Abstract

Alkaline niobates such as $K_xNa_{1-x}NbO_3$ are considered to be a promising class of lead free piezoelectric materials representing an environment-friendly alternative to Pb(Zr, Ti)O_3. On the other side, however, the consolidation to full density of these compounds is problematic. Therefore, ultrafine powders with improved sinterability are desirable for the preparation of dense piezoceramics on the basis of these niobates. Many physical properties of nanocrystalline transition metal-based oxide particles strongly depend on their size and shape. Here we focus on $K_{0.5}Na_{0.5}NbO_3$ as a technically interesting composition and investigate the size effect on the crystallographic phase transformation.

Raw powders with an average particle size of 30 nm were synthesized using microemulsion mediated hydrolysis of mixed metal alkoxides. Upon annealing below 600 °C, the mean particle diameter moderately increased up to 100 nm. For annealing temperatures above 600 °C, drastic particle growth up to 10 micron was observed after annealing at 1000 °C. Raman spectra (Ar^+ laser excitation, Lambda = 514.5 nm, < 50 mW power) were collected for these powders. Bands at the low frequency region below 160 cm^{-1} can be assigned to K^+/Na^+ translations and rotations of NbO_6 octahedra. These modes and the internal vibrational modes of the NbO_6 octahedra above 200 cm^{-1} sharpened with increasing particle size. X-ray powder diffraction in combination with Raman spectroscopy showed that the crystallographic structure of particles larger than 200 nm annealed at 700 °C or above can be assigned to the monoclinic $P2$ (C_2^1) or Pm (C_S^1) space group. They have the normal modes $4A+8B$ and $8A'+4A'$, respectively. On the other hand, particles smaller than 200 nm annealed at 625 °C or below have a triclinic $P1$ (C_1^1) space group with the irreducible representation of $27A$. Furthermore, in the intermediate temperature region both structures were observed.