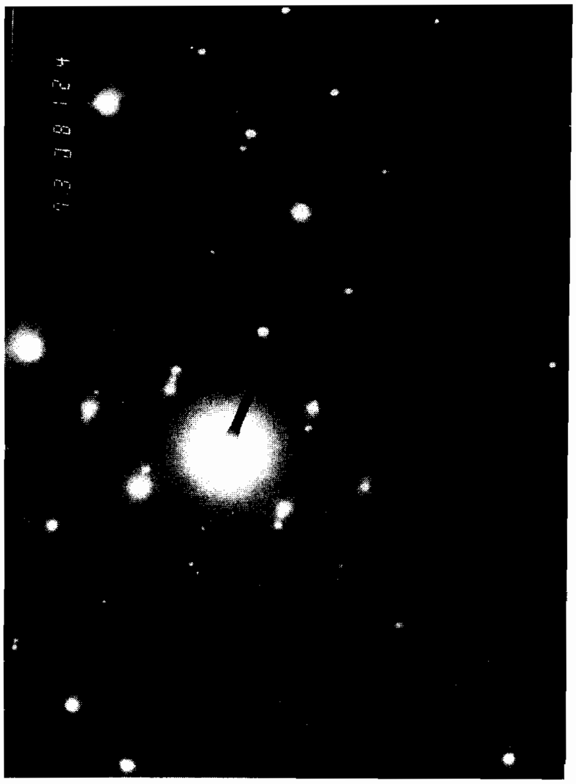

Fig. 1. Diffraction pattern of praseodymium oxide, Pr_2O_3: Epitaxy of the monoclinic (B) type along [392] on the hexagonal (A) type along [00.1].

Fig. 2. Diffraction pattern of hexagonal $Pr_{12}O_{22}$ along [00.1].

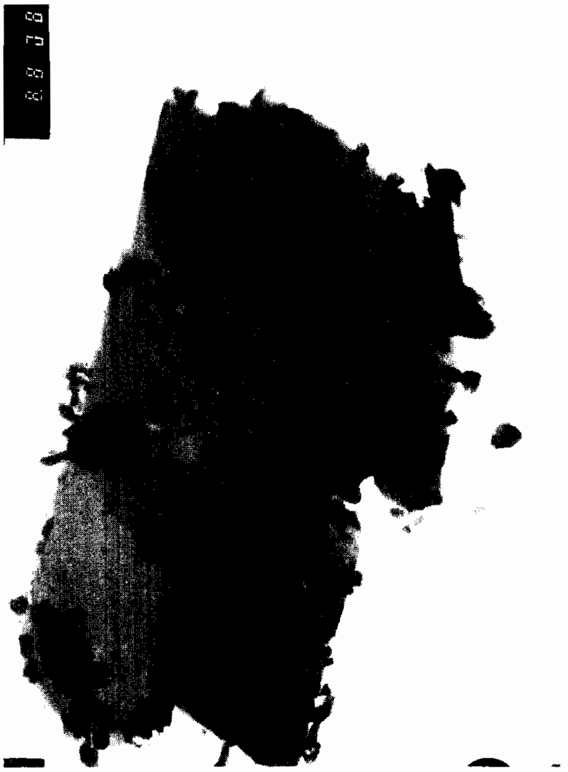

Fig. 3. Micrograph of a thin flake of $Pr_2(CO_3)_3 \cdot nH_2O$.

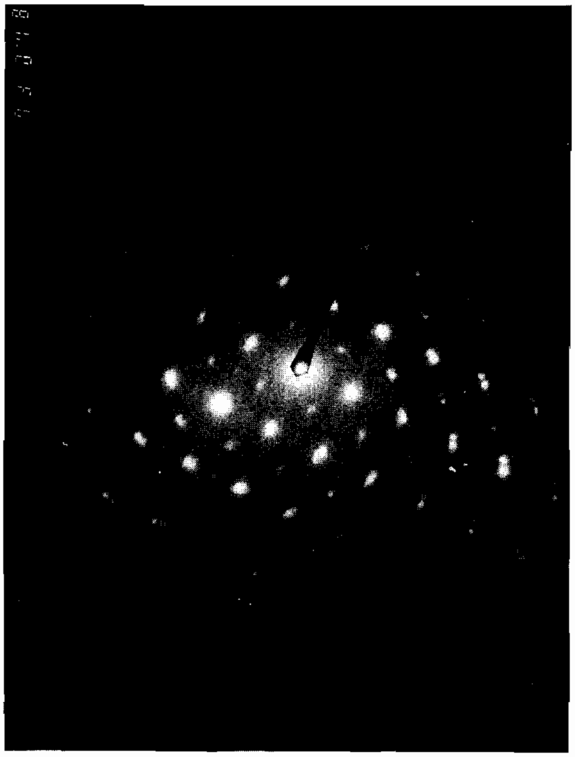

Fig. 4. Diffraction pattern of orthorhombic carbonate $Pr_2(CO_3)_3 \cdot 8H_2O$ along [101].

tron diffraction patterns show the presence of the $Pr_2(CO_3)_3 \cdot 8H_2O$ compound (Fig. 4). At the impact of the electron beam the crystals are unstable and are transformed into compounds unknown in the bulk. By heating at moderate temperature the platelets become immediately amorphous. At higher temperature they crystallize into several different phases: the A-Pr_2O_3 with some amounts of C-Pr_2O_3 appear, then the A-Pr_2O_3 and PrO_2 oxides are predominant. The powder heated before observation at 473 K shows decomposition products. Nothing happens until moderate annealing with the electron beam and no PrO_x phases are observed.

Like praseodymium platelets, the lanthanum ones are very unstable and are decomposed into intermediate compounds at the impact of the electron beam. Freshly prepared powders exhibited an unknown f.c.c. or b.c.c. structure. After a delay of some days under vacuum, it was possible to observe the $La(CO_3)_2 \cdot 8H_2O$ compound. By heating first the I-$(LaO)_2CO_3$ oxycarbonate appeared and then the A-La_2O_3 sesquioxide [9].

Conclusions and Tentative Explanation

These experiments demonstrate the great importance of water or OH radicals for the phase transformations, stabilities and reversibilities of the rare earth oxides in thin films. Especially the appearance of the RO_x systems seems to be very sensitive to the presence of water. A terbium oxide thin film, exposed for some time to ambient normal atmosphere, was analysed by means of a SIMS apparatus (secondary ion mass spectroscopy). Only Tb^+, TbH^+, TbO^+ and $TbOH^+$ ions were detected at the sample surface, the $TbOH^+/Tb^+$ ratio being roughly equal to 14% [13]. When carbonate groups alone are present in the material as impurity the situation does not seem to be as critical as it is with water. Oxycarbonates are very stable chemical species and CO_2 or CO_3 groups presumably do not enter the rare earth oxide lattices.

The existence of B-Pr_2O_3 among the phases produced by the impact of the electron beam on the water-treated thin films is a key observation to understand the processes at work. The presence of the B-phase was confirmed by other experiments undertaken on neodymium. The B-phase is a high pressure phase for these elements. This suggests that some kind of high pressure generating phenomenon is the source of those paradoxical observations. It is known from experiments on semiconductors that the impact of a laser beam can be the source of intense phonon emission in the material [14]. It arises from the condensation of electron-hole pairs (excitons) into electron-hole droplets (EHD). EHD are extremely mobile and strongly interact with the 'phonon wind' in the material to which they themselves contribute through their de-excitation processes. In this way high frequency acoustic waves can be generated with phonon energies in the 100 cm^{-1} range. In our high temperature experiments we create an electron-hole plasma and the phonon wind can be very intense. If impurities such as OH^-, or more likely the OH^-/H^+ couple, are present they may contribute through excitonic processes to strong phonon wind 'waves', and may be even focalized, travelling through the sample as high pressure shockwaves which will be the source of the strange phase transitions and unusual chemistry observed.

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