Dielectric Properties of new Ferroelectric Lead Potassium Niobate $Pb_{0.9}K_{0.2}Nb_2O_6$

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Abstract: In this paper we report the dielectric properties of ferroelectric compound $Pb_{0.9}K_{0.2}Nb_2O_6$ (PKN-0.1) that was elaborated by a standard solid-state reaction technique and characterized by X-ray diffraction, Raman diffusion and scanning electron microscope techniques confirming its tetragonal tungsten bronze (TTB) crystallographic structure. The dielectric permittivity and the loss tangent of the sample have been measured in a frequency range 20Hz–1MHz and a temperature range 35–550°C. The ferroelectric-paraelectric phase transition was observed at T_c=518°C witch follow the Curie-Weiss law. AC impedance plots were used as tool to analyse the electrical behaviour of the sample as function of frequency at different temperature. The obtained results indicate the non-Debye type dielectric relaxation.

Keywords: Ferroelectric, Tetragonal Tungsten Bronze (TTB), Phase transition, lead potassium niobates, impedance spectroscopy

I. Introduction

The most important property of ferroelectric materials is the existence of spontaneous polarization which direction can be reversed by the applied electric field. This makes them as emergent materials for new technology usage [1] like e.g. the memory-storage elements, piezoelectric transducers, sensors etc. A large number of pure or complex ferroelectric oxides have been examined as suitable candidates for such applications. One of them is the tetragonal tungsten bronze (TTB) family which was discovered in 1949 by Magneli on example of $K_{0.57}WO_3$ compound [2].

The structure of this family is different from the traditionally studied perovskite structure and is described as framework of MO_6 octahedra sharing corners as shown in Fig. 1. Such geometry leads to three kinds of tunnels with pentagonal (p), square (s), and triangular (t) sections. The first two sites of coordination number respectively 15 and 12 can be occupied by ions of large size while the third one of coordination number 9 can be only occupied by small size ions [3]. The formula unit of the generating cell is given by $(A_2^1A_4^2)C_4B_{10}O_{30}$. If all A and C sites are occupied, the structure is called completely filled structure [4]. The possibility of varying of occupation of A and B cite offers the flexible possibility to tune the materials properties [5].

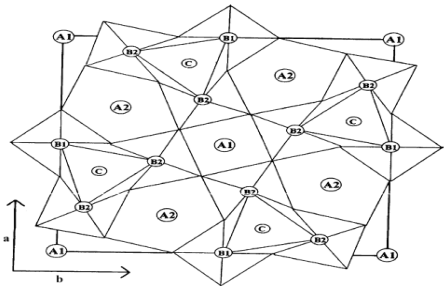

Figure 1: Schematic projection of the TTB crystalline network along the c axis

One of the most promising material of TTB family, important for piezo-electric, electro-optic and photo refractive applications is the lead potassium niobate with general formula $Pb_{1-x}K_{2x}Nb_2O_6$ (PKN). At room temperature it is isomorphic to ferroelectric $PbNb_2O_6$ [6] having the space group Cm2m (C^{14}_{2V}) and unit cell with four formula units [7].

The objective of the current paper is to understand the electrical properties of PKN ceramics resulting from different contributions from various components and processes in the material. Generally, the charge transport can take place via different modes such as charge displacement, dipole reorientation, and space charge dynamic relaxation.

For such study we used the Complex Impedance Spectroscopy (CIS). Consisting in the application of

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AC signal as an input perturbation, this technique is the principal non-destructive method for such type of analysis, especially suitable for polycrystalline compounds. The output response, presented in a complex plane as the superposition of different semi-circles (Cole-Cole plot), can separate the grain, grain boundary and electrode contributions with different time constants [8].

PKN series is a limited solid solution between Pb-niobate ($PbNb_2O_6$) and K-niobate ($KNbO_3$) for x varying from 0 to 0.34 [9]. To the best of our knowledge several authors had studied the dielectric properties for PKN compositions: Rao et al for f x=0.2 and 0.32 [6, 10, 11], Yamada and al, and Hussain for x=0.2 [12, 13, but no study of the composition with x=0.1 is reported in the literature.

Consequently in view of the importance of the material PKN, the present work discusses the preparation, dielectric and impedance spectroscopy properties of the new composition $Pb_{0.9}K_{0.2}Nb_2O_6$ of ferroelectric of TTB family that is called further as PKN-0.1. We refine its symmetry by X-ray diffraction and investigate the ferroelectric transition by dielectric measurements. The electrical parameters of the material are also examined using the complex impedance spectroscopy.

II. EXPERIMENTAL:

II-1. Synthesis:

Polycrystalline lead potassium niobates PKN-0.1 has been synthesized by solid state reaction route, using high purity (99.9%) carbonates and oxides; PbO, K_2CO_3 and Nb_2O_5. These ingredients (carbonates and oxides) were mixed in a desired stoichiometry and grounded in methanol medium for an hour with agate mortar with pestle before each thermal treatment. The obtained powder was calcined at 900°C/4h. The process has been repeated three times to achieve homogenous state with single phase powder. The formation of the single phase compound was confirmed via X-ray powder diffraction (XRD). The fine homogenously calcined powder was then added with required organic binder poly ethylene glycol (PEG) which evaporates at low temperature to provide strength and flow ability of granules and to reduce the brittleness of sample. The granulated powder compacted under a hydraulic press with 250MPa pressure was prepared into discs of 13 mm diameter and of 1.1 mm thickness approximately. Then the obtained pellets were placed into alumina crucible and sintered at 1100°C/1h. The obtained sintered ceramic sample was crack-free.

II-2. Structure and microstructure characterization:

A preliminary structural study was carried out using an X-ray diffraction technique with X-ray powder diffractometer (XPERT-PRO) for the confirmation of formation of the correct compound. CuKα radiation (λ=1.5406Å) was employed in the wide range of Brag angles (10°≤2θ≤90°). Micro-Raman spectra measurements were performed on a JY HR800 Raman spectrometer. The surface morphology and microstructure of a sintered pellet were studied by scanning electron microscopy (SEM) on apparatus Jeol JSM-5500. A pellet was carbon coated before scanning under high resolution field emission gun of SEM.

II-3. Dielectric measurements:

To measure the electrical properties of the compound, air drying silver paint was applied on both flat faces of the sample. Capacitance (C_p), loss tangent (D) and impedance were measured as function of frequency from 20Hz to 1MHz at different temperatures 35-550°C using a computer controlled LCR-meter (HP 4284) with an incertitude of 0.05% in conjunction with a laboratory-made sample holder and heating arrangement with an ac signal of 1V. The effect of moisture on the above properties was overcome by pre-heating of the sample to 200°C with annealing time of 2h, and then cooled to room temperature prior to the measurements.

III. RESULTS AND DISCUSSION:

III-1. structure

Formation of the desired compound PKN-0.1 has been checked by preliminary X-ray structural analysis. The XRD pattern of PKN-0.1 is shown in Fig. 2. The structure was refined basing on the orthorhombic structure with a space group of Cm2m. The lattice parameters has been found to be a = 1,7697 nm, b=1,7963 nm and c = 0,3872 nm at room temperature.

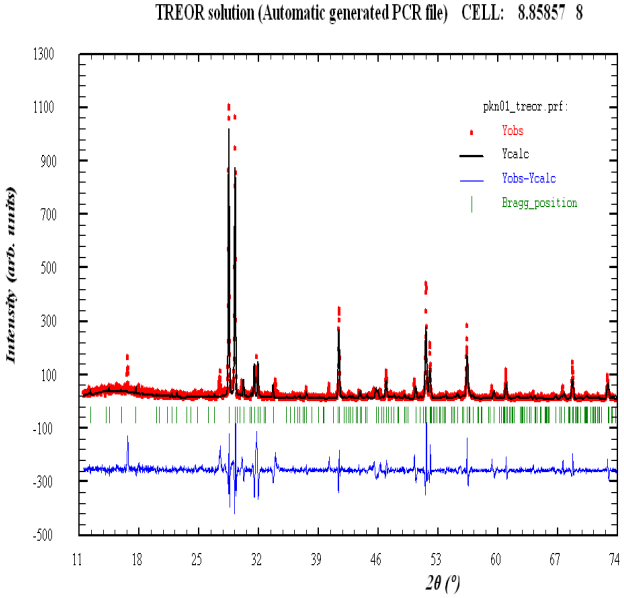


Figure 2: Room temperature XRD pattern of the calcined powder of PKN-0.1 ceramic

The micro-Raman spectra of the polished PKN ceramic at different temperatures are presented in Fig.3. We observed two broad and strong bands about 250 and 621 cm^{-1} which are characteristic for TTB structure [15], and two additional weak peaks at 390 and 806 cm^{-1}. The peak at 250 cm^{-1} is assigned to the deformation of O–Nb–O bond, the peak at 621 cm^{-1} is due to the elongation of O–Nb bond, whereas the peak at 806 cm^{-1} is associated to the deformation of NbO6 octahedron. [16,17] The very weak peak at 390 cm^{-1} is the A1 mode of Nb–O elongation in PKN-0.1 [18]. The bandwidth of the Raman peak increases with increasing of the temperature, which may be accompanied by an increased order in TTB structure.

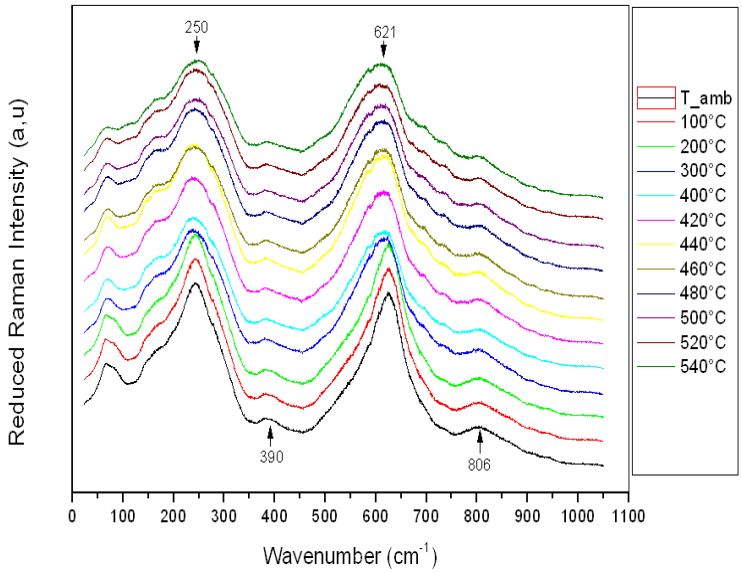
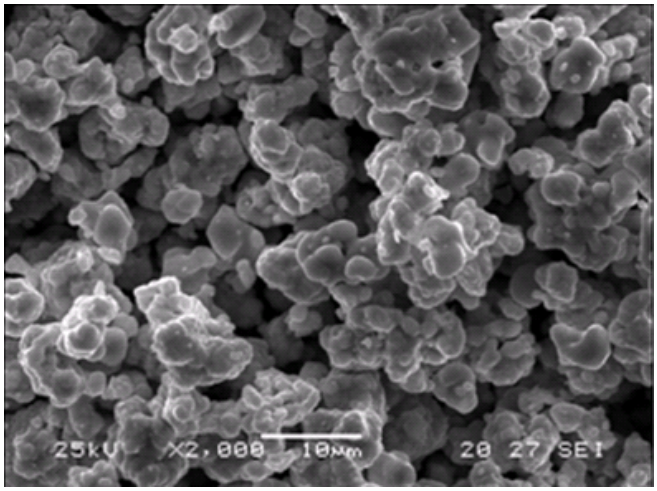


Figure 3: Micro-Raman scattering spectra for PKN-0.1 ceramic

In figure 4 we reported the tow aggrandizement of the scanning electron micrographs for the sintered pellet of the ceramic PKN at room temperature witch describes their surface properties and microstructure.



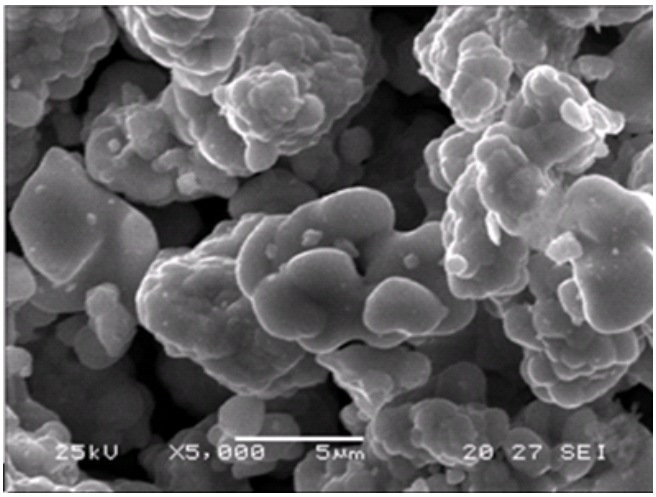


Figure 4: SEM micrograph of the sintered pellet at room temperature.

The nature and distribution of the grains in the sample suggests the formation of the single phase compound which is compatible with the X-ray results. Also, the grains are uniformly distributed through the surface of the sample showing its compactness (high density) for dielectric measurement. The grain size is about 4 microns.

III-2. Dielectrics measurements:

The evolution of the dielectric constant versus temperature during heating and cooling of ceramic PKN-0.1 for frequency f = 30 kHz is shown in Fig. 5.

A maximum of the real dielectric constant related to Para-Ferroelectric transition is observed at Curie temperature Thc = 518°C. The same dielectric anomaly is observed during the cooling at Tcc =512°C. This anomaly corresponds to the Ferro-Paraelectric transition [19]. The process of heating and cooling shows the thermal hysteresis in the ferroelectric phase. The cooling stage is marked by the lower transition temperature and the higher dielectric permittivity than those in the heating stage. This may be explained by the high mobility of ions in the paraelectric phase [20].

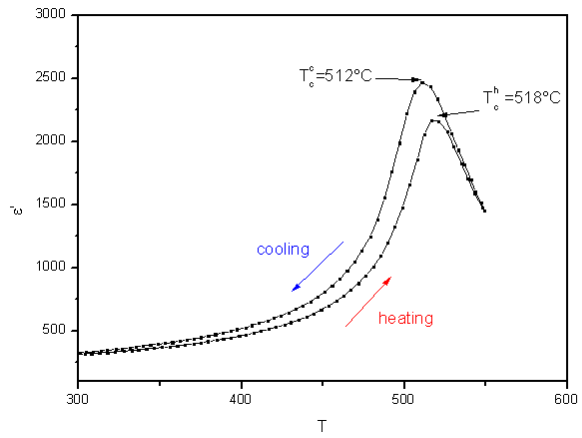


Figure 5: Dielectric constant versus temperature on heating and on cooling for PKN-0.1 ceramic at f=30 KHz

The temperature dependence of the dielectric permittivity at different frequencies for the PKN-0.1 ceramic is shown in the Fig.(6-a). As can be seen, in the whole studied interval, there is no appreciated shift of the transition temperature (T_c) with increase of the frequency, which is the fundamental characteristic of ferroelectrics with conventional Para-Ferroelectric phase transition.

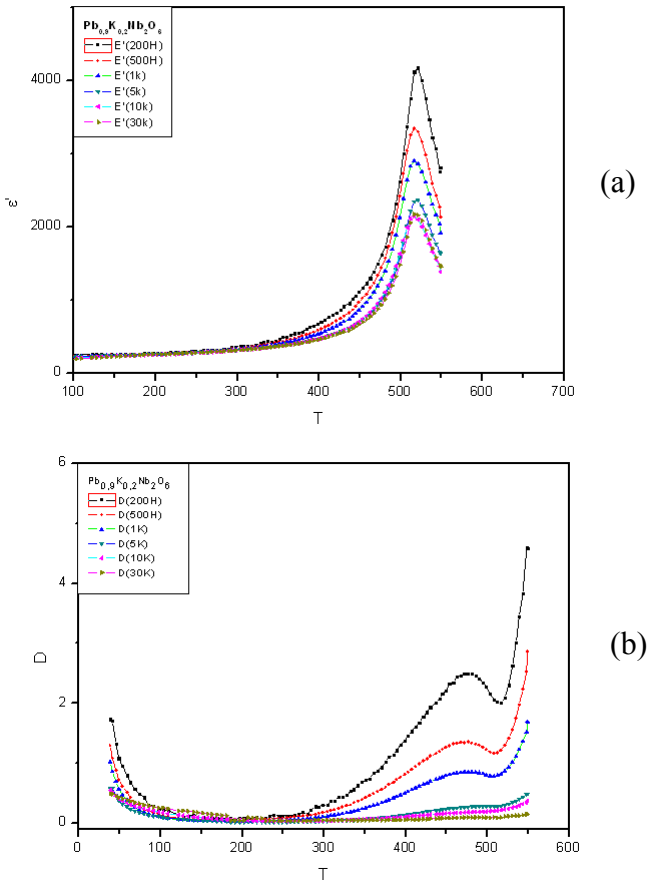


Figure 6. Temperature dependence of real dielectric constant (a) and dielectric loss (b) at different frequencies in PKN-0.1 ceramic

However a slight frequency dispersion of the maximum of dielectric permittivity was observed around T_c, in agreement with results obtained in [21]. This behaviour has been associated to the domain walls motion in ferroelectric phase where the micro-domains that marks a normal-type transition prevail [22].

The shown in Fig.(6-b) the dielectric loss tan(δ) decreases as frequency increase. The anomalous behaviour at temperature which coincides with T_c at different frequencies has been observed. The decrease of tan(δ) at T_c is attributed due to the reduction in the domain wall contribution to the dielectric loss [4]. The observed dispersive loss at high temperature is probably due to localised ionic conductivity [20].

The thermal variation of 1/ε' is of the Curie-Weiss type (ε'=C/T-T_0) and is displayed in Fig. 7, with C=125000 and T_0=473°C [23].

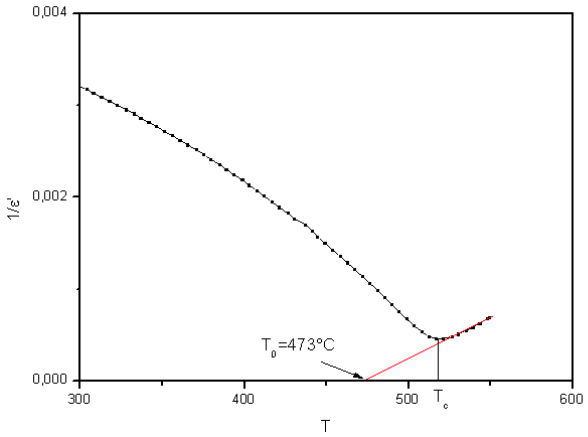


Figure 7: Temperature dependence of 1/ε' at f=30 KHz for a PKN-0.1 ceramic

Cole-Cole plots (Fig. 8) of impedance in PKN at different temperatures (400-560°C) in the frequency range (20Hz-1MHz) shows a linear response in Z" at lower temperature (<400°C) which indicates the insulating behaviour in the sample. As the temperature increases above 400°C the linear response gradually change to semicircles which became smaller and shifts towards lower Z values, indicating a reduction in grain (R_g) and grain boundary (R_{gb}) resistance [6]. The centre of semi-circles lies below the x-axis at an angle Φ indicating non-Debye type relaxation process [4]. Detailed impedance spectroscopy studies will be investigated soon.

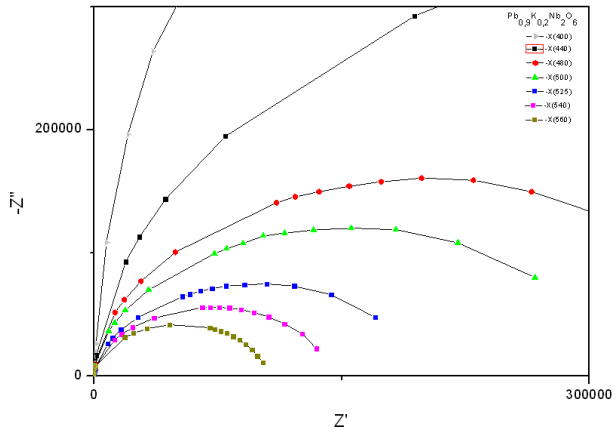


Figure 8: Cole-Cole plots for PKN-0.1 creamics at different temperatures.

IV. Conclusion

Ferroelectric compound of TTB structure: $Pb_{0.9}K_{0.2}Nb_2O_6$ (PKN) was synthesized. XRD analysis on ferroelectric (PKN) ceramic confirmed homogeneous, single phase with orthorhombic structure. The frequency dependency of dielectric and impedance has been studied as a function of temperature and phase transition temperature 518°C in PKN has been found from real dielectric constant versus temperature response. Note that the centre of semi-circles at Cole–Cole plot lies below the x-axis and indicates the non-Debye type relaxation process.

This work anticipates our future investigation of ferroelectric TTB family $Pb_{2-x}K_{2x}Nb_5O_{15}$ that will allow us compare all obtained results on ceramics with those on single crystal and to study the impedance spectroscopy and electric modulus to understand the mechanism of conduction in these ceramics.

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V. References

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