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New scheelite-type oxynitrides in systems RWO$_3$N - AWO$_4$ (R = rare-earth element; A = Ca, Sr) from precursors obtained by the citrate route

François Cheviré, Franck Tessier, Roger Marchand

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Abstract

RWO$_3$N oxynitrides were isolated as single phases for R = Nd and Pr, after thermal ammonolysis of reactive precursors prepared using the citrate complexation/calcination route. Both stoichiometric compounds crystallize with a scheelite-type tetragonal unit cell, with $a = 5.2821(3)$ Å, $c = 11.5893(8)$ Å (NdWO$_3$N) and $a = 5.299(3)$ Å, $c = 11.631(9)$ Å (PrWO$_3$N). Neutron diffraction experiments performed on the Nd-phase did not evidence any oxygen/nitrogen order within the scheelite anionic subnetwork (S.G. I4$_1$/a). (Nd,A)W(O,N)$_4$ (A = Ca, Sr) solid solution domains were identified between NdWO$_3$N and the AWO$_4$ oxide composition.

KEYWORDS: A. nitrides, B. chemical synthesis, C. neutron scattering, D. crystal structure.

1. Introduction

Two coordinating atoms are known to date to give oxynitrides with the scheelite structure: Os$^{\text{VIII}}$ in KOsO$_3$N (I4$_1$/a, $a = 5.646(2)$ Å, $c = 13.027(4)$ Å) [1] and W$^{\text{VI}}$ in the RWO$_3$N series (R = Nd, Sm, Gd, Dy) [2-4]. This series derives from the scheelite representative term CaWO$_4$ by applying the cross-substitution principle: R$^{3+} + \text{N}^{3-} = \text{Ca}^{2+} + \text{O}^{2-}$. Whereas KOsO$_3$N was synthesized in aqueous solution, a quite unusual synthetic route for a nitride-type compound, the RWO$_3$N compositions resulted from a solid-gas reaction at 700-750°C between corresponding tungstates R$_2$W$_2$O$_9$ and flowing ammonia. In fact, only SmWO$_3$N and GdWO$_3$N were isolated as single phases; in the case of neodymium in
particular, simultaneous presence of both a scheelite phase and a nitrogen-rich perovskite-type phase NdW(O,N)₃ was systematically observed, the formation of the latter being favored by higher temperatures and/or longer reaction times.

Due to their too high value of thermal neutron cross-section [5], neither Sm ($\zeta = 5900$ barns) nor Gd ($\zeta = 49700$ barns) are suitable elements for a neutron diffraction study. Consequently, in order to conclude about a possible oxygen/nitrogen order within the scheelite anionic subnetwork, we have performed new investigations in the RWO₃N series by using more reactive oxide precursors prepared via a *chimie douce* process - the amorphous citrate method [6]. NdWO₃N has been synthesized as a pure scheelite and studied by neutron diffraction, and the RWO₃N series extended to R = Pr. The amorphous citrate method has been also utilized to investigate $A_{1-x}Nd_xWO_4_N_x$ ($A = Ca, Sr$) possible solid solutions.

2. Experimental

Lanthanide oxides (Nd₂O₃, Pr₆O₁₁; 99.99%, Alfa Aesar), alkaline-earth carbonates (99%, Alfa Aesar) and tungstic acid ($\geq 99\%$, Acros) were used as starting materials and separately dissolved, for oxides or carbonates, in concentrated nitric acid (65%, Merck) or, for $H_2WO_4$, in a commercial ammonia solution (25%, Merck). Citric acid ($C_6H_8O_7$, $\geq 99\%$, Merck) dissolved in a minimum amount of water was added to each solution in the proportion of one mole per cation valence, the addition being followed by a 30 min stirring step at 120°C. As the complexation of cations by citric acid is improved at pH $\geq 7$ [6], the acidic solutions (containing the rare-earth or the alkaline-earth cation) were neutralized by ammonia solution. All the solutions were then mixed and the resulting solution stirred at 150°C for 15 min to promote chelate formation. A rotavapor (Buchi R3000) was used to remove a maximum of water until formation of a clear and highly viscous liquid. The liquid was then progressively heated up to 250°C, leading after 15 h to an expanded black solid residue. This solid was finally grinded and calcined at 600°C in an alumina crucible until total elimination
of carbon. The resulting \( \text{R}_2\text{W}_2\text{O}_9 \) and Ca(Sr)-containing tungstate powders showed a color characteristic of the rare-earth, light blue for \( R = \text{Nd} \), light green for \( R = \text{Pr} \).

Nitridation experiments were carried out in alumina boats placed inside an electric furnace through which ammonia gas flowed at a flow rate of 30-40 \( \text{l.h}^{-1} \). The temperature was raised in the 550-700°C range at a heating rate of 10°C.min\(^{-1}\). After a 15 h reaction time, the furnace was switched off and the nitrided powders were allowed to cool down to room temperature under nitrogen atmosphere.

Nitrogen contents were determined by the Grekov method based on the reaction of the nitride ion \( \text{N}_3^- \) with a strong base and the formation of ammonia which is then titrated [7].

The oxide precursors prepared by *chimie douce* as well as the oxynitrides were identified by X-ray Diffraction. The XRD powder patterns were recorded using a Philips PW 3710 diffractometer operating with CuK\(_\alpha\) radiation (\( \lambda = 1.5418 \text{ Å} \)). X’PERT softwares – Data Collector, and Graphics and Identify – were used, respectively, for recording and analyzing the patterns. The lattice parameters were refined using Dicvol [8].

Neutron diffraction experiments were performed on the two-axis powder diffractometer 3T2 at the Orphée 14 MW reactor of the CEA Saclay (France), using \( \lambda = 1.2251 \text{ Å} \) as the neutron wavelength. The diffraction pattern was recorded over the angular range 6° < 2\( \theta \) < 120° in steps of 0.05°. The crystal structure of \( \text{NdWO}_3\text{N} \) was refined using the Rietveld method with Fullprof [9,10].

### 3. Results and Discussion

#### 3.1. \( \text{NdWO}_3\text{N} \) and \( \text{PrWO}_3\text{N} \)

Nd- and Pr-containing oxynitride scheelites were obtained by reacting oxide precursors prepared via the amorphous citrate method [4,6]. This method utilizes the complexing properties of citric acid to prevent any undesired precipitation within a solution containing all the considered cations. After total evaporation, then calcination of resulting
metal-organic complexes, homogeneous and reactive fine powders are obtained. Thus, the citrate route applies to a large number of oxide compositions which cannot be reached via traditional methods, in particular complex stoichiometries involving several cations in different proportions.

In the nitridation of the neodymium oxide precursor, the competition between the formation of the scheelite NdWO$_3$N and the perovskite NdW(O,N)$_3$ is a difficult parameter to control. Antoine et al. [2,11] have shown previously that, while the perovskite is only present at high temperature (a black-colored phase due to mixed-valent tungsten), both phases are observed since the nitridation onset (700-750°C), thus preventing any possibility to prepare a pure scheelite phase.

A neodymium tungstate precursor (Nd/W = 1) has been prepared via the amorphous citrate route in order to decrease the nitridation onset by taking advantage of the reactivity and the chemical homogeneity of such precursors. In the light of the results for neodymium, the synthesis of a novel scheelite-type oxynitride - PrWO$_3$N - has been carried out to extend the R-containing scheelite domain towards larger rare-earth elements.

A calcination temperature of 600°C of the oxide precursors revealed to be necessary to totally remove carbon. But, the resulting powders presented a very low crystallization state, the broad XRD peaks not allowing any identification of lanthanide tungstates or binary oxides. Subsequent nitridation experiments evidenced a high reactivity of such oxide powders, however, they provided amorphous nitrided powders which did not crystallize even after long nitridation times at 650°C and, consequently, could not be identified. Hence, the oxide precursors were systematically annealed in air at 750°C; under those conditions pure Nd$_2$W$_2$O$_9$ and Pr$_2$W$_2$O$_9$ were clearly evidenced by XRD (cf. Figs. 1 and 2). Using those crystalline but still reactive starting oxides, nitridation experiments were carried out at different temperatures ranging between 550 and 700°C. Corresponding XRD powder patterns
are shown in Figs. 1 and 2. A nitridation onset as low as 550°C was observed, and formation of the perovskite phase only from 650°C. So, for both Nd and Pr, nitridation of the precursor at 600°C for 15 h provides pure scheelite phases.

These oxynitride scheelite powders display a light grey color different from the brown color reported for SmWO$_3$N and GdWO$_3$N [2]. However, from $T = \sim 650°C$ the powders became progressively darker, indicating a partial reduction of tungsten and presence of the perovskite phase which was confirmed after longer nitridation times. Table 1 gives the XRD powder patterns and tetragonal unit cell parameters of NdWO$_3$N and PrWO$_3$N. The variation of the unit cell parameters versus the $R^{3+}$ ionic radius is shown in Fig. 3 for the whole RWO$_3$N series ($R = \text{Pr} \rightarrow \text{Dy}$). Attempts to synthesize La- and Ce-containing analogous scheelite-type oxynitrides were unsuccessful. In the case of lanthanum, only the perovskite phase LaW(O,N)$_3$ was observed [12,13], while in the case of cerium, oxidation of Ce$^{III}$ into Ce$^{IV}$, which occurs during the citrate process, prevented synthesis of the Ce$_2$W$_2$O$_9$ oxide precursor.

Chemical analysis results are shown in Table 2. As mentioned above, the experimental formulations are obtained by taking into account the nitrogen content and the electroneutrality of the formula considering W in its highest oxidation state VI.

Using neutron diffraction, oxygen and nitrogen can be clearly distinguished because of very different coherent nuclear scattering lengths [5]: $b(\text{N}) = 9.36$ fm, $b(\text{O}) = 5.805$ fm. Among the oxynitrides studied to date, only a few exhibit a partial or total nitrogen/oxygen order: TaON [14] with the ZrO$_2$ baddeleyite-type structure, Nd$_2$AlO$_3$N [15] and Sr$_2$TaO$_3$N [16, 17] with the K$_2$NiF$_4$ structure, LaTaON$_2$ and SrTaO$_2$N [18] with the perovskite structure when synthesis is mineralizer-assisted.

The crystal structure of NdWO$_3$N was refined in the space group I4$_1$/a using KO$_3$O$_3$N, which structure was determined from a single crystal study [1], as an isostructural model. As
shown in Fig. 4, the scheelite-type tetragonal structure consists of isolated \([WO_3N]\) tetrahedra linked to each other by 8-fold coordinated Nd cations. The refinement results are given in Table 3 and Fig. 5, and the structural parameters gathered in Table 4. The neodymium position was taken as 4a, the tungsten as 4b and the oxygen and nitrogen, initially taken in a 3:1 ratio, were assigned to the 16f position. The occupancy of the anion position 16f was refined considering its full occupancy, but with no constraint on the O/N proportion. The resulting composition \(\text{NdWO}_{2.99}\text{N}_{1.01}\) is in good agreement with this calculated from chemical analysis (Table 2). The Rietveld refinement confirms the distribution of oxygen and nitrogen over the same position without O/N ordering. The interatomic distance \(W-(O,N)\) (1.808 Å) matches well with the average distance observed in \(\text{Na}_3\text{WO}_3\text{N}\) (\(W-(O,N) = 1.801 \text{ Å}\)) [19]. In the case of the Nd-(O,N) distance, no reference is available in the literature where Nd is 8-fold coordinated. However, it is possible to compare the distances in \(\text{NdWO}_3\text{N}\) (Nd-(O,N) = 2.470 Å and 2.489 Å) to those given in \(\text{NdN}\) (Nd-N = 2.576 Å, coordinence number 6) [20] and \(\text{NdTaO}_4\) (Nd-O = 2.451 Å, coordinence number 8) [21]. Thus, we can estimate from those data the average distance \(\text{Nd-(O,N)} = \frac{3}{4}\text{Nd-O} + \frac{1}{4}\text{Nd-N} = 2.482 \text{ Å}\), which is in good agreement with those determined in our study.

3.2. \((\text{Nd},A)_4\text{W}(O,N)\_4\) solid solutions \((A = \text{Sr, Ca})\)

According to a partial cross-substitution \(\text{A}^{II}/\text{Nd}^{III} - \text{O}^{II}/\text{N}^{III}\) (\(A = \text{Ca, Sr}\)), attempts have been carried out to prepare solid solution terms between the scheelite oxynitride \(\text{NdWO}_3\text{N}\) and the isostructural pure oxide phase \(\text{AWO}_4\). Table 5 summarizes the different compositions prepared in both \(\text{A}_1-x\text{Nd}_x\text{WO}_{4-x}\text{N}_x\) systems and the corresponding experimental parameters. The thermal stability domain of the scheelite phase in these systems is very limited as nitridation occurs from 550°C only, and a perovskite phase forms as low as 600°C (cf. Fig. 6). In the case of calcium, the pure scheelite XRD powder patterns seem to indicate formation of a solid solution along the whole domain without any shift with respect to the
diffraction peak positions of CaWO$_4$, or indication of superstructure, as shown in Fig. 7. We correlate those similar patterns to the same effective ionic radius of Ca$^{2+}$ and Nd$^{3+}$ in 8-fold coordination (1.12 Å) [22]. Thus, it is not possible to be sure that a solution exists between CaWO$_4$ and NdWO$_3$N.

Strontium has a significantly higher effective ionic radius (1.26 Å in 8-fold coordination [22]). The XRD powder pattern of the nitrided $x = 0.5$ precursor composition manifests coexistence of two scheelite-type patterns which do not correspond either to SrWO$_4$ or NdWO$_3$N, but have intermediate diffraction peaks (Fig. 8). Experiments carried out on different Sr$_{1-x}$Nd$_x$WO$_4$ compositions ($x = 0.2, 0.3, 0.8, 0.9$) give rise to a single phase. Those results support existence of two different solid solution domains, one for $0 \leq x < 0.5$, the second for $0.5 < x \leq 1$ (NdWO$_3$N), with the composition $x = 0.5$ located out of these two domains. As shown in Table 5, with increasing neodymium content, a progressive nitrogen enrichment occurs to balance the higher cationic formal charge in the scheelite composition Sr$_{1-x}$Nd$_x$WO$_{4-x}$N$_x$.

4. Conclusion

In the study of systems RWO$_3$N - AWO$_4$ (R = rare-earth; A = Ca, Sr), the amorphous citrate route has demonstrated its efficiency to provide oxide precursor powders with an improved reactivity. Thermal ammonolysis of such precursors yields the pure scheelite oxynitrides NdWO$_3$N and PrWO$_3$N that was not possible via the conventional solid state route, as well as RWO$_3$N - AWO$_4$ solid solutions between NdWO$_3$N and AWO$_4$ (A = Ca, Sr). A neutron diffraction study of NdWO$_3$N has evidenced no O/N anionic order.

Acknowledgments

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Rennes 1, France) for his advices about Fullprof and WinPlotr softwares.

References

Figures Captions

Fig. 1 XRD powder patterns of the Nd/W = 1 oxide precursor and oxynitrides.

Fig. 2 XRD powder patterns of the Pr/W = 1 oxide precursor and oxynitrides.

Fig. 3 Variation of the RWO₃N tetragonal unit cell parameters as a function of the R³⁺ ionic radius (after Shannon [22]).

Fig. 4 Crystal structure of the oxynitride scheelite NdWO₃N.

Fig. 5 Experimental (points) and calculated (solid line) neutron powder diffraction profiles from the Rietveld refinement of NdWO₃N (intensities in arbitrary units); the difference /esd profile is also given.

Fig. 6 Nitridation of Ca₁₋ₓNdₓWO₄₋ₓ/₂ oxide precursors at 550 and 600°C, and corresponding XRD powder patterns.

Fig. 7 XRD powder patterns of Ca₁₋ₓNdₓWO₄₋ₓNₓ oxynitrides.

Fig. 8 XRD powder patterns of Sr₁₋ₓNdₓWO₄₋ₓNₓ oxynitrides.
Fig. 1
Fig. 2
Fig. 3
Fig. 4
Fig. 5
Fig. 6
Fig. 7
Fig. 8
Table 1. XRD powder pattern and tetragonal unit cell parameters of RWO$_3$N oxynitrides (R = Nd, Pr).

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<tr>
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<th>d$_{calc.}$ (Å)</th>
<th>I/I$_0$</th>
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<tr>
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Table 2. Chemical analysis results and corresponding oxynitride formulations.

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Table 3. Neutron diffraction refinement results of NdWO$_3$N.

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Table 4. Atomic parameters for NdWO$_3$N.

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<th>Position</th>
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Table 5. (Nd,A)W(O,N)$_4$ solid solutions (A = Sr, Ca): nitridation parameters and results.

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<th>Nitridation time (h)</th>
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<td>Sr$<em>{0.8}$Nd$</em>{0.2}$W</td>
<td>550</td>
<td>30</td>
<td>0.81</td>
<td>0.88</td>
<td>O$<em>{3.77}$N$</em>{0.21}$</td>
</tr>
</tbody>
</table>

P: Perovskite