The Effects of Low Oxygen Activity Conditions on the Phase Equilibria and Cation Occupancy of Strontium Barium Niobate

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Strontium barium niobate (SBN) is a tungsten bronze family ferroelectric which shows promising thermoelectric properties under reducing conditions. It is found here that the enhanced electrical conductivity of oxygen-deficient SBN correlates with the formation of a NbO_2 secondary phase. The effects of the reducing environment and the NbO_2 phase formation are studied via a detailed defect chemistry analysis. Increasing amounts of the NbO_2 phase are accompanied by an interesting mechanism where the A-site occupancy of the SBN matrix increases. The resulting donor defects source the large carrier concentrations which cause the enhanced electrical conductivity necessary for thermoelectric performance. In investigation of the phase equilibria, it is found that a solid solution between $(Sr_{0.6},Ba_{0.4})Nb_2O_6$ and $(Sr_{0.6},Ba_{0.4})_{1.2}Nb_2O_6$ exists and that the A-site filling is found to occur at more modest reduction conditions in Sr- and Ba-rich compositions. Finally, thermogravimetric analysis of the reoxidation process is performed, and the results suggest that the A-site filling is compensated ionically. Not only do the presented results explain the enhanced electrical conductivity of oxygen-deficient strontium barium niobate but also modification of the site occupancies by reduction and reoxidation may widen the design space for property modification in tungsten bronze-structured materials in general.