Study of Structural Phase Transitions in $\text{Na}_{1-x}\text{Sr}_{x/2}\text{NbO}_3$

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Abstract: The solid solution $\text{Na}_{1-x}\text{Sr}_{x/2}\text{NbO}_3$ is prepared by solid state reaction method. Detailed analyses of powder x-ray diffraction data clearly suggest a change of structure from ABO$_3$ perovskite (NaNbO$_3$ like) to complicated Tungsten Bronze SrNb$_2$O$_6$ like. The presence of additional reflections clearly suggests that cell multiplicity for $x \geq 0.20$ is different to that of pure NaNbO$_3$. For composition $x \geq 0.20$, the lattice parameters are related with pseudocubic perovskite cell parameters as follows: $A_0 = 4a_p$, $B_0 = 3b_p$, $C_0 = 5c_p$. The lattice parameters and volume increases monotonically with increasing concentration of Sr$^{2+}$ in NaNbO$_3$ matrix.

1. Introduction:
Perovskite oxide family has long been investigated especially in view of the ferroelectric properties that they commonly exhibit. Ferroelectric properties of oxide perovskite have potential applications in piezoelectric transducer and actuators, non-volatile memories etc. These materials also find important application as dielectrics for wireless communication, microelectronics, non-linear optical applications, medical imaging. NaNbO$_3$ is well documented as antiferroelectric at room temperature and have orthorhombic symmetry. But, the presence of substitutional impurities like Li$^+$, K$^+$ at the Na$^+$ site or Mn at the Nb site in NaNbO$_3$, stabilize long range ferroelectric ordering. These structural phase transitions are associated with condensation of zone centre and zone boundary phonon and driven force is strain. The nature of these transitions depends largely on the concentration of impurity. For example, polar phase can be stabilized at room temperature in the Na$_{1-x}$K$_x$NbO$_3$ (KNN) and Na$_{1-x}$Li$_x$NbO$_3$ (LNN) systems, for $x=0.50$ and 0.12 respectively. It is also interesting to note that both the systems to exhibit morphotropic phase boundary (MPB) near to these compositions and one of the end members is ferroelectric in nature. In addition to this, solid solutions of alkaline niobate are of great current interest due to their piezoelectric properties and their environmentally friendly nature makes them superior to lead based materials[1,2]. It is believed that substitutional impurities to take off-centre position of cuboctahedron formed by the 12 nearest neighbour oxygen atoms due to mismatch in the radius of ionic radii. In this communication, we present the results of Sr$^{2+}$ substitution at the

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Na$^{2+}$ site and find the possibilities of presence of morphotropic phase boundary in this system. It may be noted that similar to KNbO$_3$ and LiNbO$_3$, SrNb$_2$O$_6$ is a well known ferroelectric.

2. Experimental
Specimens of Na$_{1-x}$Sr$_{x/2}$NbO$_3$ (SNN) were prepared by solid state reaction method using powders of Na$_2$CO$_3$, SrCO$_3$ and Nb$_2$O$_5$ each of minimum assay of 99.0%. These powders were thoroughly mixed in stoichiometric amounts using mortar and pestle using acetone as the mixing medium. Calcination of the mixed powder was carried out at 1150 $^\circ$C for 6 hours. The calcined powder was pressed into circular pellets of 10mm diameter using a uniaxial hydraulic press at an optimized load of 10 tons. Sintering of the green pellets was carried out at 1250 $^\circ$C - 1300 $^\circ$C, depending upon the composition, for 6 hours in air. For powder diffraction experiments, the sintered pellets were crushed to fine powder and subsequently annealed at 500$^\circ$C to remove strains introduced, if any, during crushing. Rietveld analysis of the powder diffraction data was carried out using structure free model in the program FULLPROF.

3. Results and Discussion:
3.1 Powder diffraction pattern of SNN(0.0$\leq$x$\leq$0.5)

Figure 1 depicts the evolution of the x-ray powder diffraction patterns for SNN in the composition range 0$\leq$x$\leq$0.5 for a limited 2$\theta$ range of 20-60 degrees. The powder diffraction patterns in Figure 1 contain the main perovskite and super lattice reflections. These super lattice reflections assume Miller indices represented by odd integers while the main Bragg reflections are represented by even integered indices with respect to the doubled pseudo-cubic unit cell (i.e. 2$a_p$, 2$b_p$, 2$c_p$, $\alpha_p$, $\beta_p$, $\gamma_p$, where $a_p$, $b_p$, and $c_p$ are the cell parameter of the elementary pseudo-cubic perovskite cell). All-odd integered (i.e., ‘ooo’ type indices) super lattice reflections correspond to the out of phase (- tilt) tilts of the adjacent octahedra whereas presence of super lattice reflections with two odd and one even integer indices (i.e., ‘ooe’ type) implies presence of in-phase (+ tilt) tilt of the adjacent octahedral. It is important to mention here that in-phase and anti-phase tilts of octahedral are known to be driven by M (q=0.0, ½,) and R(q= ½, ½, ½) point instabilities of the cubic Brillouin zone respectively. Pure NaNbO$_3$ (x=0) shown in Fig. 1, one observes odd-odd-odd and odd-odd-even type reflections but with additional fractional indices (11 5/2, near 2$\theta$ = 37degree) reflection. The fractional indices indicate the quadrupling of one of the elementary perovskite axes.
3.2 Rietveld analyses:

Cochran and Zia [2] have shown that this quadrupling of the elementary pseudocubic cell in the room temperature phase of NaNbO$_3$ results from a freezing of the $\Delta$ point $(q=0,0,\frac{1}{4})$ soft phonon mode. All superlattice peaks are nicely accounted by orthorhombic structure with Pbcm space group during Rietveld data analysis. A compound tilt system, $[(a_b-a')(a_b'a')_2]$, in the space group Pbcm has been found to be consistent with all these features for pure NaNbO$_3$[3,4] although the possibility for slight monoclinic distortion cannot be ruled out. It is evident from the Fig. 1, that there is a drastic change in the profile near $2\theta \approx 46$, 52 and 57 degrees in the powder x-ray diffraction pattern as concentration of Sr$^{2+}$ increases in NaNbO$_3$ matrix. Appearance of additional peak (marked with arrow) at lower two-theta sides of around 46 and 57 degree Bragg profile and change in Bragg profile at two theta 52 degree are clearly observed in Figure 1. All these features can be explained in terms of a change of crystal structure of Na$_{1-x}$Sr$_{x/2}$NbO$_3$ from ABO$_3$ perovskite like NaNbO$_3$ to complex Tungsten Bronze type SrNb$_2$O$_6$ like for $x \geq 0.20$ reveals a structural phase transition. The presence of these additional reflections clearly suggest that cell multiplicity for $x \geq 0.20$ is different than pure NaNbO$_3$. The lattice parameters are related with pseudocubic perovskite cell parameter as follows: $a_p = 4a$, $b_p = 3b$, $c_p = 5c$. This was further confirmed by structure free Rietveld refinement of SNN using the orthorhombic symmetry with space group P222. In the structure free Rietveld refinements, pseudo-Voigt function was chosen to define the peak profiles. Background was described in terms of a sixth order polynomial.

Figure 2 shows the observed, calculated and difference profiles for Na$_{1-x}$Sr$_{x/2}$NbO$_3$ ($x=0.20$). As can be seen from this figure, the fit between observed and calculated profiles is quite satisfactory and include the weak super lattice reflections.

![Figure 2](image-url)
3.3 Variation of lattice parameters with composition:

For the sake of easy comparison with corresponding cell parameters of orthorhombic phases, we have plotted the cell parameters of these phases in terms of equivalent elementary perovskite cell parameters. It is evident from Figure 3 that with increasing concentration, the lattice parameters and volume increase monotonically. It is expected that as the Sr$^{2+}$ is substituted at the Na$^{2+}$ site, the lattice expands as ionic radius of Sr$^{2+}$ is larger than ionic radius of Na$^{2+}$. To explore the possibilities of presence of morphotropic phase boundary in this system, assignments of correct space group and study of the dielectric behaviour is under investigation.

![Figure 3: Evolution of lattice parameters of SNN with composition](image)

4. Conclusions:
In conclusion, detailed analysis of powder x-ray diffraction data clearly shows a change of structure from NaNbO$_3$ like to SrNb$_2$O$_6$ like. The lattice parameters and volume increases monotonically with increasing concentration of Sr$^{2+}$ in NaNbO$_3$ matrix.

5. References:
[1] Yasuyoshi Saito, Hisaaki Takao, Toshihiko Tani, Tatsuhiko Nonoyama, Kazumasa Takatori, Takahiko Homma, Toshiatsu Nagaya & Masaya Nakamura, 2004 Nature 432, 84.
[2] Yu.I. Yuyuk, E. Gagarina, P. Simon, L A Reznitchenko, L Hennet and D. Thiaudiere, Phys. Rev B 69, 144105 2004 Phys. Rev B 69, 144105.
[3] Cochran and Zia W. Cochran and .4. Zia, 1968 Phys. Status Solidi 25, 273.
[4] Darlington C N W, Knight K S 1999 Physica B 266, 368.

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