

First Principles Investigation of Anion Ordering in (Ba, Sr, Ca)TaO₂N

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BaTaO₂N and SrTaO₂N (crystal structure given in Fig. 1) are two oxynitride perovskites with high dielectric permittivities of approximately 4900 and 2900 respectively over a wide temperature range of at least 180 to 300K without a phase transition [1]. They are classified into relaxor ferroelectrics [2, 3], which are promising candidates in many applications especially because Pb is not included unlike in many relaxor ferroelectrics. Withers *et al.* proposed formation of structurally frustrated one-dimensional polar nanoregions (1D PNRs)[2] along the <001> axis as the reason for relaxor-type ferroelectric behavior in BaTaO₂N. They also claimed that random local strain fields from chemical disorder suppresses transverse correlations of chain dipoles and the development of a long range ordered ferroelectric state [4].

Some degree of anion ordering is apparent in SrTaO₂N. There are two anion sites in the idealized tetragonal perovskite structure of SrTaO₂N: the minority axial sites (1/3 of anion sites: blue balls in Fig. 1) and the remaining majority equatorial sites (purple balls in Fig. 1). Neutron diffraction experiments of tetragonal SrTaO₂N found that the O:N ratios at two anion sites are approximately 1:1 and 3:1 respectively [5-7]. Preference for “cis-type” TaO₄N₂ octahedra with 90-degree N-Ta-N bonds as opposed to “trans-type” octahedra with 180-degree N-Ta-N bonds has been experimentally and theoretically proposed in BaTaO₂N [8-10] (Fig. 2).

The anion ordering should be closely related to the formation of PNRs, and hence to the high dielectric permittivity. Theoretical calculations that can be used to quantify the anion ordering would be the best approach to verify this hypothesis. In the present study, we have systematically investigated the anion ordering in three oxynitrides, i.e., (Ba, Sr, Ca)TaO₂N, adopting a variety of models with Z= 1, 2, and 4, where Z denotes the number of atoms in the supercell per the chemical formula. Total energies were obtained by the projector augmented-wave (PAW) method [11,12] within the generalized gradient approximation (GGA) to density functional theory [13] as implemented in the VASP code [14,15]. The formation of “cis-type” TaO₄N₂ octahedra is preferred in all three (Ba, Sr, Ca)TaO₂N systems.

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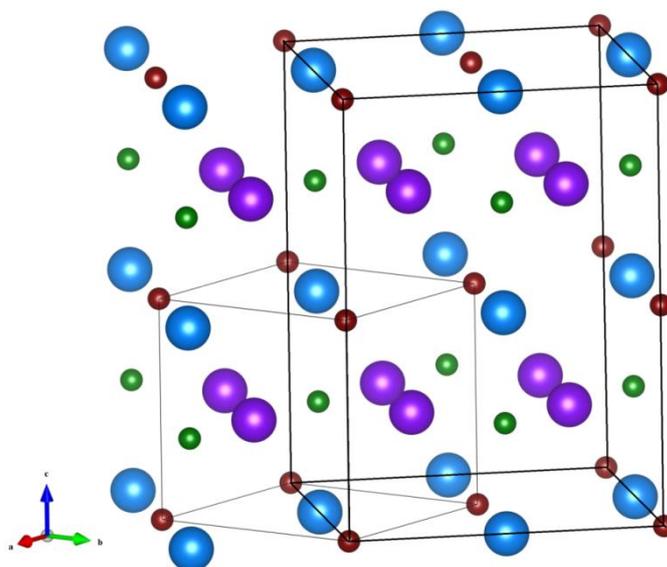


FIG. 1. Crystal structure of $(\text{Ba}, \text{Sr}, \text{Ca})\text{TaO}_2\text{N}$. Thin lines indicate the perovskite unit, thick lines indicate the tetragonal supercell. Legend: brown = Sr, green = Ta, blue = axial anion sites (4a sites of the tetragonal supercell), purple = equatorial anion sites (8h sites).

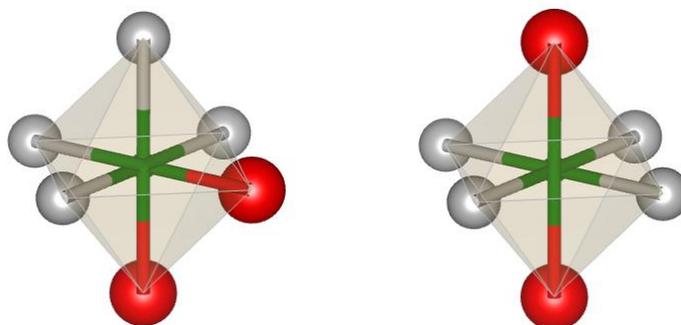


FIG. 2. (left) *cis*- and (right) *trans*- TaO_4N_2 octahedra. Legend: green = Ta, gray = O, red = N.