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Morphology and the Structural Study of the TTB Ferroelectric $Sr_{2(1-x)}Na_{(1+x)}Gd_xNb_5O_{15}$ (SNGN)

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Abstract*—We synthesized The nanopowders ferroelectric $Sr_{2(1-x)}Na_{(1+x)}Gd_xNb_5O_{15}$ by solid-state method. Using X-ray diffraction (XRD) and scanning electron microscopy (SEM) technique we studied the $Sr_{2(1-x)}Na_{(1+x)}Gd_xNb_5O_{15}$ (SNGN) ceramics over the composition range $0 \le x \le 1$. The X-ray results reveal an orthorhombic phase, with space group Pmmm for $0 \le x \le 0.8$ and a tetragonal phase, with space group P4mm (a = b = 12.3343 Å et c = 3.9778 Å), for $0.9 \le x \le 1$. These results are confirmed by the SEM technique who provide strong evidence of the reduction of the disorder in the TTB structure when going from Sr^{2+} to Gd^{3+} (from x = 0 to x = 1). This disorder is connected to the orthorhombic distortion, which is reduced when going from orthorhombic to tetragonal phase*

Keywords— *Solid-state, X-ray diffraction, Space group, Ferroelectric*

I. INTRODUCTION

Recently, considerable attention has been focused on the study of tetragonal tungsten bronze (TTB) type ferroelectrics. These compounds constitute one of most important families of ferroelectric materials. Fig. 1 shows a schematic representation of the TTB structure with general formula $A_2BC_2M_5O_{15}$ (M = Nb, Ta), projected along the [001] direction. as it is shown in Figure 1 The network is built from NbO_6 corner-sharing octahedra that provide cavities of three types, A, B and C, with coordination numbers 15, 12 and 9, respectively, forming square, pentagonal and triangular tunnels capable of capturing positively charged ions [1]. In fact, large ions, like K^+, Rb^+, Cs^+, $Pb^{2+,}$ Ba^{2+} or Na^+, can only be located in A or B sites, while smaller ions, for example Li^+, can penetrate to the C-type cavity. The great variety of TTB-type compounds is provided by the different choices of the inserted ions.

Although the prototype paraelectric phase of the whole family of $A_2BC_2M_5O_{15}$ compounds has a tetragonal symmetry (P4mm), the ferroelectric phase can be either of tetragonal or of orthorhombic symmetry. The tetragonal symmetry of the ferroelectric phase occurs mostly in Strontium-free TTB-type compounds such as $Na_2GdNb_5O_{15}$ (NGN) [2]. The Strontium-containing compounds such as $Sr_2NaNb_5O_{15}$ (SNN) [3–5] present generally an orthorhombic distortion in the ferroelectric phase provided by the strong polarizability of the Sr^{2+} ion that involves a structural anisotropy and distortion of oxygen octahedra [4]. Note, however, the special case of the compound $Sr_2NaNb_5O_{15}$.

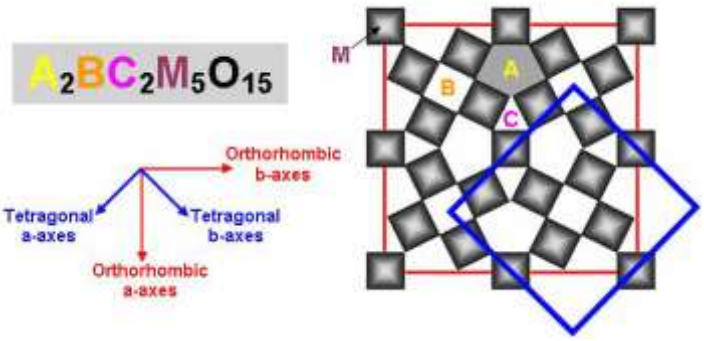

Fig. 1. Schematic projection of the TTB crystalline network along the fourfold c axis (A, B and C correspond to cationic sites with coordination number 15, 12 and 9, respectively, in the unit cell $A_2BC_2M_5X_{15}$).

II. EXPERIMENTAL PROCEDURES

We synthesized the ferroelectric compound (SNGN) by solid-state method from the following chemical formula:

$$2_{(1-x)}\,SrCO_3 + \frac{1+x}{2}\,Na_2CO_3 + \frac{5}{2}Nb_2O_5 + \frac{x}{2}Gd_2O_3 \Longrightarrow Sr_{2(1-x)}Na_{(1+x)}Gd_xNb_5O_{15}$$

The precursors are placed in alumina boats and heated at high temperature. Heating is provided by programmable ovens up to 1300 °C. The mixtures of carbonates ($SrCO_3$, Na_2CO_3) and oxides (Nb_20_5, Gd_2O_3) are finely ground and undergo a heat treatment at 1200 ° C for 24 hours in oxygen atmosphere, this is after a pretreatment at 700 ° C for 10 hours (fig. 2). The powder obtained from this calcination was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The diffraction pattern was refined in according to the Rietveld method. The refinement was performed using the program Fullprof. The reason for having interest in the TTB family, it has been found that their physical properties can be modified by different ionic substitution at above mentioned sites [7]. The ferroelectric niobate materials with TTB structure are quite attractive materials due to their remarkable electro-optic, pyroelectric, piezoelectric, nonlinear optical properties [8].

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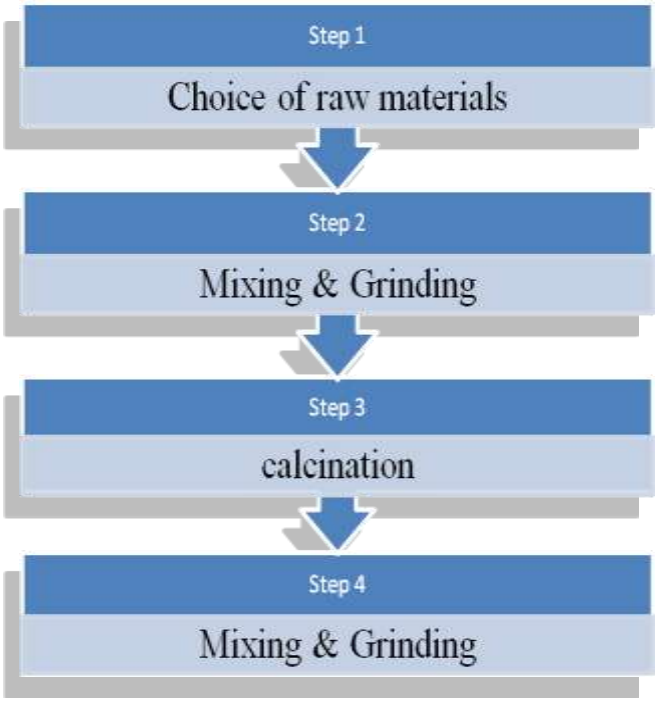
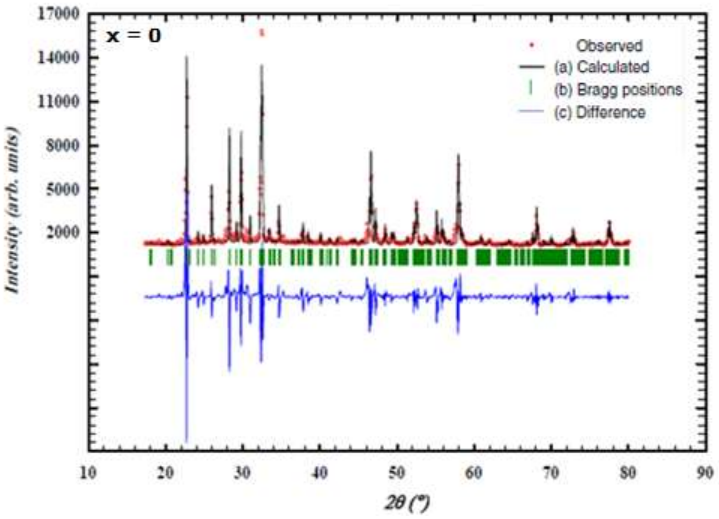
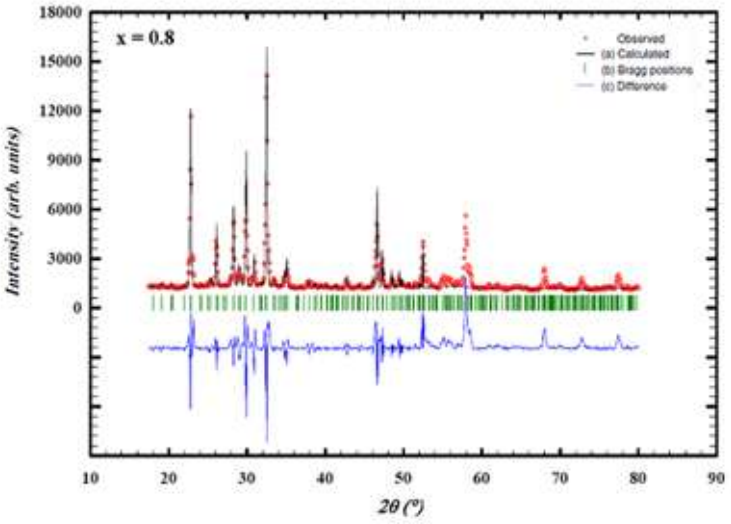


Fig. 2. Main steps in the manufacture of $Sr_{2(1-x)}Na_{(1+x)}Gd_xNb_5O_{15}$

III. RESULTS AND DISCUSSION

A. X-ray diffraction results





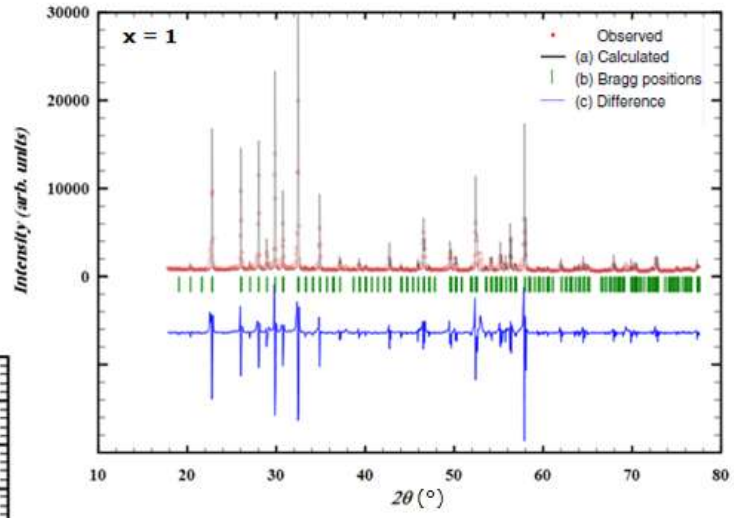


Fig. 3. Observed, calculated and difference X-ray diffraction patterns for compounds with x=0, x=0.8 and x=1.

Figure 3 shows the room temperature XRD patterns of $Sr_{2(1-x)}Na_{(1+x)}Gd_xNb_5O_{15}$ (SNGN) with x=0 (first compound), x=0.8 (intermediate compound) and x=1 (last compound). The patterns of three compositions indicate that the powders are pure and that they been have crystallized in a TTB-type structure. The intensity of some peak is weak for the sample SNN (x=0). After introducing of Gd^{3+} concentration the intensity of most peaks increases remarkably in intermediate compound (x=0.8) and it reaches great values in last compound (x=1) , deducing that a certain distortion of the crystalline structure appears in the Nb sites. The diffraction patterns of the samples were refined according to the Reitveld method, using the Fullprof program integrated in WINPLOTR software, to determine the symmetry group and the parameters (a, b and c) for three compositions (figure 4).

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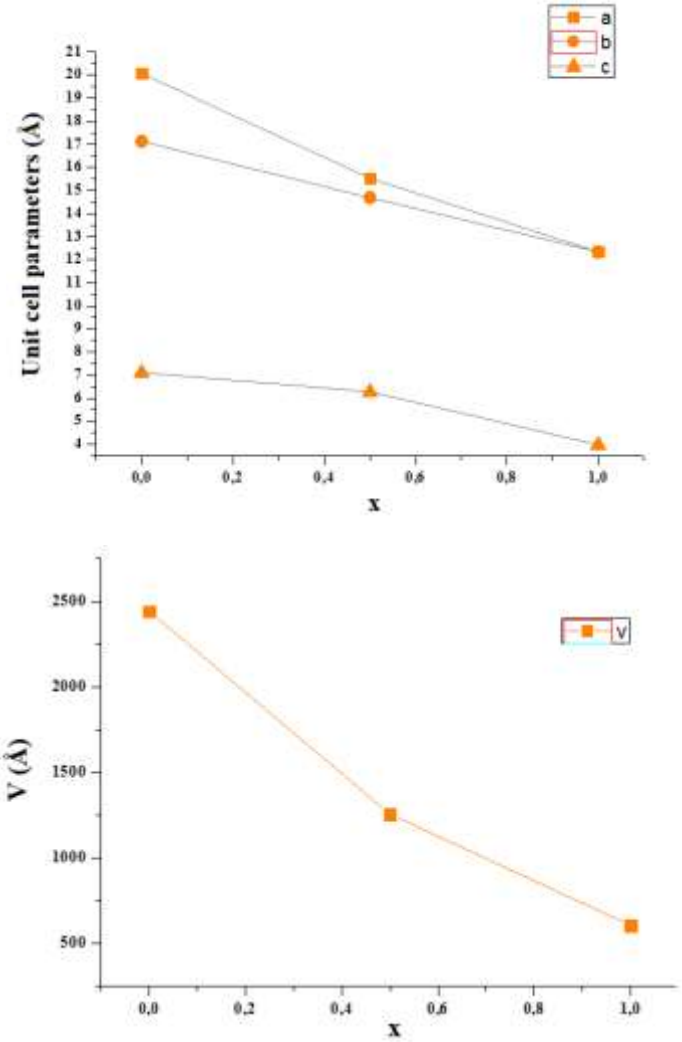

Fig. 4. Evolution of the lattice parameters and volume of Sr2(1-x)Na(1+x)GdxNb5O15 as a function of the gadolinium content x.

In this Figure we note that when the substitution rate x increases the parameters (a) and (b), for each composition, decreases while the parameter (c) remains relatively constant before undergoing significant decrease for the large values of the substitution rate (x). Indeed, more the rate of gadolinium cation (Gd^{3+}) is important in the crystal lattice, the cell volume decreases, so the structure becomes more stable. The shrinkage of the unit cell can be reasonably attributed to the smaller ionic size of Gd^{3+} (r = 0.94 Å) compared to that of Sr^{2+} (r = 1.18 Å) and Na^{+} (r = 1.02 Å).

B. SEM results

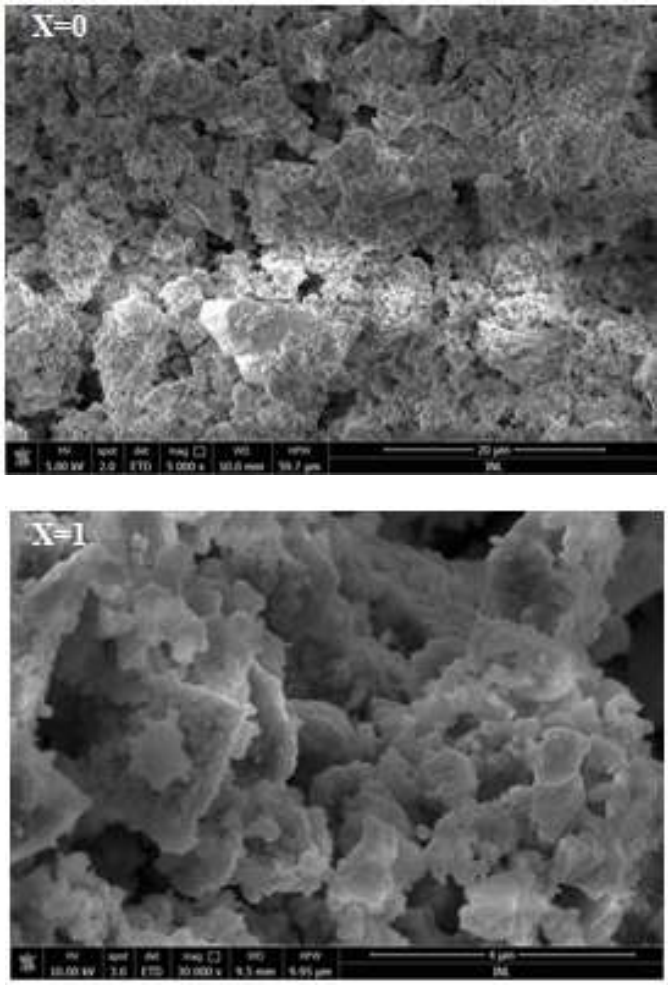

Fig. 5. SEM images of the initial phase (x=0) and the final phase (x=1) of SNGN powders

For the initial phase (x=0) we see some crystallites that are not similar but they are homogeneous as well as the shapes of the layers are well organized and oriented in three dimensions. We also find the deep pores. The size of these particles is on a microscopic scale, and from this image we find the real distance on the sample equal to 59.7µm while the scale bar indicates that the actual distance is 10 µm.

For the final phase (x=1) we can see clearly the tetragonal form of grains with very smooth surfaces whose arrangements are more or less irregular and not uniform, some of these grains appear to be oriented perpendicular to the surface moreover the surface is well surrounded by the dopant.

IV. Summary and Conclusion

We prepared a series of new family of TTB ferroelectric Materials $Sr_{2(1-x)}Na_{(1+x)}Gd_xNb_5O_{15}$ with $0 \leq x \leq 1$ using a solid-state method. The X-ray diffraction indicates that the powders are pure and crystallize in a TTB-type structure. We have successfully refined the diffraction patterns and determined the lattice parameters of each composition. Our results show two ferroelectric phases: an orthorhombic phase

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with space group Pmmm for $0 \leq x < 0.8$ and a tetragonal phase, with space group P4mm, for $0.8 \leq x \leq 1$. This result is confirmed by the SEM technique which demonstrated that the SNGN compound has an unstable orthorhombic structure for low gadolinium levels $x < 0.8$ and the progressive replacement of Sr^{2+} by the Gd^{3+} cation induces a decrease in orthorhombic distortion until its complete disappearance at x=1 so the SNGN structure becomes quadratic more stable.

Moreover, we concluded than more the substitution rate x is big, more the cell volume is small. This work anticipates our future investigation of the ferroelectric TTB family

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