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Ferroelectric Phases in Rare-Earth TTB Ferroelectric Compounds $Pb_{2(1-x)}\ K_{(1+x)}Gd_xNb_5O_{15}$

Y. GAGOU,[1] J.-L. DELLIS,[1] M. EL MARSSI,[1]
I. LUKYANCHUK,[1,*] D. MEZZANE,[2] AND M. ELAATMANI[3]

[1]LPMC, Université de Picardie Jules Verne, 33 rue Saint-Leu, 80039 Amiens Cedex, France
[2]LMCN, FSTG, University Cadi Ayyad Marrakech, Morocco
[3]LCMS, FSS, University Cadi Ayyad Marrakech , Morocco

A new family of rare-earth ferroelectric Tetragonal Tungsten Bronze (TTB) - type compounds with general formula $Pb_{2(1-x)}\ K_{1+x}Gd_xNb_5O_{15}$ was elaborated by solid state reaction. Structural and dielectric properties were investigated using X-ray diffraction and dielectric measurements. The symmetry of the ferroelectric phase strongly depends of the lead concentration. The ferroelectric phase of the compounds with high lead concentration ($x < 0.35$) was found to be described by the symmetry group Cm2m *whereas the compounds with low lead concentration ($x > 0.35$) have the symmetry space group Pba2. The ferroelectric transition temperature was shown to decrease with the concentration of lead.*

Keywords Ferroelectrics; new family; structure; dielectric properties; phase diagram

I. Introduction

Ferroelectric oxides having the Tetragonal Tungsten Bronze (TTB) structure form one of the largest and yet purely studied families of ferroelectric materials [1-4]. These compounds are of substantial interest since several phenomena are involved in the ferroelectric transition. Coupling of the polarization with crystal elasticity and with subsystem of free-tunneled small-size ions provides a reach phase diagram having the series of intermediate phases. The diffusive nature of ferroelectric phase transition provides the enhanced dielectric and piezoelectric constants. The high electro-optic coefficient and strong photorefractive effect make the TTB oxides attractive for the technological applications [5–8].

In the present work we study the new group of these compounds that contains Gadolinium (Gd) and has a general formula $Pb_{2(1-x)}\ K_{1+x}Gd_xNb_5O_{15}$ (PKGN).

II. Experimental

PKGN samples were prepared by solid reaction starting from oxides (PbO, Gd_2O_3, Nb_2O_5) and carbonate K_2CO_3. The finely crushed mixtures undergone the pre-heating at 650°C during 6 h, and then were held at 1100°C during 20 h under the X-ray control. Sintered

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*Corresponding author. E-mail: lukyanc@ferroix.net

cylindrical pastilles of density 96% having 13 mm in diameter and of 1mm in thickness were then elaborated.

X-ray measurements were performed using Bruker AXS – D8 advanced diffractometer with a Cobalt radiations $\lambda_{K\alpha 1} = 1.788970$ Å and $\lambda_{K\alpha 2} = 1.792850$ Å. The sample powders were sealed in a glass capillary and the transmitted beam is focused to a punctual scintillation (NaI) detector.

Dielectric measurements were carried out by SOLARTRON SI-1260 spectrometer in the 10^1–10^7 Hz frequency domain. The platinum electrodes were sputtered at two faces of the pastille. The temperature variation was provided by TS 93 Linkam hot stage having a temperature stability of ±0.1 K.

III. Results and Discussions

1. X-Ray studies

Six compounds (x changes from 0.2 to 1) have been studied by X-ray measurements at room temperature at the same experimental conditions. These measurements substantially improve the previous X-ray study of the Gd containing TTB compounds [9].As shown in Fig. 1 (grey rectangles), several peaks observed in X-ray diffractograms are different for the composition with $x > 0.35$ and with $x < 0.35$. This indicates that a structure of compounds with $x > 0.35$ and $x < 0.35$ can be different.

The crystallographic structure of compounds has been refined using the Rietveld method available in the program *Fullprof* [10]. Assumptions were made in the *pattern matching mode*, taking into account cell parameters, space groups and instrument characteristics. Results are justified by minimizing statistical standard deviation and R-factor. Such structural refinement shows that for compound with $x > 0.35$ the orthorhombic structure is well refined by *Pba*2 symmetry group, while for $x < 0.35$ the structure seems to be better fitted by *Cm*2*m* symmetry group. This permits us to suggest the existence of structural phase transition at the intermediate $x \sim 0.35$.

Therefore our main result is that, depending on the lead (or gadolinium) concentration the ferroelectric transition occurs from the high-symmetry paraelectric tetragonal phase P4/mbm to either one of the two phases:

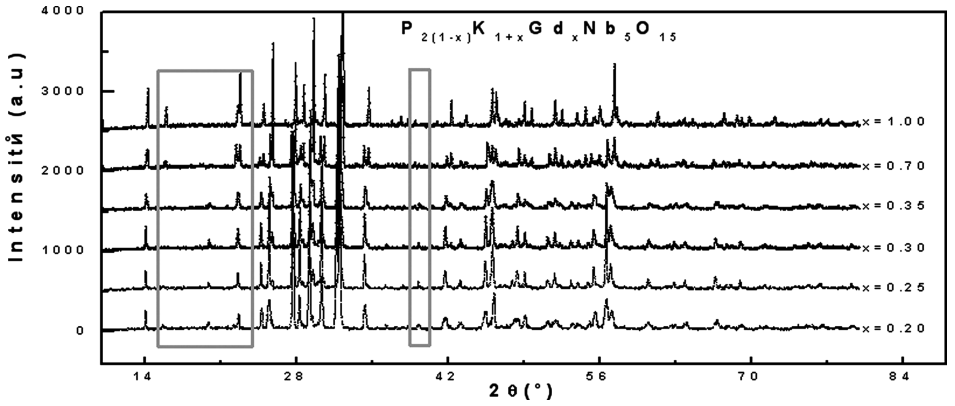

Figure 1. X-ray diagrams of the PKGN compounds.

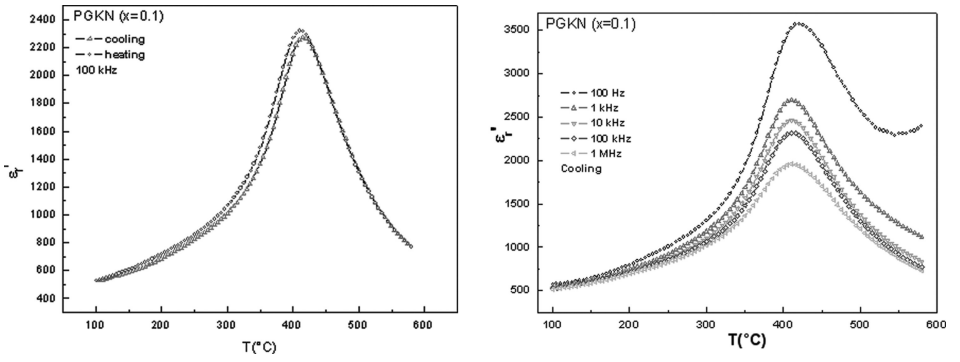

Figure 2. Dielectric constant versus temperature for x = 0.1. (See Color Plate IX).

– For high lead concentration (x < 0.3) the ferroelectric phase is described by the symmetry group *Cm*2*m* in which the orthorhombic deformation is naturally induced by the in (a, b)-plane oriented polarization. Such situation is typical for the traditional lead-containing TTB ferroelectrics as $Pb_2KNb_5O_{15}$, $Pb_2NaNb_5O_{15}$ etc.
– For low lead concentration (x > 0.3) the polarization in the ferroelectric phase is oriented along c-axis. The symmetry group of this phase *Pba*2 reveals the spontaneous orthorhombic deformation that can be provided by the specific interaction of ferroelectric and ferroelastic degrees of freedom.

Such situation is quite rare and was observed previously in the TTB ferroelectric compound $PbK_2LiNb_5O_{15}$ [11,12]. These compounds can be considered therefore as an intermediate stage between lead-containing orthorhombic TTB ferroelectrics with (a, b) oriented polarization and the leadless tetragonal TTB ferroelectrics (like $Ba_2NaNb_5O_{15}$) with c-oriented polarization.

2. Dielectric Measurements

The temperature dependences of the real part of dielectric constant for samples with x = 0.14 and x = 0.4 are shown in Figs. 2 and 3. The peak of dielectric anomaly is well defined for the sample with x = 0.1 and becomes broader in the sample with x = 0.4. This

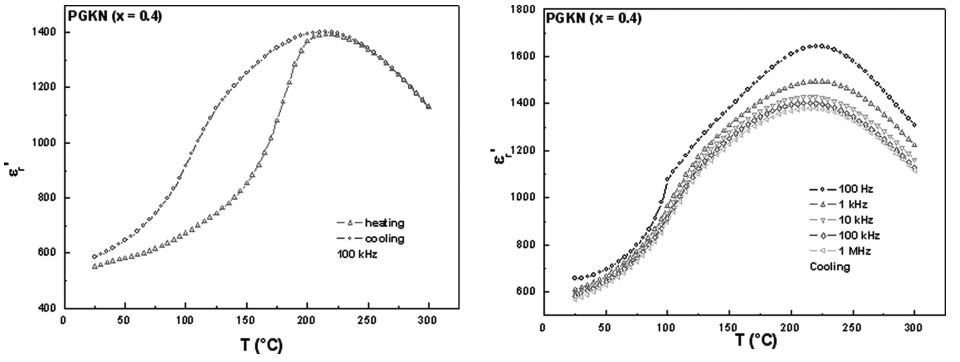

Figure 3. Dielectric constant versus temperature for x = 0.4. (See Color Plate X).

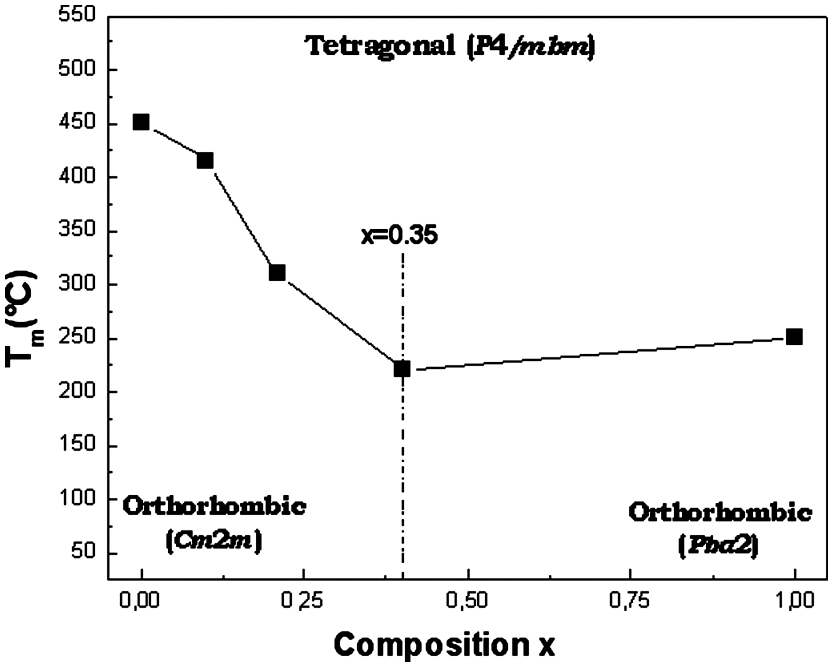

Figure 4. Proposed phase diagram of PGKN compounds.

tendency of the peak broadening with increasing of x is confirmed by measurements of the samples with other intermediate values of the lead concentration. However the investigated compounds did not exhibit the relaxor behavior as is seen from the right panels of Figs. 2 and 3, where we plot the dielectric constant for several frequencies. Another important observation is that, the hysteresis loop is wider in the compound with $x = 0.4$ than that in the compound with $x = 0.1$.

The maximum of dielectric constant is obtained at $T_m = 410°C$ for the compound $x = 0.1$ and at $T_m = 225°C$ for the compound with $x = 0.4$. However, the characteristic temperature of the peak T_m (that should correlate with transition temperature) changes non-monotonously with concentration x. It decreases until $x = 0.3$ and then begins to increase slowly with increasing of x as shown in Fig. 4. Such behavior of the dielectric constant confirms that the ferroelectric properties of the phase with $x = 0.1$ and $x = 0.4$ are different and indicates on the possibility of the structural phase transition at $x \sim 0.3$.

IV. Conclusion

Gadolinium containing TTB compounds with general formula $Pb_{2(1-x)}K_{1+x}Gd_xNb_5O_{15}$ have been elaborated by solid state reaction and studied using X-ray and Impedance spectrometry measurements. It was shown that phases with $x < 0.35$ and with $x > 0.35$ have the different structural and dielectric properties. The symmetry group *Cm*2*m* and *Pba*2 were assigned to these phases. Figure 4 presents the suggested phase diagram for the family PKGN based on the analysis of evolution of T_m versus x and on the X-ray data. We think that a critical concentration $x \sim 0.3$ where the polarization drops from **P**|**c** to **P**|**a,b** direction is the point of special interests where the important piezoelectric properties and morphotropic

region as in several perovskite compounds [13] can be expected. Experiment is in progress to resolve the whole phase diagram.

Acknowledgment

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