Structures and properties of the perovskite type compounds $Na_{1-x}Sr_xNbO_3$ ($0.1 \leq x \leq 0.9$) a composition-induced metal-insulator transition

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Composition-induced metal-insulator transitions in complex perovskite-type oxides containing transition metals with $d^0 - d^1$ electronic configuration are rare. For such a transition to take place the presence of enough charge carriers is necessary and in addition the occurrence of suitable paths of overlapping orbitals, which requires that the tilt of the NbO_6 octahedra should not be too large. In the $d^0 - d^1$ oxotantalate system $Na_{1-x}Sr_xTaO_3$ ($0.0 \leq x \leq 0.4$) the electrical resistivity decreases with increasing strontium content, but metallic conductivity is not reached even for the highest possible strontium content $Na_{0.6}Sr_{0.4}TaO_3$ [S.Y. Istomin *et al.*: Journal of Solid State Chemistry **154**, 427 (2000)]. As reduced oxides with the lighter homologue Nb are more stable the system $Na_{1-x}Sr_xNbO_3$ with samples $0.1 \leq x \leq 0.9$ was investigated. They all crystallize as variants of the cubic perovskite type structure (a_{per}). As a result of the substitution of Na^+ by the larger Sr^{2+} associated with the partial reduction of the small Nb^{5+} to the larger Nb^{4+} the volume of the perovskite subcell in $Na_{1-x}Sr_xNbO_3$ increases with the Sr content x, see Fig. 7.

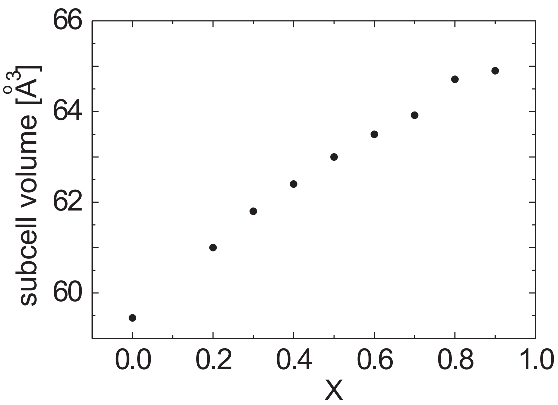

Figure 7: *The volume of the perovskite subcells (a^3_{per}) of $Na_{1-x}Sr_xNbO_3$ vs. the Sr content x.*

X-ray powder diffraction (XRD) studies of the $0.2 \leq x \leq 0.7$ phases indicate a tetragonal structure (*P*4/*mbm*) with unit cell parameters $a \approx \sqrt{2} \cdot a_{per}$, $c \approx a_{per}$, and for $x = 0.8$ and 0.9 the space group *P*4/*mmm* was found with $a \approx a_{per}$ and $c \approx a_{per}$. Rietveld refinements based on XRD and neutron diffraction data confirmed this for samples with $0.3 \leq x \leq 0.7$. However, SAED (**s**elected **a**rea **e**lectron **d**iffraction) and CBED (**c**onvergent **b**eam **e**lectron **d**iffraction) studies show that in crystallites of the $x = 0.2$ and 0.3 phases the tetragonal symmetry is broken, these phases being isotypic with $GdFeO_3$, space group *Pnma* with unit cell parameters $a \approx \sqrt{2} \cdot a_{per}$, $b \approx 2 \cdot a_{per}$, $c \approx \sqrt{2} \cdot a_{per}$. Crystallites of the $0.4 \leq x \leq 0.9$ samples consist of intergrown domains between this orthorhombic structure and a tetragonal variant of the perovskite structure (*P*4/*mbm*) associated with local variations in the Na and Sr content within the crystallites, a result which is interesting in the general context of phase separation.

The magnetic susceptibilities of $Na_{1-x}Sr_xNbO_3$ samples indicate paramagnetism within the entire range $0.1 \leq x \leq 0.9$, see Fig. 8.

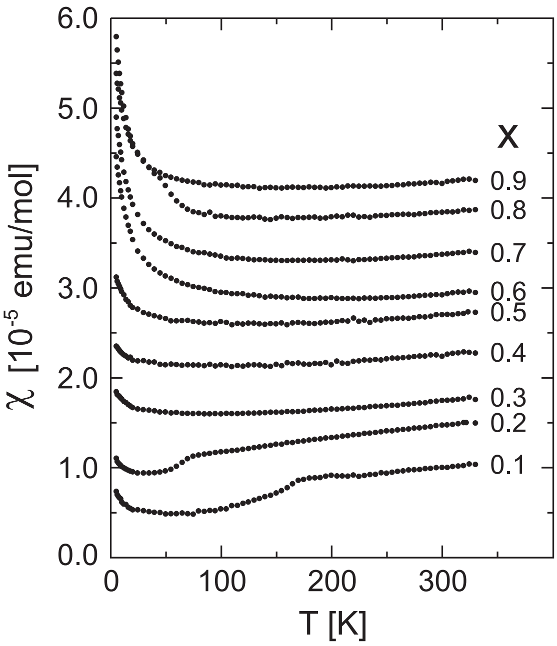

Figure 8: *Temperature dependence of the magnetic susceptibilities vs. temperature for samples $Na_{1-x}Sr_xNbO_3$ ($0.1 \leq x \leq 0.9$).*

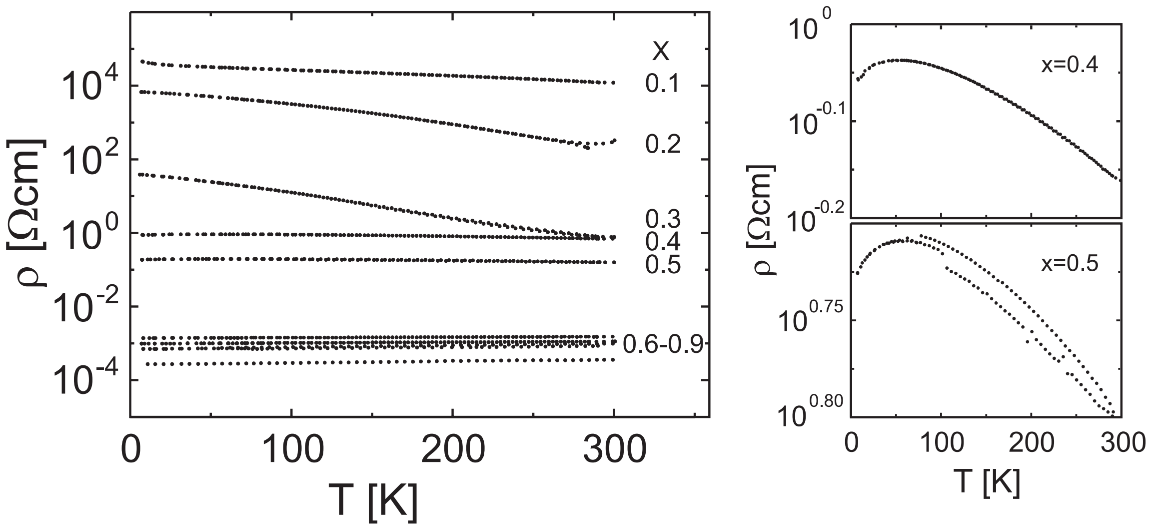

Figure 9: *Resistivity vs. temperature for $Na_{1-x}Sr_xNbO_3$ ($0.1 \leq x \leq 0.9$) together with the corresponding curves for the x = 0.4 and x = 0.5 samples with an enlarged scale (right).*

The paramagnetic susceptibilities are proportional to the carrier concentration. For samples with small carrier concentrations (x = 0.1 and 0.2) discontinuities of the temperature dependence of χ are observed at approximately 160 K and 60 K, respectively. However, these changes of χ are so small that they are probably related to structural changes rather than to changes in the magnetic structure.

The electrical resistivities of $Na_{1-x}Sr_xNbO_3$ samples with $0.1 \leq x \leq 0.9$ range over 8 orders of magnitude from approximately 10^4 Ωcm to 10^{-4} Ωcm, see Fig. 9. Samples with low carrier concentrations (x = 0.1–0.3) are insulating. An unusual *non*-monotonic temperature behavior is found for the x = 0.4 and 0.5 samples. Their resistivities increase with temperatures up to a maximum around $T \approx 75$ K. Such a maximum of the resistivity was also observed for $La_{0.75}TiO_3$, whose composition lies between the insulating $La_{0.7}TiO_3$ and metallic $La_{0.8}TiO_3$ and is discussed in terms of disorder-induced localization [M.J. Maceachern *et al.*: Chemistry of Materials **6**, 2092 (1994)]. The complex temperature dependent behavior of the electrical resistivity of the $Na_{1-x}Sr_xNbO_3$ samples with x = 0.4 and 0.5 might therefore also be related to a fluctuation of the charge carrier concentrations in different crystallites caused by local variations in the Na/Sr ratio combined with vacancies at these positions.

Samples $Na_{1-x}Sr_xNbO_3$ with $0.6 \leq x \leq 0.9$ are metallic, and the linear dependence of the resistivity vs. temperature $\rho = \rho_0 + AT$ indicates an electron-phonon scattering mechanism. Obviously the composition-induced transition from semiconducting to metallic behavior takes place between x = 0.5 and 0.6 with no major structural change occuring but simply due to a large enough carrier concentration. The complex superstructures and electronic features of the perovskite type niobates $Na_{1-x}Sr_xNbO_3$ ($0.1 \leq x \leq 0.9$) call for further studies, e.g., the clarification of the origin and nature of the metal-insulator transition in this system.