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研究課題名(和文) Synthesis of Novel Oxynitride With Derivate Perovskite Structure

研究課題名(英文) Synthesis of Novel Oxynitride With Derivate Perovskite Structure

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研究成果の概要(和文)：このプロジェクトでは、我々はLiNbO<sub>3</sub>型とダブルペロブスカイト型の結晶構造を持つ物質の合成と物性について研究した。これらの物質は高圧高温下で合成しました。従来の酸窒化物は、酸化物をアンモニア雰囲気かつ高温の条件下で処理するのにに対し、我々は還元雰囲気のない高圧合成法を用いた。我々はZnTaO<sub>2</sub>Nの結晶構造と物性について研究し、LiNbO<sub>3</sub>型のほとんどの酸化物は室温でカチオンが秩序化しているのに対し、本物質は秩序化しておらず反転対称性があることがわかった。La<sub>2</sub>MnTaO<sub>5</sub>Nについては、部分的にアニオンが秩序下していることが分かり、磁気構造についても研究した。

研究成果の概要(英文)：During this project we have investigated the synthesis and properties of LiNbO<sub>3</sub>-type and double perovskite structures. The materials were prepared using the high pressure and high temperature technique. While most oxynitrides have been prepared using precursor oxides at high temperature under ammonia flow, we have used the high pressure approach to yield less reducing conditions. We have studied ZnTaO<sub>2</sub>N crystal structure and properties which shows cationic disorder and centrosymmetry at room temperature while most oxides of the LiNbO<sub>3</sub>-type are usually ordered at this temperature. The crystal structure of La<sub>2</sub>MnTaO<sub>5</sub>N was also investigated and showed partial order of the anions in the structure. The magnetism of the structure has been investigated.

研究分野：Solid State Science

キーワード：Perovskite Oxynitride High-Pressure

### 1. 研究開始当初の背景

Perovskite  $ABO_3$  is one of the most common structure encountered in nature and one of the most versatile frameworks in terms of compositions. Most known perovskite structure contain only the oxide anion  $O^{2-}$ . The wide range of accessible compositions allow for applications from superconductors, magnetoresistance, dielectrics, catalysts, etc... Unlike oxides that can be prepared in different conditions, oxynitrides containing both the  $O^{2-}$  and  $N^{3-}$  ions are difficult to prepare. Oxynitrides are however very interesting with numerous functionalities from water-splitting catalysis, magnetoresistance and dielectrics.[1] To prepare them, the conventional technique is the annealing of oxides under ammonia flow so-called ammonolysis. The high temperature and use of  $NH_3$  create strongly reducing conditions which severely limit the range of compositions. Therefore, a different approach is necessary to develop new materials.

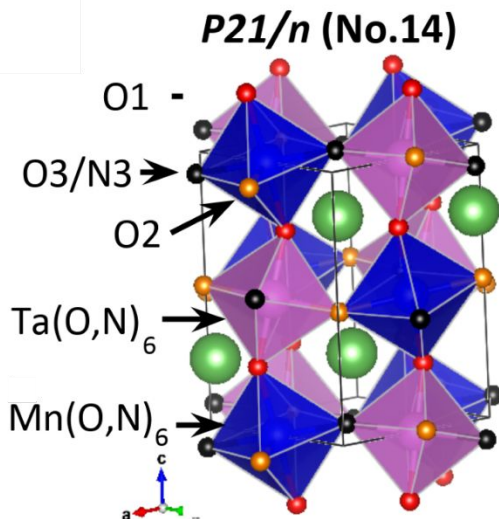


Figure 1. Schematic  $La_2MnTaO_5N$  structure.

### 2. 研究の目的

The purpose of this research was to develop novel oxynitride structure and investigate their different properties from photocatalysis to magnetism. In this aim, we used a different approach with commonly used path for oxynitrides that is ammonolysis. In this research, we have used the high-pressure and high-temperature synthesis. In this technique, the oxide and nitride anion

come from the precursors of the reaction. This allows a simpler control of the anionic composition with respect to the  $NH_3$ -flow technique.

Using the high-pressure approach, different elements from those conventionally used can be explored. Unlike ammonolysis, high-pressure synthesis should allow yielding less reducing conditions. We therefore explored different oxynitride composition with different types of structures notably the  $LiNbO_3$ -type and the B-site ordered perovskite type  $A_2BB'O_6$  where two different B octahedral sites exist.

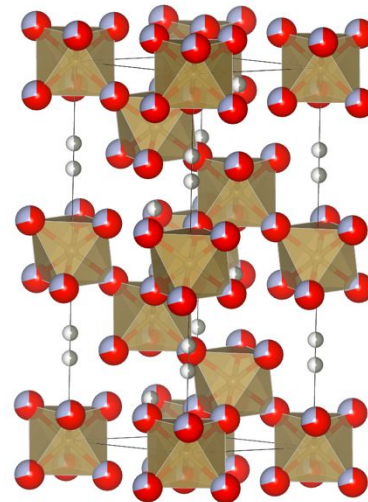


Figure 2. Schematic  $ZnTaO_2N$  Structure. Red, purple, brown and grey spheres indicate oxygen, nitrogen, tantalum and zinc.

### 3. 研究の方法

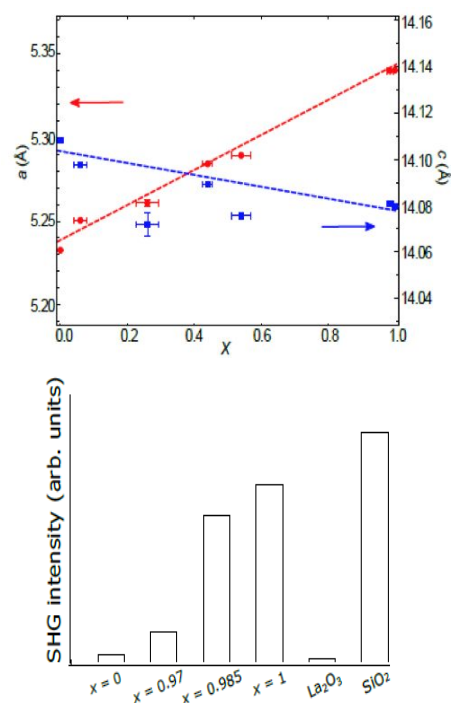
To yield novel perovskites we used the high pressure and high temperature technique. In order to introduce nitride ion in the structure, oxides were mixed with nitrides, typically TaON and sealed the starting mixture in platinum foils within a glove box. The mixtures were first pressed to the desired pressure and then heated at high temperature. Once the sample was cooled, pressure was decreased slowly to ambient atmosphere. The samples were studied first with laboratory XRD and their structure were determined using both synchrotron and neutron radiation powder diffraction. The symmetry of the materials were checked using second harmonic generation. The magnetism of the manganese was studied using a magnetic property measurement system and

neutron diffraction at low temperature.

#### 4 . 研究成果

We have mainly studied two structures in this project  $\text{La}_2\text{MnTaO}_5\text{N}$  and  $\text{ZnTaO}_2\text{N}$  (Figure 1 and 2, respectively).  $\text{ZnTaO}_2\text{N}$  has a hexagonal  $\text{LiNbO}_3$  structure but was found to be centrosymmetric. The model structure  $\text{LiNbO}_3$  is a non-centrosymmetric hexagonal phase at room temperature. Due to the small size of  $\text{Li}^+$ ,  $\text{NbO}_6$  octahedra collectively tilt and which leads to low coordinated A-site (six-fold) and an  $R\bar{3}c$  space group which lacks an inversion center. This structure is found to have a high temperature phase transition at 1470 K [2] to a  $R\bar{3}c$  space group, centrosymmetric. This transition is due to the  $\text{Li}^+$  cations disorder at high temperature which leads to the symmetry switch.  $\text{ZnTaO}_2\text{N}$  has the  $R\bar{3}c$  symmetry because of  $\text{Zn}^{2+}$  disorder even at room temperature. This is unusual because most  $\text{LiNbO}_3$  type structures require high temperatures ( $>1000$  K) to disorder. The structure is also different with that of  $\text{MnTaO}_2\text{N}$  [3] which is also an oxynitride we previously synthesized but contains ordered  $\text{Mn}^{2+}$  and is therefore non-centrosymmetric. Studies of the structure indicated that the nature of the Zn-anion bonds could be responsible for the exotic disorder. Investigation of the solid solution between Mn and Zn showed that a small amount, as low as 3% of Zn in  $\text{MnTaO}_2\text{N}$  lead to the change of symmetry (Figure 3). No ordering between  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$  could be observed.

The second compound  $\text{La}_2\text{MnTaO}_5\text{N}$  is of the double perovskite family with order between the Mn and Ta octahedral sites. Order in these materials occur because of the charge difference between the cations at the B site,  $2+$  and  $5+$  here. The size of these cations needs to differ as well and here  $\text{Mn}^{2+}$  is 83 pm and  $\text{Ta}^{5+}$  is 64 pm.[4] As-shown in figure 1, the structure has been refined using neutron and synchrotron diffraction to have different anionic content as a function of the crystallographic site. This partial ordering arises from the different crystallographic site that occur in the structure in reason of the ordering of Mn and Ta and because of the tilting pattern of the structure. In  $\text{ZnTaO}_2\text{N}$  only one site exists and  $\text{O}^{2-}$  and  $\text{N}^{3-}$  are disordered. The magnetic Figure 3. (Top) Evolution of the lattice



parameters of the  $\text{Zn}_{1-x}\text{Mn}_x\text{TaO}_2\text{N}$  solid solution and (Bottom) second harmonic generation (SHG) response from the solution.

properties of this materials are under investigations and will be reported in a peer-reviewed journal. Due to the pseudo ordering of the  $\text{O}^{2-}$  and  $\text{N}^{3-}$ , the magnetic interaction should be different as a function of the direction within the crystal and should result in different properties with conventional double perovskite oxide structures. We also have attempted the synthesis a  $\text{La}_2\text{ZnTaO}_5\text{N}$  structure, which should be similar with that of  $\text{La}_2\text{MnTaO}_5\text{N}$ . Although the crystal structure should be similar, subtleties could be observed using diffraction and improvement in the synthesis is necessary. Several attempts to yield an oxynitride with ordered A-site were also done notably based on  $\text{CaTaO}_2\text{N}$  to introduce  $\text{Ca}^{2+}$  in the structure along with  $\text{Mn}^{2+}$  but all attempts were found unsuccessful.

#### Conclusion

This funding allowed us to investigate the feasibility of novel perovskite oxynitrides using the high pressure and high temperature technique. The investigation of different composition enabled us to better comprehend the structure that can be done and those that are more challenging. In this project we have focused on the use of TaON as a source of

nitride for the high-pressure synthesis. It will be interesting in the future to consider pure nitrides or oxynitrides of other species ( $Zr^{4+}$ ,  $Ge^{4+}$ ,  $Ga^{3+}$ ) in order to generate novel structures. An interesting challenge could be also to use a path to generate nitride anions within the high-pressure apparatus during the synthesis in order to nitridize some oxide precursors.

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#### 5 . 主な発表論文等

(研究代表者、研究分担者及び連携研究者には下線)

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