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Characterization of Nd_2AlO_3N and Sm_2AlO_3N oxynitrides synthesized by carbothermal reduction and nitridation

François Cheviré*, Arthur Pallu, Erwan Ray, Franck Tessier

UMR CNRS 6226 "Sciences Chimiques de Rennes", Equipe Verres et Céramiques, Groupe Matériaux Azotés et Céramiques, Université de Rennes 1, 35042 Rennes Cedex, France

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ABSTRACT

The Nd_2AlO_3N and Sm_2AlO_3N oxynitrides with the K_2NiF_4-type structure have been prepared from oxide mixture at 1250 °C using the carbothermal reduction and nitridation route (CRN). Optimization of the process is discussed to prevent surface oxidation of the oxynitrides during the synthesis. The absorption of Nd_2AlO_3N and Sm_2AlO_3N, orange and yellow respectively, has been characterized by diffuse reflectance as well as their thermal stability versus oxidation by thermogravimetric analyses.

1. Introduction

Over the recent years, a great interest has been shown for multinary oxynitrides containing main group elements especially in the fields of phosphors [1] or visible light-driven photocatalysts [2,3]. However, if a tremendous work has been done on nitridosilicates and nitridoaluminosilicates based materials, very little is know about multinary (oxy)nitride systems based on aluminum (ex: R_2AlO_3N [4], $BaAl_{11}O_{16}N$ [5]), gallium (ex: La_2GaN_3 [6]) or phosphorus (ex: Zn_2PO_3N [7]). The R_2AlO_3N system with $R = La \rightarrow Eu$ has already been studied by Marchand previously [4]. These compounds which were air stable and told yellow have been prepared by heating R_2O_3/AlN mixtures in a sealed nickel ampoule under N_2 at 1350 °C. Several heating cycle were necessary to achieve a nearly pure sample. These oxynitrides exhibit a K_2NiF_4-type structure which correspond to the $n = 1$ member of the Ruddlesden–Popper series $A_{n+1}M_nX_{3n+1}$ [8]. A neutron diffraction study performed by Marchand has evidenced an oxygen/nitrogen ordering within the anionic sub network with the nitrogen atom occupying an apical position of the AlO_5N octahedra resulting in a lower symmetry of the cell, i.e. S.G. $(K_2NiF_4) = I4/mmm \rightarrow$ S.G. $(R_2AlO_3N) = I4/mm$, as illustrated in Fig. 1 [9].

However, one major limitation is the synthetic process which is not cost efficient and only permit small quantities to be prepared at once. In this work, we have successfully investigated an alternative and easier synthetic approach: the carbothermal reduction and nitridation route (CRN [10]) which allows to prepare larger quantities starting from cheaper precursors, i.e. oxides.

2. Experimental

Neodymium and Samarium sesquioxides (Nd_2O_3, Sm_2O_3, 99.99%, Alfa Aesar), aluminum oxide (Al_2O_3, Degussa) and carbon graphite powder (325 mesh, Alpha Product) were used as starting materials and mixed thoroughly in isopropanol using an agate mortar. The masses are determined according to the following reaction formula:

$$2R_2O_3 + Al_2O_3 + 3C + N_2 \rightarrow 2R_2AlO_3N + 3CO\ (R = \text{Nd or Sm}) \quad (1)$$

The slurry is dried at 60 °C for a couple of hours in an oven and the resulting powder placed into an alumina boat and heated at temperatures between 1000 °C and 1350 °C by 10 h cycles. In this reaction, carbon acts as a reducer and oxygen is progressively removed from the sample as carbon monoxide; the product becomes then more reactive and reacts with nitrogen to form the oxynitride. In order to limit any oxidation of the product or any parasitic consumption of the carbon graphite by oxygen or moisture traces from the nitrogen gas (99.995%, Air Liquide), a very simple device has been setted up. As described in Fig. 2, active carbon chunks (Carbio) are set in the alumina boat in front of the reacting mixture and an alumina plate is used to cover the boat. With this device, the nitrogen reacting with the mixture has to previously flow through the active carbon which react as a getter to eliminate oxygen and moisture impurities from the gas.

XRD powder patterns were recorded using a Philips PW3710 diffractometer operating with Cu K_α radiation ($\lambda = 1.5418$ Å). X'PERT softwares – Data Collector and Graphics and Identify – were used, respectively, for recording, analysis, and phase matching of the patterns.

Nitrogen contents were determined with a LECO TC-600 Analyzer using the inert gas fusion method in which nitrogen was detected by thermal conductivity.

Diffuse reflectance spectra were collected using a Varian Cary 100 Scan spectrometer equipped with the Varian WinUV software and the integrating sphere Labsphere (DRC-CA-30I). Prior to measurements, the absolute reflectance of the samples was calibrated with a certified "spectralon" standard (Labsphere Cie). Experimental data were collected within the 250–800 nm range with 1 nm step and 0.5 s integration time.

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* Corresponding author. Tel.: +33 2 2323 6234; fax: +33 2 2323 5683.
E-mail address: francois.chevire@univ-rennes1.fr (F. Cheviré).

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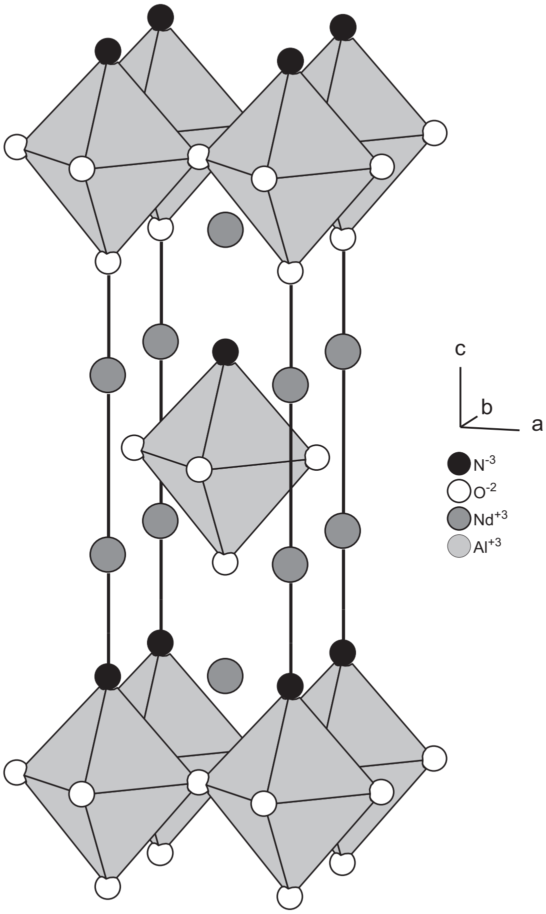

Fig. 1. Crystal structure of Nd_2AlO_3N [9].

Thermal stability of the products was determined from thermogravimetric experiments conducted at 10 °C min^{-1} and performed with a TA instruments SDT 2960. The overall accuracy of this instrument is expected to be within ±2 °C.

3. Results and discussion

Here, we have studied the potential of the CRN route for the synthesis of R_2AlO_3N with R = La, Nd, Sm and Gd. Firstly, we have focused our attention on the preparation of the Nd_2AlO_3N compound in order to optimize the process. Prior attempts were carried out by heating stoichiometric amounts, i.e. according to Eq. (1), of Nd_2O_3, Al_2O_3 and carbon graphite in an aluminum boat under N_2 as illustrated in the upper part of Fig. 1. Optimum reaction temperature has been determined to be 1250 °C. Below 1200 °C, the only phases observed are Nd_2O_3 and $NdAlO_3$; at 1200 °C, only very small amounts of the targeted compound can be obtained; at 1300 °C and higher, no improvement of the reaction yield is noticed. As described in Fig. 2, in order to reduce the observed surface oxidation due to some oxygen or moisture traces in the inlet gas, the experiment setup has been simply improved as explained in the experimental section. In addition, the amount of graphite has been doubled compared to Eq. (1). This new setup allows to strongly improve the yield of the reaction. As shown on the powder XRD patterns in Fig. 3, orange Nd_2AlO_3N can be obtained after only three cycles of 10 h. Small impurities of Nd_2O_3 are still present in the product but further heating cycles do not improve the purity of the sample. The same process with R = Sm leads to yellow-green Sm_2AlO_3N with no oxide impurity noticeable on the XRD patterns (Fig. 3). Attempts carried with R = La and Gd do not lead to the targeted oxynitrides but only mixtures of oxides. In the case of gadolinium, the result is consistent with the previous report and is probably due to the size of Gd^{3+} which is not compatible with the K_2NiF_4 structure in R_2AlO_3N system [4]. Nitrogen concentration measurements lead to 3.76 wt.% and 3.41 wt.% for Nd_2AlO_3N and Sm_2AlO_3N, respectively, which are in good agreement with the calculated values, i.e. 3.71 wt.% (Nd) and 3.59 wt.% (Sm).

Diffuse reflectance analyses performed on Nd_2AlO_3N and Sm_2AlO_3N reveal a valence band to conduction band type absorption at about 525 nm and 485 nm, respectively, which correspond to yellow and orange products (Fig. 4). Additionally in the case of Nd_2AlO_3N, the typical 4f–4f electronic transitions are observable on the diffuse reflectance spectra. This is in accordance with the experimental data as the Nd-containing oxynitride is an orange powder and the yellow–green color of the Sm-containing oxynitride can be seen as a mixture of a yellow sample and a very small amount of residual carbon. This result slightly differs from the literature as Nd_2AlO_3N was described as yellow by Marchand [4].

Thermal analyses carried under air on Sm_2AlO_3N show that oxidation starts at 600 °C and is rapid from 700 °C to 800 °C as illustrated in Fig. 5. The product of the oxidation has been analyzed by XRD and is a mixture of $Sm_4Al_2O_9$ with small amounts of $SmAlO_3$ and Sm_2O_3. If we only consider "$Sm_2AlO_{4.5}$" ($Sm_4Al_2O_9$) as the final product, the theoretical weight gain for the oxidation reaction is 2.56%, but the DTA curve indicates that the initial weight gain between T_1 and T_2 is about 5.14%, then a small plateau is observed from T_2 to T_3 and finally the curve lowers down towards the final oxidation product. Such phenomenon is similar to what Le Gendre et al. reported for the so-called "intermediate phases" observed in several oxynitride systems [11,12]. Such phases are described as oxides with N_2 retention within the structure. Thus here, the

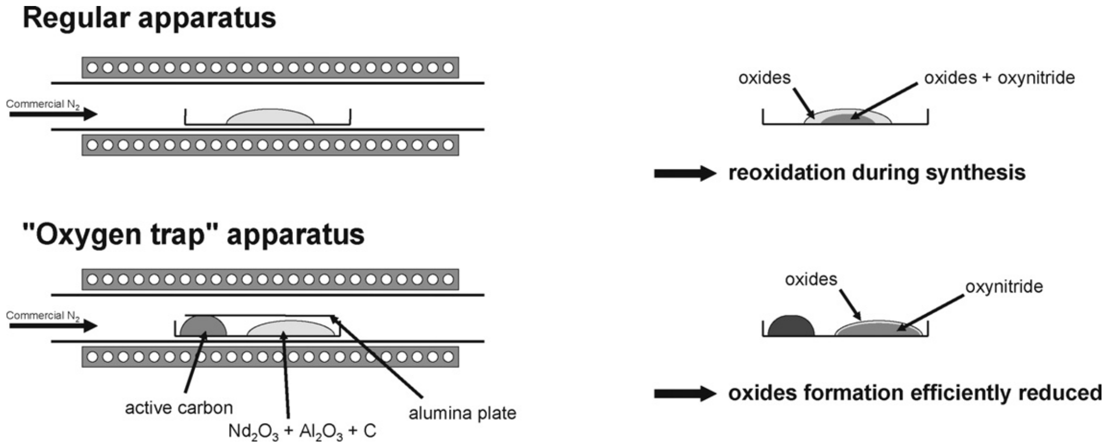

Fig. 2. Scheme of the apparatus used for the carbothermal reduction and nitridation for the synthesis of Nd_2AlO_3N and Sm_2AlO_3N.