



Contents lists available at ScienceDirect

Progress in Solid State Chemistry

journal homepage: www.elsevier.com/locate/pssc

Synthetic approaches in oxynitride chemistry

Amparo Fuertes

Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, 08193, Bellaterra, Spain

ARTICLE INFO

Keywords:

Oxynitrides
Mixed anion oxides
Anion order
Ammonolysis
High pressure synthesis
Topochemical synthesis
Perovskite oxynitrides
Water splitting photocatalysis
Oxynitride phosphors
Dielectric materials
Colossal magnetoresistance

ABSTRACT

Mixed anion oxides are emerging materials showing a variety of physical and chemical properties. Among them oxynitrides are widely investigated because of notable photocatalytic, dielectric, luminescent and electronic properties. Nitrides show more positive free energies of formation than oxides because of the higher stability of N_2 molecule with respect to O_2 and the unfavourable electron affinity of nitrogen compared to oxygen. However the stability of oxynitrides is higher than for nitrides, and they easily form from oxides in presence of reactive gases as NH_3 . In addition to ammonolysis several synthetic strategies have been developed in the last years leading to the stabilization of relevant materials with a variety of structures. In this review we will discuss recent progress in the synthesis of oxynitrides emphasizing the importance of kinetic factors and the influence of preparative parameters on the structure types and oxidation states of the cations, and the consequences on physical properties.

1. Introduction

In recent years many groups have emerged in the research field of mixed anion systems to find new properties for a variety of applications. Using the vast, previous knowledge of oxidic compounds, the general approach for the design of mixed anion oxidic materials is to substitute in a given phase some of the oxide anions by his neighbours in the periodic table F^- , S^{2-} or N^{3-} playing with the differences in electronegativity and polarizability of the anions to modify the electronic structure and therefore the properties [1–7].

Research in oxynitrides has been subjected to a large expansion in the last two decades leading to the discovery of important photocatalysts, luminescent, and electronic materials [8–14]. The substitution of oxide by nitride induces changes in the energies of the electronic levels. This is a consequence of the lower electronegativity and higher electronic polarizability of nitrogen compared to oxygen which leads to an increase of the covalent character of the bonds with metals. In semiconductors an immediate effect is the raising of the top level of the valence band and the narrowing of the band gap which for photocatalysts shifts the activity from UV to the visible light. Notable examples of visible light oxynitride photocatalysts are the perovskites $LaTiO_2N$ [15] and $LaMg_xTa_{1-x}O_{1+3x}N_{2-3x}$ ($x \geq 1/3$) that are both active in water splitting and show absorption edges near to 600 nm [16]. Another important effect in oxynitrides is the shifting to the red of the emission wavelengths of rare earths. This is because of lowering of the energy of 5d orbitals, which is a consequence of the larger nephelauxetic effect induced by covalency and the increase in crystal field

splitting induced by the higher charge of nitride (-3) versus oxide (-2). Important luminescent oxynitridosilicates are the compounds $(Sr,Ca,Ba)Si_2O_2N_2$ doped with Eu^{2+} showing high quantum efficiencies and cyan, green or yellow emissions under activation in the UV-blue range [17]. The Fermi level in a transition metal nitride is placed at higher energies than in the corresponding oxide [18]. This decreases the operating voltage in lithium or sodium batteries making the transition metal (oxy)nitrides attractive as electrode materials as it is shown by $Li_{7.9}MnN_{5.3}O_y$ [19]. For a given structure type new combinations of cations can be found in oxynitrides to compensate the higher charge of nitride. The larger covalency and polarization of bonds with metals affect the electronic properties leading to new magnetic, conducting and dielectric materials. The perovskites $EuMO_{3-x}N_x$ ($M = Nb, Ta, W$) show colossal magnetoresistance and ferromagnetism [20,21] and high dielectric constants have been reported for $BaTaO_2N$ and $SrTaO_2N$ [22]. Also remarkable is the exchange of hydride by nitride in $BaTiO_{3-x}H_x$ at low temperature that results in a new ferroelectric oxynitride material [23]. The oxynitride $MnTaO_2N$ with polar $LiNbO_3$ structure is insulating, and dielectric measurements have not been reported, but the calculated spontaneous polarization is similar to isostructural multiferroic Mn oxides [24]. Nitride introduction in the antiferromagnetic perovskites $LnCrO_3$ induces the oxidation of Cr^{3+} to Cr^{4+} and decreases the magnetic ordering temperature. The suppression of the magnetic interactions in $LnCrO_{3-x}N_x$ is a consequence of doping but this effect is less drastic than in cation doped $Ln_{1-x}A_xCrO_3$ ($A =$ alkaline earth) because of the greater covalent character of the Cr-N bonds [25]. In a similar way the introduction of nitride in $LnVO_3$ perovskites induces the

E-mail address: amparo.fuertes@icmab.es.<https://doi.org/10.1016/j.progsolidstchem.2017.11.001>

0079-6786/ © 2017 Elsevier Ltd. All rights reserved.

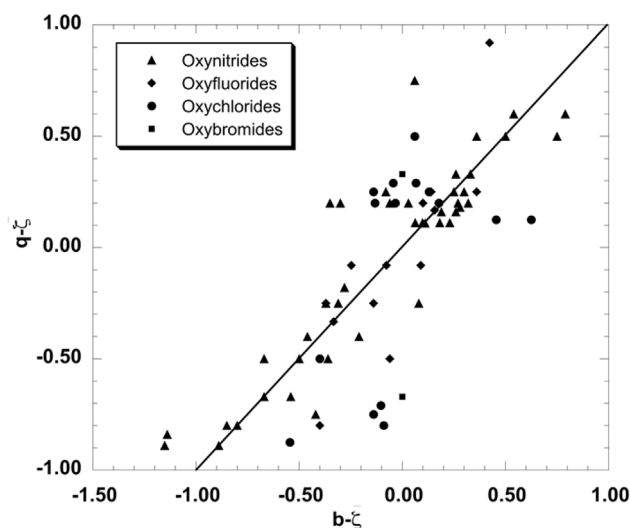


Fig. 1. Plot of the experimentally determined charge of the anion (q) versus the bond strength sum in each site (b), both corrected for the average charge of anions, \bar{z} for oxynitrides and oxyhalides. The bond strength sum b is defined according to Pauling second crystal rule as $b = \sum_i \frac{z_i}{v_i}$ where z_i is the electric charge of each cation bonded to a given anionic position and v_i its coordination number (Reproduced from Ref. [33] with permission of the American Chemical Society).

oxidation of V^{3+} to V^{4+} and a suppression of the antiferromagnetic order [26]. New antiferromagnetic double perovskites Sr_2FeWO_5N have been reported with a high degree of cation order and a Néel temperature of 13 K [27].

An important aspect of oxynitrides is anion order that has remarkable effects on properties such as ferroelectric response, dielectric constant, band gap, band edge positions and absorption coefficient [28–31]. Oxide and nitride order in many oxynitrides following the Pauling second crystal rule [32] so as the N^{3-} occupies the sites with larger bond strength sums (b) (Fig. 1) [33,34]. In perovskite oxynitrides cis order of nitrides has been observed for some compounds and this lowers the space group symmetry determined by tilting [35–38]. DFT and molecular-dynamics studies have demonstrated that the cis distribution of nitrides stabilize the structure because of the higher covalency of metal-nitrogen bonds [39,40].

The major challenge in the chemistry of oxynitride materials is the control and reproducibility of the synthesis and the development of new preparative methods. (Oxy)nitrides show smaller free energies of formation than oxides as a consequence of the high bond energy of the N_2 molecule (945 kJ mol^{-1} for $N \equiv N$ vs. 498 kJ mol^{-1} for $O = O$) [41] and unfavourable electron affinity of nitrogen (1736 kJ mol^{-1} for $N \rightarrow N^{3-}$ vs. 601 kJ mol^{-1} for $O \rightarrow O^{2-}$) [42]. The majority of oxynitrides are stable in ambient conditions and some of them do not react with strong solvents. However the higher stability of oxides makes necessary to strictly control the synthesis conditions in order to avoid the decomposition at high temperatures. In the reactions under N_2 or in sealed tubes any source of water and oxygen around the sample should be avoided which in some cases involves the use of glove box for the handling of reactants and oxygen scavengers in the reaction tube. Ammonolysis reactions of oxides have been widely used for the stabilization of ternary, quaternary and higher oxynitrides. In order to design synthesis pathways for new compounds an improved understanding of the reactivity and redox chemistry of the transition metals under NH_3 at high temperatures is needed, together with a rationalization of the effect of the relevant experimental parameters. Following this approach this review discusses relevant aspects of synthetic approaches to metal oxynitrides including traditional methods of ammonolysis of oxides and high temperature solid state reactions as well as more recently developed topochemical synthesis and soft chemistry methods, crystal growth in supercritical ammonia and ammonothermal

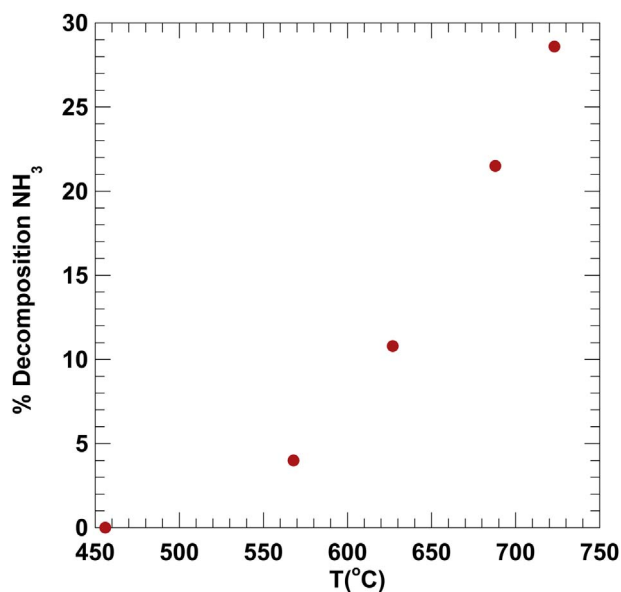


Fig. 2. % of decomposition of ammonia as a function of temperature for a flow rate of $125 \text{ cm}^3/\text{min}$ (produced with data of Ref. [45]).

and high pressure reactions.

2. Ammonolysis of oxides

Reactions of powder samples of oxides under flowing ammonia at moderate to high temperatures are the most common method for the synthesis of oxynitrides. The treatment temperatures range from $400 \text{ }^\circ\text{C}$ to $1100 \text{ }^\circ\text{C}$, with variable times from few hours to several days, and NH_3 flow rates between 50 and $1000 \text{ cm}^3/\text{min}$. Ammonia dissociates at temperatures close to $500 \text{ }^\circ\text{C}$ into N_2 and H_2 and the extent of this reaction increases with temperature following the K_p vs T empirical equation reported by Maxted [43]. The rate of decomposition depends also on the nature of the surface in contact with ammonia and on the time of exposure to heat. In a closed static system at constant volume and temperature of $1100 \text{ }^\circ\text{C}$ the decomposition is complete in twenty minutes [44]. In flowing ammonia the decomposition is largely influenced by the gas rate and for instance at $700 \text{ }^\circ\text{C}$, a typical temperature for the formation of oxynitrides, under a flow rate of $180 \text{ cm}^3/\text{min}$ the degree of dissociation is only 10%. Fig. 2 shows the dependence of the % of decomposition with temperature for flowing ammonia at constant rate of $125 \text{ cm}^3/\text{min}$ [45].

Ammonia is a Lewis base and a weak Liebig acid [46] and in consequence it can reduce and oxidize the metals evolving N_2 or H_2 respectively. Both reactions may take place during the ammonolysis of oxides. Thermodynamic calculations predicted that ternary oxides containing the electropositive alkaline, alkaline earth metals and lanthanides will not form ternary nitrides by ammonolysis but they may form oxynitrides [47]. This has been widely demonstrated by the numerous examples of preparation of oxynitrides with diverse structures and stoichiometries including anatase $TiO_{2-x}N_x$ [48,49], fluorite $CeO_{2-x}N_x$ [50], rock-salt $ZnO_{1-x}N_x$ [51], perovskites $ABO_{1+x}N_{2-x}$ ($A =$ alkaline earth or lanthanide; $B =$ Mg, Ti, Zr, V, Nb, Ta, Cr, Mo, W and Fe) [9,10,20–22,25–27,52–59], pyrochlores [60–63] and spinels [64] among others. Ammonolysis reactions have been also used to synthesize oxynitridosilicates/germanates with apatite structure such as $La_{10}(Si/Ge)_6O_{26-y}N_y$ [65] and $Y_{10}(Si_6O_{22}N_2)O_2$ starting with the corresponding oxidic compounds [66]. High temperature calorimetry studies have been recently performed to investigate the conversion by ammonolysis of ABO_4 scheelites into the perovskites $AB(O,N)_3$ [67]. The enthalpies of formation of the oxynitrides $SrMoO_2N$ and $SrWO_{1.5}N_{1.5}$ are less negative than the corresponding scheelites $SrMoO_4$ and $SrWO_4$. However

Download English Version:

<https://daneshyari.com/en/article/8961413>

Download Persian Version:

<https://daneshyari.com/article/8961413>

[Daneshyari.com](https://daneshyari.com)