11th International Conference on Advanced Materials
Rio de Janeiro Brazil
September 20 - 25
ICAM2009

Enhancement of the Lattice Polarization by the $NaSr_2(NiNb_4)O_{15-\delta}$ Solid-Solution Formation

S. Lanfredi [(1)*], S. A. Dantas[(1)], C. Poline[(1)], M. A. L. Nobre[(1)]

(1) FCT, Universidade Estadual Paulista, Campus de Presidente Prudente, S.P., Brazil, e-mail: silvania@fct.unesp.br
* Corresponding author.

Abstract –Crystalline nanopowders of the $NaSr_2(NiNb_4)O_{15-\delta}$ solid solution with average size equal to 24 nm were prepared by high energy ball milling. Structural characterization was carried out by the X-ray diffraction. Crystallite size and lattice microstrain of $NaSr_2(NiNb_4)O_{15-\delta}$ nanostructured powders were calculated. The profile of adjusting of the set of diffraction lines and refinement of the structural parameters were performed by the Rietveld method, using the FULLPROF program. Crystallographic structure was built- up using the CaRIne Crystallography 3.1® software.

Materials belong to tetragonal tungsten bronze TTB class have attracted interest of scientific and technologic areas as a promising lead-free ferroelectric material and with potential of application as sensor device, actuators, transducers and capacitors (*wireless communication*). Nanopowders of nickel doped sodium strontium niobate, $NaSr_2(NiNb_4)O_{15-\delta}$, was prepared by high energy ball milling [1]. The major crystallinity degree was attained when the precursor powder was calcined at 1150 °C during 10 hours, in oxygen atmosphere. Crystallite size and lattice microstrain were monitored by X-ray diffraction. Both parameters were derived from Rietveld method. As expected, the increase of the calcination temperature leads to an increasing of the crystallinity. According to the XRD, powders calcined below 650 °C exhibited an amorphous character. At 1150 °C, the crystallite size is equal to 35 nm. The profile of adjusting of the set of diffraction lines and refinement of the structural parameters were also performed by the Rietveld method, using the FULLPROF program. From set of crystallographic parameters, graphical representation of the structure of the $NaSr_2(NiNb_4)O_{15-\delta}$ was built- up using the CaRIne Crystallography 3.1® software, see Figure 1. The best theoretical adjust was obtained considering that pentagonal and square sites are statistically occupied by equal quantities of Na^+ and Sr^{2+} ions and each octahedral site (8d) occupied in part by nickel atoms, being Nb_I substituted by Ni atoms. The atomic coordinate, determined by Rietveld method shows z values different from z = ½ to the Nb(2) atoms, that can be characterized by a displacement of niobium atoms in the z plane, giving origin in a spontaneous polarization [2]. The displacement of niobium atoms can be associated with development of rotation and tilting of the [NbO6] octahedral. As a whole, the distortion degree of the [NbO6] is a function of the soaking time. The interatomic distances of Nb-O bonds in octahedral sites of the $NaSr_2(NiNb_4)O_{15-\delta}$ are shown in Figure 2. Both bond lengths between niobium and apical oxygen (O1 and O2) are different meaning that the niobium is off-center. Spontaneous polarization, P_S, of the [NbO6] depends on the magnitude of off-center displacement. The subtraction of the two apical lengths (Nb-O2) – (Nb-O1) is proportional to two times the niobium off-center displacement Δz. Thus, the spontaneous polarization of [NbO6] octahedral of the $NaSr_2(NiNb_4)O_{15-\delta}$ can be written by: $P_E^{Nb} = (258 \pm 9)\ x\ 0{,}248\ \mu\ C.cm^{-2}$ = 63.98 $\mu C.cm^{-2}$. This value is two times major than one obtained to the spontaneous polarization of the [NbO6] octahedral in $NaSr_2Nb_5O_{15}$ structure. Thus, the Ni cations contribute to the polarization, in specific to the structural polarization as a function of the off-center characteristics.

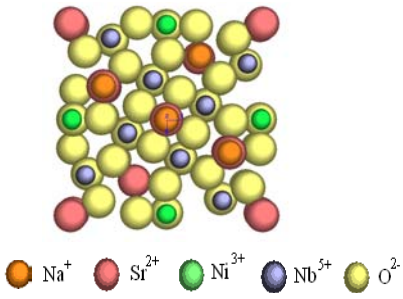

Figure 1: Unitary cell of the $NaSr_2(NiNb_4)O_{15-\delta}$.

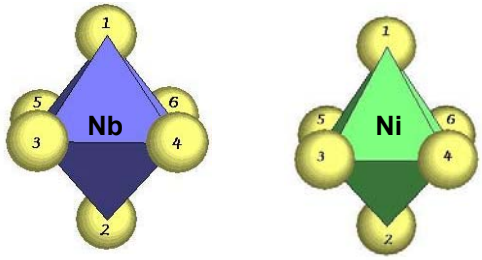

Figure 2: Representation of [NbO6] and [NiO6] octahedral in TTB structure of the $NaSr_2(NiNb_4)O_{15-\delta}$.

References

[1] S. Lanfredi, L. R. Trindade, A. R. Barros, N. R. Feitosa, M. A. L. Nobre, Cerâmica 51 (2005) 151.
[2] B. G. Hyde, M. O' Keefe, Acta. Crystallogr. , A29 (1973) 243.