

Ferroelectric materials with Tetragonal Tungsten Bronze (TTB) type structure : Synthesis and characterization

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INTRODUCTION

The compounds which crystallize in the Tetragonal Tungsten Oxygenated Bronze type structure (TTB: Tetragonal Tungsten Bronze) are one of the most important classes of ferroelectrics (niobates and tantalates families). They have been the subject of many studies such as structurals, dielectrics, Pyroelectric and so on. More recently, new applications have been revealed for these materials containing rare earth cations.

The main goal of this work is to study the ferroelectric properties of ceramics, especially the substitutions of the square sites A (coordination number 12) and pentagonal sites B (coordination number 15). The studied compositions in this work have the following formula: $Pb_{2(1-x)}K_{1+x}Gd_xNb_5O_{15}$ (PKGK) ($0 \leq x \leq 1$). Powders are prepared by solid phase reaction. The characterization is carried out by Raman spectroscopy at room temperature in order to investigate the influence of Pb^{2+} substitution by Gd^{3+} one in the structure of these compositions.

ELABORATION

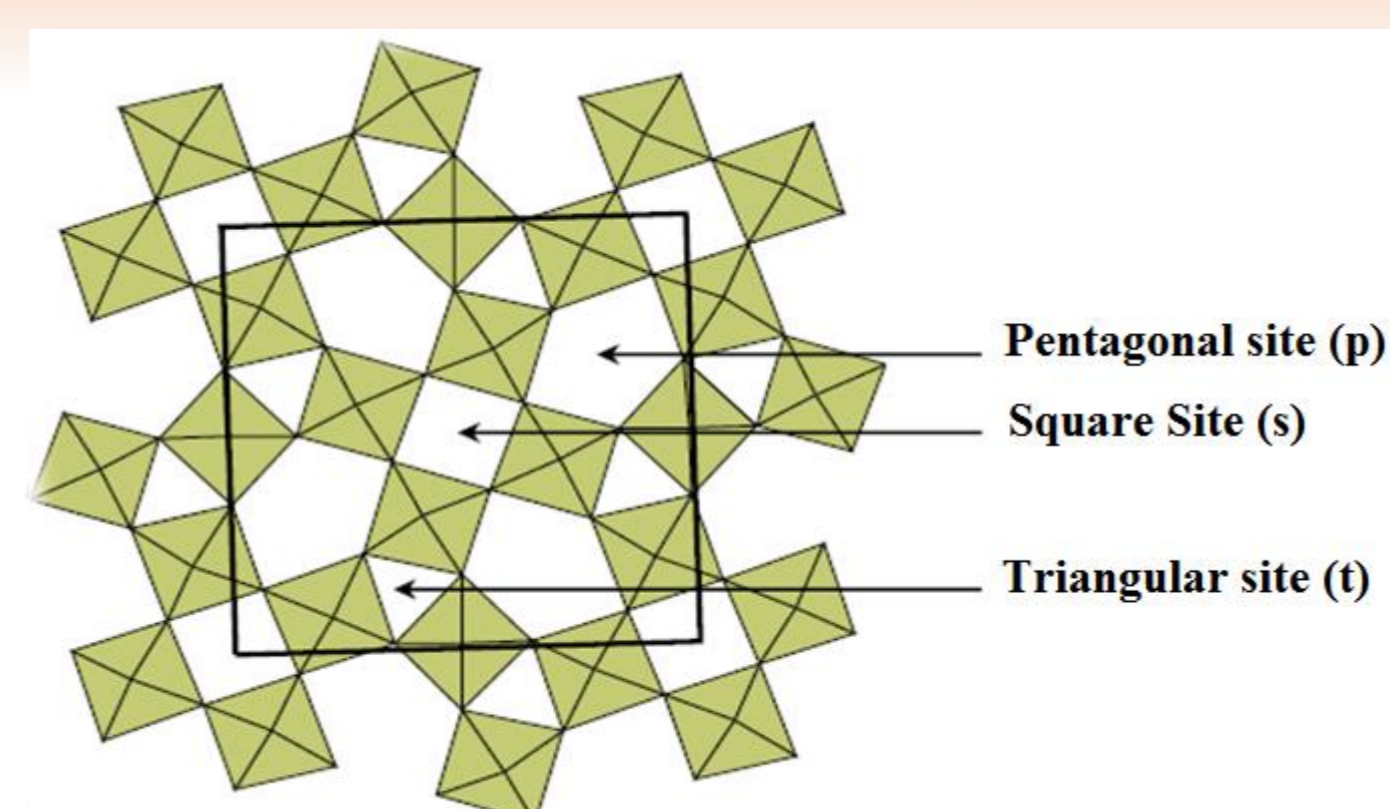


Fig. 1: TTB type structure. (p), (s) and (t) represent pentagonal, square and triangular sites, respectively



Fig. 2: Principal steps in the fabrication of ceramic.

DESCRIPTION

1-The tetragonal tungsten bronze structure can be described by an octahedras network MO_6 ($M =$ transition metal) connected between them by their vertices and showing along the χ axis the cavities within the form of tunnels of pentagonal (p), square (s) or triangular (t) section. The first two sites of coordination number 15 and 12, respectively may be occupied by cations of large size (generally alkali or alkaline earth), while the (t) site of coordination number 9, by small cations such as lithium.

2-The PKGN compound is produced by the solid process which consists to mixing a stoichiometric amount of different precursors, which are generally the oxides, by manual grinding. The pulverized mixture is reacted at $1200^\circ C$ to ensure the reaction between the various precursors and to form the crystalline phase. This step is followed by grinding to break up the agglomerates formed and to homogenize the final powder. The method by solid process is an easy process whose implementation aspect is very economical.

RESULTS

Analysis using Raman spectroscopy at room temperature

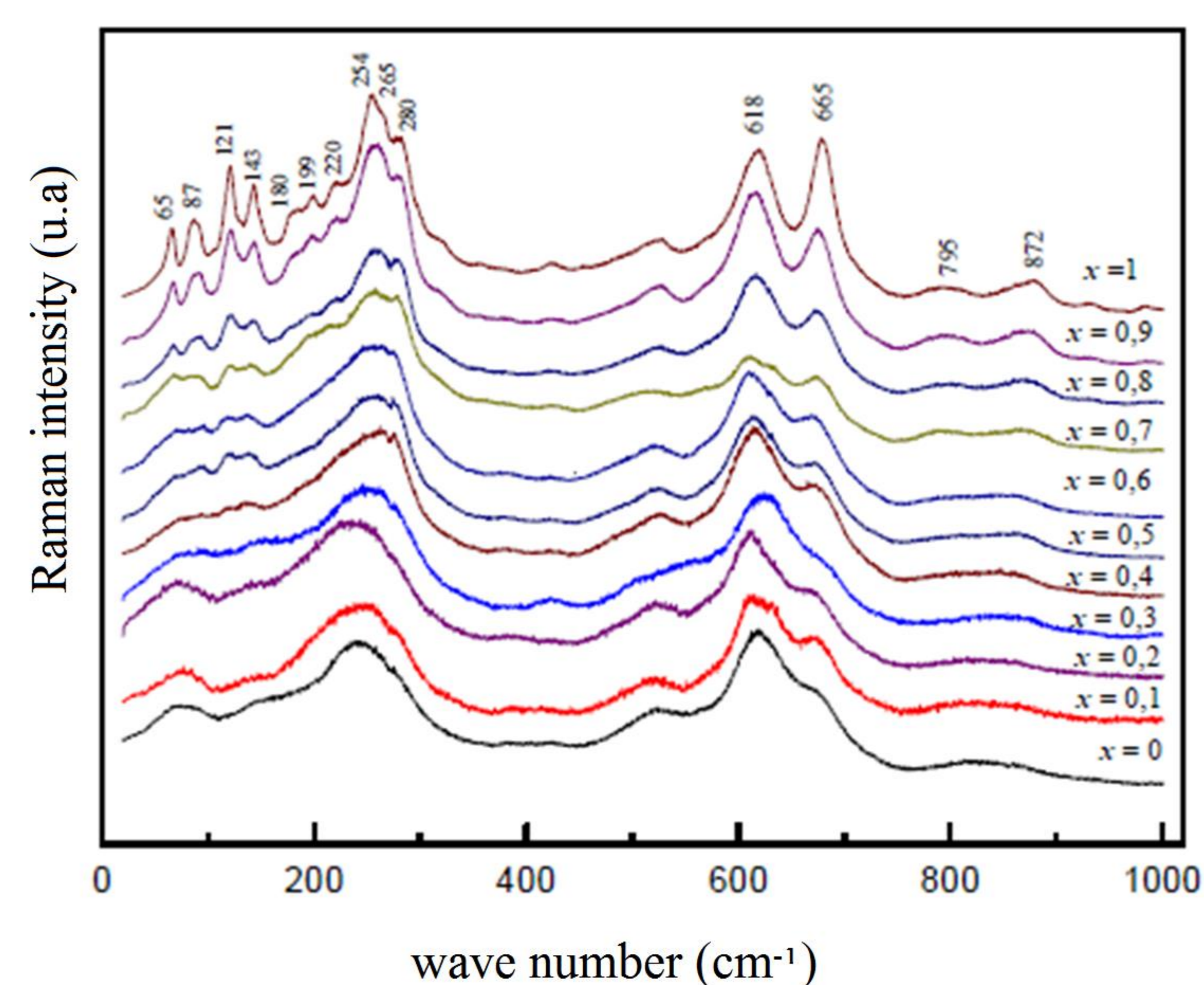


Fig. 3 : Raman spectra of $Pb_{2(1-x)}K_{1+x}Gd_xNb_5O_{15}$ solid solution as a function of x ($0 \leq x \leq 1$) at room temperature.

Raman spectra have wide bands which persist until to $x = 0.7$. This explains the reduction of cationic disorder by substitution of lead by gadolinium. Thus confirming the preferential occupation of pentagonals sites by K^+ and squares sites by Gd^{3+} .

The obtained results have shown that the internal vibration modes dependent differently of Gd. The Nb-O elongation mode shows two rays about 618 cm^{-1} and 665 cm^{-1} which become narrower when x increases without duplication or frequency shift for all compositions. However, the vibration mode of O-Nb-O deformation shows a decrease of the wide in the half-height and a shift to the high frequencies, followed by a duplication for the compositions rich in gadolinium. This behavior confirms the reduction of the disorder in the GKN phase ($x = 1$).

CONCLUSION

These results have enabled to study the influence of Gd^{3+} ions substituted on the structural distortions. Some substitutions are envisaged in order to optimize the ferroelectrics and dielectrics properties of these materials. The ultimate goal is the use of materials exempts the lead in the context of environmental protection as dielectrics for capacitor materials, Pyroelectrics for electronics materials, etc....

These results offer many perspectives, one of the main concerns the characterization by magnetic measurements to find multifunctional materials.