# The influence of non-stoichiometry and chemical doping on the electrical properties of Na1/2Bi1/2TiO3 ceramics

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ABO3-type perovskite oxides exhibit a diverse range of useful functional properties from ferroelectric BaTiO3 materials for dielectric applications in multilayer ceramic capacitors to (La,Sr)(Ga,Mg)O3- solid electrolytes and (La,Sr)MnO3- mixed oxide-ion, electronic conducting electrodes for solid oxide fuel cells. The ferroelectric perovskite Na1/2Bi1/2TiO3 (NBT) is known to exhibit interesting and diverse structure-composition-property relationships.1-2 A combination of A-site (Na, Bi) disorder, Bi- and Ti- displacements and in-phase and out-of-phase octahedral tilting ensures the crystal chemistry and polymorphism of NBT remain a challenging subject, especially below *ca*. 520 oC where distortions from the ideal ‘cubic’ cell are reported to occur. Furthermore, the electrical conductivity of undoped NBT materials are known to be critically dependent on low levels of A-site non-stoichiometry, commonly ± 0.02 from the nominally stoichiometric 0.50Na:0.50Bi ratio.3

Here we review the structure-composition-property relationships of NBT materials based on a combination of A-site non-stoichiometry and chemical doping. We use results4,5 from a combination of X-ray, Neutron and Electron Diffraction, Impedance Spectroscopy (IS), O18 Time-of-Flight Secondary Ion Mass Spectrometry (ToF SIMS) and oxygen concentration cell (electromotive force, emf) measurements to show nominally Na-rich (eg Na0.51Bi0.50TiO3.005) or Bi-deficient NBT (eg Na0.50Bi0.49TiO2.985) ceramics to be excellent oxide-ion conductors with oxide-ion transfer numbers (tion) exceeding ~ 0.9 at 600 oC whereas nominally Na-deficient (eg Na0.49Bi0.50TiO2.995) or Bi-excess NBT (eg Na0.50Bi0.51TiO3.015) ceramics are electrically insulating but retain tion ~ 0.1 at 600 oC.This shows undoped NBT ceramics to be mixed ion-electron conducting materials where the magnitude of the bulk conductivity, b, and tion are heavily dependent on the nominal Na:Bi ratio in the starting composition. We attribute the source of oxygen vacancies in nominally stoichiometric NBT to be associated with low levels of Bi2O3-loss during ceramic processing.

Chemical doping4,6 with acceptors such as Sr for Bi or Mg for Ti can significantly increase the oxide ion conductivity in NBT with tion approaching unity to promote solid electrolyte behaviour whereas Nb-doping for Ti can suppress the oxygen vacancy concentration and oxide-ion conductivity such that excellent dielectric behaviour can be obtained with tan  < 0.02 at 600 oC. Such behaviour is desirable for NBT-based dielectric applications, eg as Pb-free piezoelectrics and/or as a solid solution member in temperature stable, high permittivity multilayer ceramic capacitors (MLCCs) operating at > 175 oC. Finally, we discuss the differences in the defect chemistry of NBT compared to conventional titanate perovskites, such as (Ba,Sr)TiO3.

# References

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