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Local anionic ordering and anisotropic displacement in dielectric perovskite $SrTaO_2N$

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The perovskite oxynitride $SrTaO_2N$ as a promising candidate for lead-free dielectric materials has been studied with a special emphasis on the structural characterization using neutron powder diffraction. $SrTaO_2N$ powders were prepared by means of ammonia nitridation via precursors obtained from a soft chemistry method and a solid state reaction route. All the products crystallized in tetragonal $I4/mcm$ space group with only slight variation in the lattice constant, e.g., $a = 5.7023(1)$ Å and $c = 8.0786(1)$ Å for the soft-chemistry derived sample. Neutron diffraction analysis suggested the short-range O/N ordering involving a *cis* configuration in TaO_4N_2 octahedra together with large anionic displacement within the *ab* plane on their axial position in the average crystal lattice. These facts are associated with local tilting of the TaO_4N_2 octahedra which is likely to play a key role in the unusual dielectric behavior of $SrTaO_2N$.

Key-words : Perovskite oxynitrides, Dielectric properties, Neutron diffraction, Crystal structure, Anionic ordering

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1. Introduction

Perovskite oxynitrides have received considerable attention both for their structural challenges and novel physical properties. Partial substitution of oxygen by nitrogen in perovskite oxides containing early transition metals with the d^0 electronic configuration has profound effects on their optical and electric properties. The band gap reduction induced by nitrogen incorporation makes the highly colored oxynitrides promising materials as non-toxic pigments[1] and visible-light driven photocatalysts.[2] Apart from the optical characteristics, the increased covalency in oxynitrides leads to modifications in the magnetoelectric[3] and dielectric properties.[4–6] Since most of the d^0-type perovskite oxynitrides are eco-friendly and stable in air, water and even in concentrated acids, oxynitrides with high permittivity can be considered as promising candidates for lead-free dielectric materials to replace the widely used but toxic $Pb(Zr,Ti)O_3$ (PZT)-based ceramics.[7,8]

Recently, Kim et al. reported that $BaTaO_2N$ and $SrTaO_2N$, i.e., oxynitride derivatives of the prototypical dielectrics $BaTiO_3$ and $SrTiO_3$, possessed bulk permittivity of ~4900 and ~2900 with moderate temperature coefficients.[4] To date, the unusual dielectric behavior has been discussed mainly on $BaTaO_2N$ in relation to its crystal structure.[9–11] While the structure of this oxynitride was refined with cubic $Pm\bar{3}m$ space group,[12] local structure relaxation was suggested to induce marked dielectric polarization. Nevertheless, direct observations of the anionic ordering or local distortion are practically impossible by X-ray diffraction (XRD)[4] and neutron diffraction (ND),[12] because there is only one anion site in the cubic structure model. Accordingly, many other techniques[9–11,13] were utilized to investigate the local structure. First principles calculations on $BaTaO_2N$ predicted lowering of local symmetry due to differences in the interatomic distance and covalency of Ta–O and Ta–N bonds in $Ta(O,N)_6$ octahedra.[9] The low-symmetry coordination environment around Ta was indicated by extended X-ray absorption fine structure (EXAFS) experiments.[10] Furthermore, short-range O/N ordering caused by a *cis* arrangement of N in TaO_4N_2 octahedra was revealed by pair distribution function (PDF) analysis of neutron scattering data.[11] Lately, local displacive disorder in $BaTaO_2N$ was proved through the electron diffraction investigation by Withers et al.[13] They suggested that the inherently polar, off-center and anti-correlated displacements of Ta and the nearest neighboring O/N ions along the ⟨001⟩ direction, giving rise to one-dimensional polar nanoregions, were responsible for the dielectric behavior of $BaTaO_2N$.[13]

In contrast to $BaTaO_2N$, limited efforts have been devoted to the studies on structure–property correlation in similar dielectric perovskite $SrTaO_2N$. So far the crystal structure of $SrTaO_2N$ has been refined based on three different space groups, i.e., cubic $Pm\bar{3}m$,[14] tetragonal $I\bar{4}2m$[15] and $I4/mcm$.[4,16,17] Even for the most acceptable tetragonal $I4/mcm$ model, discrepant conclusions have been reached in terms of the preferential site occupations for O/N anions. Both a complete O/N ordering[16] and a statistical anion distribution among the available sites[17] were reported. Very recently, the occurrence of well-defined O/N ordering in $SrTaO_2N$ was suggested from 200 up to 750°C.[18] And there is a chance to observe the local structure deviation in the pseudosymmetric $I4/mcm$ crystal lattice by analyzing the anisotropic displacements of the anions. Therefore, systematic investigations on synthesis and structure of $SrTaO_2N$, placing emphasis on the site occupancy and local displacement, are indispensable to elucidate the origin of the unusual dielectric property of $SrTaO_2N$. And ND analysis is particularly appropriate to study local structure and anionic ordering in oxynitrides, owing to the considerably different scattering lengths for O (5.803 fm) and N (9.360 fm).[19]

In the present study, ND analysis was carried out on $SrTaO_2N$ powders prepared with different synthesis conditions. A close attention was paid to the anionic distribution and displacement to understand the behavior of short-range ordering and local distortion in an average crystal lattice of $SrTaO_2N$.

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