Synthesis and Crystallization of Pure Ytterbium Nitride under High Pressure (2000 bar) and Temperature (1600 °C)*

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High reactivity, non stoichiometry, decomposition and high melting points (in the region of 2500 °C) make some rare earth (RE) compounds a preparative challenge. Development of new methods of synthesis and crystal growth and investigations of their defect structure and thermochemical properties are necessary in order to manipulate their physical properties. The growth of high purity crystals of some rare earth nitrides (ScN, GdN, YbN, CeN) [1, 2], and hydrides (CeH_3) [3], has been successful, but the conditions of synthesis and crystal growth are limited by mechanical and thermal properties of the crucible and ampoule materials. The use of sealed tungsten crucibles allows temperatures up to 2500 °C for the nitrides, but the vapor pressure can be varied in the sealed crucibles only in a limited range and with very rough control. For the hydrides the situation is even worse. For high temperature work (necessary for crystal growth) quartz glass ampoules are the only available material, which limits the P, T conditions to 5 bar and 1150 °C. Therefore, the available P, T field for chemical manipulation of reactive compounds is quite extended in the direction of the T axis but very narrow in the direction of the P axis. Increase of the maximum pressure is very important to control several effects at high temperature, provided, of course, that contamination is avoided.

The need for a high pressure of the volatile component of a compound cannot be satisfied up to now in a clean atmosphere. To increase our capabilities for varying the stoichiometry, make thermodynamic investigations and grow crystals, we have developed a new high purity autoclave system [4]. The main requirements of the design were: extreme purity (oxygen level down to 0.1 ppm) and perfect control of atmosphere in the high pressure crucible.

To control the purity of the gas atmosphere in the autoclaves, we used a Balzers quadrupole mass spectrometer QMG 101 with an inlet allowing continuous monitoring of the gas composition. To determine the amount of impurities (mainly oxygen) in the gas, a calibration curve for various mixtures of oxygen in nitrogen has been measured down to 0.1 ppm of oxygen. Using this curve we have found that the nitrogen atmosphere of the autoclave contains approx. 0.1 ppm of O_2, thus meeting the requirements.

As a first material for synthesis under high pressure we chose YbN. Several investigations of the carrier concentrations of rare earth nitrides in our institute [5], undertaken up to now, have indicated that if one of these compounds could be semiconducting, it would be YbN. Our goal was to obtain stoichiometric crystals which would allow measurements of physical properties. Because of the very high melting temperature (≈2500 °C) the only way to grow crystals is sublimation of polycrystalline starting materials in electron beam sealed W crucibles at a temperature of about 2200 °C [2]. The results are rather interesting: two phases, one blue and one silver colored, appear in the crucible after sublimation. Change of valence, which could be possible in a Yb compound, could not be confirmed because the difference in the lattice constant of the two phases is rather small. We assumed, therefore, that the decrease of the N_2 partial pressure was the reason for the appearance of the blue phase. In fact, chemical analysis showed a slightly lower nitrogen content for this phase. In view of the tremendous sensitivity of the evaporation equilibrium of the RE nitrides on the P_{N_2} [2] it is very easy to suppress completely the sublimation in the sealed tungsten crucible by increasing the P_{N_2} in the furnace chamber. Estimation of the equilibrium constant suggested $10^{-3} < P_{N_2} < 10^{-1}$ torr. In view of the difficulty in estimating the permeability of tungsten to N_2, which determines the actual P_{N_2} inside the sealed W crucible, we have tried a furnace atmosphere of 99.1% Ar and 0.1% N_2. The result was clear: two sublimations gave homogeneous silver colored sublimates.

High nitrogen pressure under high purity conditions is an excellent tool to increase the nitrogen content of nitrides. Two kinds of experiments were performed in the autoclave:

(1) Synthesis from the elements, using 4 N ytterbium (Johnson Matthey). Three parameters: pressure, temperature and time have been varied. Figure 1 shows the experimental results. With increasing nitridation time and pressure, nitrogen contents and lattice constants increase up to the stoichiometric composition $x = 1.00$ and $a = 4.781$ Å.

(2) Increase of the nitrogen content of the YbN crystals grown by sublimation ($\Delta T = 30$–50 °C). The results are also shown in Fig. 1. For a low nitrogen content nitridation of the crystals in the autoclave ($P = 900$ bar, $T = 1500$ °C) results in an appreciable increase of the nitrogen content. The form of the dependence of the lattice constant on the nitrogen

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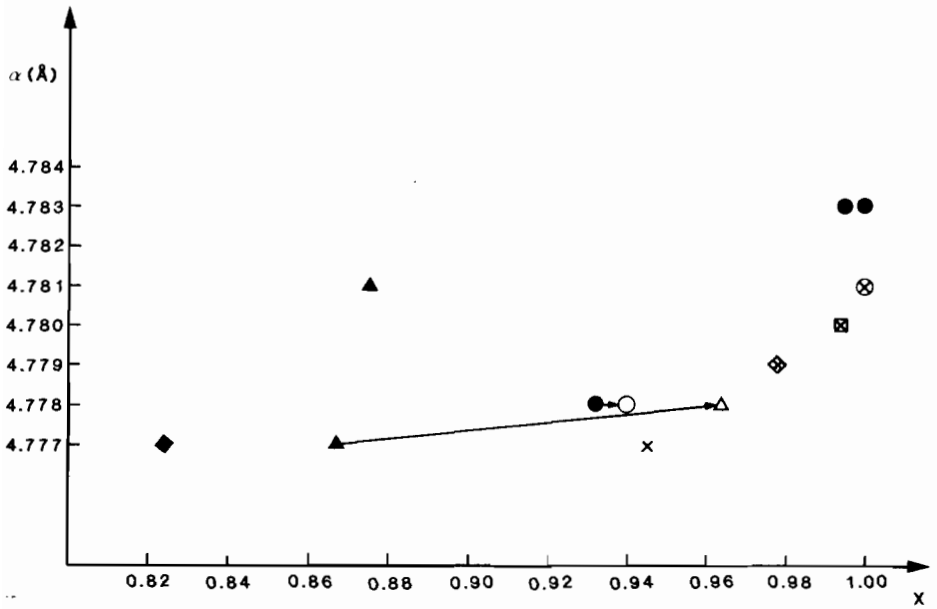

Fig. 1. Lattice parameter of YbN_x as a function of composition x. Polycrystalline YbN_x obtained by high pressure nitridation at: ⊗ 1500 °C, 600–800 bar, 142 h; ⊠ 1500 °C, 90–110 bar, 112 h; ⊕ 1600 °C, 1600–2000 bar, 5 h; × 1400 °C, various pressures 10–1500 bar, 5 h; ● crystals grown at 2000 °C by sublimation (top of sealed crucible); ◆ blue phase and ▲ recrystallized YbN (bottom of sealed crucible (2000 °C, partly contaminated)); ○ and △ crystals grown in sealed crucible after high pressure treatment at 1500 °C, 800–1000 bar, 144 h.

content indicates the existence of a phase boundary at the exact stoichiometry which, up to P_{N_2} = 1000 bar, probably cannot be exceeded.

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