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Remarkable effects of local structure in tantalum and niobium oxynitrides

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ABSTRACT

Compounds that contain two types of anion are attracting attention as a new field of solid state chemistry. The nitride anion is similar to the oxide anion in size and nature. They coordinate together to cations in oxynitrides to form characteristic local structures around them in a certain way. Special properties induced by the specific local structure have been observed in oxynitrides. Ferroelectricity was identified in oxynitride perovskites, especially those of tantalum, because the oxide and nitride anions form a polar ordered local crystal structure around Ta^{5+} in the $5d^0$ electron configuration. The critical current density in superconductivity was enhanced by the formation of clusters in niobium oxynitrides with the rocksalt-type structure. Main group elements doped into the niobium oxynitrides, especially silicon, are coordinated mainly by oxides with some amount of nitrides to form silicon oxide-like clusters. The niobium in the oxynitride has some 4d electrons to maintain the superconductivity in the niobium oxynitride host. Here, the preparation, crystal structure and properties of oxynitrides formed with tantalum and niobium are reviewed.

Contents

1. Introduction

Oxynitrides have been assumed to be either partially substituted nitrides together with some amount of oxides or as oxide compounds containing nitrides [1–3]. Oxynitrides have found some applications, such as phosphor materials in white LEDs and as visible light driven photocatalysts. Many review papers have been published on optical oxynitrides in the past decade [1–7]. Two types of anions had been considered to be present on the same crystallographic sites in the oxynitride crystal structure. Their electron configuration is formally the same in $1s^22s^22p^6$ although the atomic numbers for nitrogen and oxygen are different at 7 and

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8, respectively. It is thus difficult to distinguish nitride and oxide anions in oxynitrides by X-ray diffraction because their X-ray scattering powers are very similar [1]. These anions are very different from each other in their bonding nature, especially with respect to covalency. The optical application of oxynitrides has been discussed in relation to the change in the band gap and valence band top position in the anion exchange between oxide and nitride. Two types of anions with different bonding nature should be present at individual sites, at least locally, even if they are together in the same site in an average of the crystal structure. Layered crystal structures appear in compounds that contain two distinct anions that are quite different in size and nature, such as oxychlorides, oxybromides, oxysulfides and oxypnicogenides [8–10]. These anions are separately in their respective sites in the crystal structure.

Local *cis*-ordering of nitrogen atoms was reported for $BaTaO_2N$ with the cubic $Pm\text{-}3m$ structure from a neutron pair distribution function analysis [11]. The existence of polar one-dimensional displacive disorder was discussed but not directly related to the O/N ordering [12]. In $SrTaO_2N$ and $SrNbO_2N$, symmetry lowering from $I4/mcm$ to $I112/m$ was assumed from weak extra reflections in the (100) and (010) electron diffraction planes as a consequence of nitride *cis*-ordering [13]. The structural model for $SrTaO_2N$ had been firstly reported as anion ordered in c.a. 50/50 O/N occupancies at 4*a* sites and 75/25 at 8*h* sites in $I4/mcm$ although there was no idea about *cis*-ordering of nitrogen atom [14]. Neutron diffraction provided direct observation of the nitride *cis*-ordering in tetragonal $I4/mcm$ $SrTaO_2N$ from the 4*a* and 8*h* site occupancies, whereby octahedral tilting was also clarified [15]. The order was assumed to be stable until high temperatures above 2000 °C and anions were segregated when the materials were synthesized [16]. The preferred *cis*-arrangement of nitrides in oxynitride perovskites of d^0 transition metals was explained in terms of the maximum utilization of vacant d-orbitals in π-bonding with the anion lone pair [17]. The local structure is very important to obtain superior dielectric properties in $SrTaO_2N$ and $BaTaO_2N$ [18–20]. The correlated anion order was also identified in the $NdVO_2N$ perovskite containing V^{4+} in the 3d [1] configuration [21]. Zigzag chains of *cis*-VN were stabilized by the second order Jahn-Teller effect and the 3d electrons were itinerant. The electrical properties were modified by the formation of oxynitride solid solutions in $LnMO_{3-x}N_x$ (Ln = La, Pr, Nd, M = Cr, V, $0 \le x \le 1$) [22,23].

Niobium oxynitride perovskites are slightly more conductive than tantalum oxynitrides because the electronic configuration is $[Kr]4d^45s^1$ in Nb and $[Xe]4f^{14}5d^36s^2$ in Ta [24]. A small amount of d-electrons that contribute to the electrical conduction remain more easily on niobium than on tantalum oxynitrides because of the smaller atomic number in Nb [25]. Niobium oxynitride with the rocksalt-type structure is another target that exhibits interesting properties induced by a different type of local structure. Main group elements doped in the niobium nitride segregate and form oxide-like clusters that are coordinated by mostly oxide with a small amount of nitride anions [26]. The doped niobium oxynitrides maintain their average crystal structure as the rocksalt-type. These oxynitrides exhibit an increase in critical current density (*Jc*) in their superconductivity because the formed clusters pin the superconducting flux in the crystal structure [27].

In the present paper, we would like to review the importance of local structure in the two kinds of oxynitrides. Tantalum oxynitride perovskites exhibit promising dielectric properties because they have anisotropic nitride anions ordering in *cis*-type TaO_4N_2 octahedra. Thermal stability and ceramic fabrication are reviewed and their structure is investigated. Niobium oxynitrides with the rocksalt-type crystal structure are investigated to enhancement of the *Jc* of these superconductors. Large *Jc* values are necessary to realize the application of superconductivity together with the critical transition temperature *Tc*, and critical magnetic field, *Hc*. Doped foreign cations such as Si form clusters with mostly oxides in niobium oxynitride with the rocksalt-type structure. The preparation, structure and superconductivity of the niobium oxynitrides are reviewed.

2. Polar ordered ferroelectric tantalum oxynitride perovskites

Anisotropic coordination of the *cis*-type has been reported for the oxynitride perovskites AMO_2N with M = Ta, Nb and V [13,15,21]. The presence of polar nanoregions was suggested from experimental measurements [11,12] and then related to an M-N coil of d^0 and d^1 transition elements in the perovskites [13,28]. Oxynitride perovskites are easily reduced and release a portion of nitrogen when sintered at high temperature [29,30]. They become slightly electrically conductive with a small amount of electrons and exhibit a spuriously large permittivity value [19,20]. The loss of nitrogen from oxynitride perovskites has occurred even under high pressures of gigapascal order [31]. Highly insulating ceramics are required to observe real dielectric behavior while excluding the electronic contribution. A high relative density is also required to study the ferroelectric properties and to improve the dielectric properties. Processing has thus been reviewed with respect to the improvement of dielectric sample preparation, although problems remain in achieving this [32].

2.1. Crystal structural study of $SrTaO_2N$ and $La_{1-x}Sr_xTiO_{2+x}N_{1-x}$

The existence of a nanopolar region in cubic $Pm\text{-}3m$ $BaTaO_2N$ was proposed from neutron pair distribution function analysis [11], extended x-ray absorption fine-structure spectroscopy [12] and electron diffraction [33], probably because better dielectric behavior was expected for $BaTaO_2N$ than $SrTaO_2N$. The anisotropic local structure was not clearly observed on $BaTaO_2N$, even if neutron diffraction was applied to distinguish oxide and nitride. The structure was averaged due to the high symmetry of the cubic crystal lattice and there was only one anion site at 3*c*. A neutron diffraction study was then performed on tetragonal $I4/mcm$ $SrTaO_2N$ to confirm the proposed nanopolar region in $BaTaO_2N$ [15]. There are two anion sites with O/N population ratios of approximately 50/50 at 4*a* and 75/25 at 8*h* sites. These values suggest that nitrogen atoms are in *cis*-type octahedral coordination around tantalum to form Ta-N coils, as shown in the left panel of Fig. 1. Helical coils were statistically formed with both clockwise and anticlockwise configurations [28]. The previously reported symmetry lowering [13] was not observed, because the anion ordering was not significantly extended through the crystal lattice due to the similar size of oxygen and nitrogen. The 4*a* site showed a large anisotropic displacement, which suggests the *cis*-TaO_4N_2 octahedra tilt each other to form Ta-N coils of various length, as depicted in the right panel of Fig. 1. First-principles calculations indicated that stable anion orderings in $BaTaO_2N$ and $SrTaO_2N$ have two types of similar 3-dimensional Ta-N coiled motifs that can switch with each other, the formation mechanism of which breaks long-range order and increases the diversity of anion ordering around Ta^{5+} [28]. Both materials have two sets of low-energy displacements that form opposite directions of polarization that can be easily altered at the picosecond scale, as represented in Fig. 2.

Neutron diffraction was also applied to $La_{1-x}Sr_xTiO_{2+x}N_{1-x}$ (x = 0, 0.2) belonging to the triclinic space group $I\text{-}1$ [34]. The refined O/N occupancies of the #1, 2, and 3 anion sites were 0.748/0.252, 0.482/0.518, 0.770/0.230 for x = 0, and 0.861/0.139, 0.509/0.491, 0.830/0.170 for x = 0.2, respectively. These are similar to the previously reported values of 0.73/0.27, 0.52/0.48, 0.72/0.28 for

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