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Temperature induced dielectric polarization evolution in polycrystalline $Pb(Cd_{1/3}Nb_{2/3})O_3$

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Abstract

The results of X-ray diffraction (XRD), scanning electron microscopy (SEM), dilatometric and dielectric measurements performed for the same polycrystalline $Pb(Cd_{1/3}Nb_{2/3})O_3$ (PCN) sample are presented. These results reveal the complex character of polycrystalline PCN dielectric properties; in particular, no structural phase transition (PT) was observed. The thermal expansion coefficient indicates glass-like behaviour of PCN. The frequency and temperature dependencies of complex dielectric permittivity were measured and analyzed in terms of diffused/relaxor transition of the ferroelectric polarization. Temperature induced evolution of the relative dielectric permittivity was found to involve two processes. Dielectric permittivity changes, originating from thermally induced evolution of thermal equilibrium of interactions between main structural lattice and two sub-lattices present in the sample were interpreted in terms of thermal evolution of polar cluster sizes in the region of relaxor/glass-like transition.

Keywords: Dielectric properties; Relaxor ferroelectrics; Diffused phase transition; Ceramics

1. Introduction

$Pb(Cd_{1/3}Nb_{2/3})O_3$ (PCN) is classified in the literature as a ferroelectric material of perovskite structure. It is also attributed to a group of ferroelectric materials with diffused phase transition (DPT) and relaxor behaviour. Among many others, $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), $Pb(Ni_{1/3}Nb_{2/3})O_3$ (PNN) and $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) also belong to this group [1]. These materials are used as dielectrics in capacitors and as piezoelectric ceramics [2].

The structure of PCN at room temperature has been determined to be cubic or pseudo-cubic. Maximum values of the dielectric permittivity ε have been observed within a broad temperature range [3–5]: the values of T_m, the temperature of the maximum relative dielectric permittivity ε_m, range from about 550 K for monocrystalline PCN, to about 600 K for polycrystalline PCN. For polycrystalline PCN, T_m depends on the frequency of the applied electric field, as is typical of relaxors [6–8]. In these materials, an increase of frequency (ν) usually causes a decrease of ε_m and a shift of T_m towards higher values. However, in PCN a decrease of T_m as ν increased above 43 kHz was also observed [9]. The temperature expansion of polycrystalline PCN has been described as "glass-like" [10]. Finally Ichinose et al. [11] have suggested the occurrence of polar clusters in PCN.

The high-symmetry cubic structure of PCN at room temperature, a lack of sharp structural phase transition, as well as behaviour ranging from a diffused phase transition to a glass-like one, contrast with typical properties of ferroelectrics. Typical ferroelectrics are characterized by structural PT occurrence with coexistence of paraelectric and ferroelectric phases at T_m. The ferroelectric phase is connected to hysteresis loop presence (observed in PCN) and spontaneous polarization below T_m. Moreover, in ferroelectrics the coexistence of structural and dielectric phases should be accompanied by long-range interactions.

The discrepancies discussed above, relating to the material properties and character of the PT, motivated this author to perform a detailed examination using X-ray diffraction (XRD), scanning electron microscopy (SEM), thermal expansion measurements and dielectric spectroscopy.

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2. Results and discussion

Polycrystalline PCN samples were prepared by hot pressing. XRD measurements were performed by means of a DRON3 apparatus (Cu Kα line, monochromator: monocrystal LiF, at detector NaJ side) with a 2θ angle step of 0.02° within the range 10–120°.

Thermal expansion measurements were carried out using an interferometric dilatometer (MLU-Halle-Wittenberg). Structure morphology images were made using a Philips SEM525 M electron microscope at room temperature.

Dielectric measurements were performed using a QUATRO 4.0 cryosystem with an Agilent 4824A precise LCR meter, BDS 1100 cryostat and WIN Data 5.62 – program Novocontrol.

An X-ray image of the PCN sample is shown in Fig. 1. Sharp peaks and Miller's indicators for cubic structure can be seen. The PCN cubic cell constant equals 0.414 nm at room temperature.

The presence of cubic phase indicates a lack of well-defined relation between the observed dielectric anomalies and changes of PCN crystalline structure. It is worth mentioning here that, in the ferroelectrics literature, the term ''phase transition'' is very often used simultaneously for structural transition and polarization (or dielectric transition). This can be a source of misunderstanding or improper interpretation.

Images taken by SEM show the polycrystalline structure of the PCN sample. Well-developed crystallites were observed at a magnification of 6000× (Fig. 2).

Dilatometric examinations [9] indicate a glass-like PT. The $\alpha(T)$ dependence was determined as follows:

$$\alpha = \frac{d(\Delta l / l_0)}{dT}, \tag{1}$$

with the corresponding value of glass-like temperature T_g, equal to about 560 K (Fig. 3).

The temperature, called Burns (glass) temperature, was for the first time also determined by optical measurement of PLZT [12,13]. This temperature was connected with the development of dipole type polarization (P_d). Similar, glass-like changes were observed in a polycrystalline sample of $Ba(Ti_{0.90}Sn_{0.10})O_3$ [14].

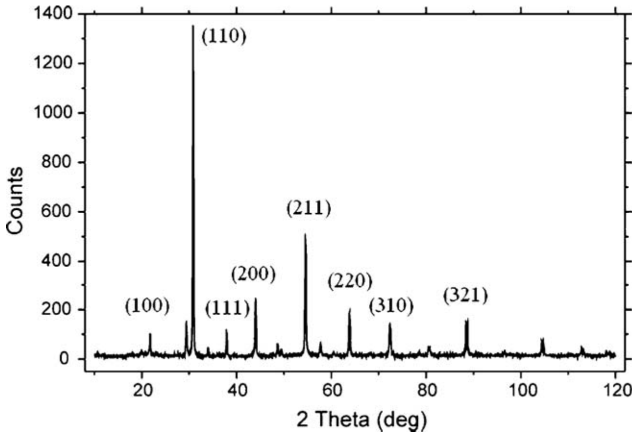

Fig. 1. XRD diagram of polycrystalline PCN sample at room temperature.

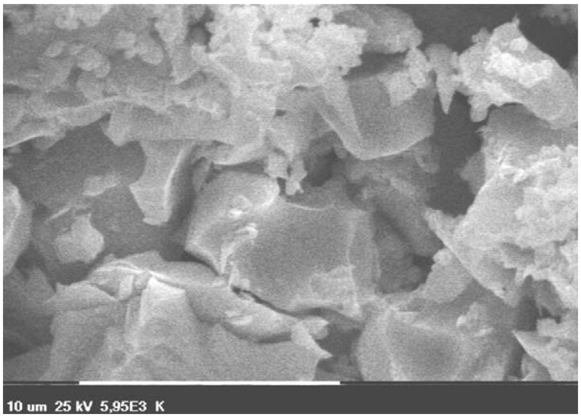

Fig. 2. SEM image of PCN crystallites; magnification 6000×.

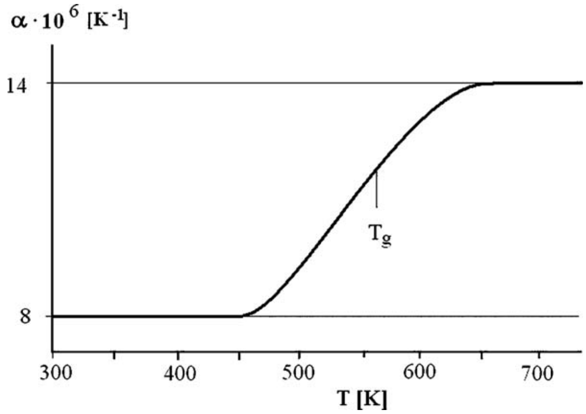

Fig. 3. Thermal linear expansion coefficient of the PCN sample.

X-ray and dilatometric examinations of PCN confirm Schmidt's suggestion [15], combining the degree of broadening of the PT with the degree of paraelectric phase freezing. This is connected with relaxation phenomena and with the degree of polar region freezing. Such clusters can develop in the paraelectric phase during sample cooling.

Dielectric measurements of polycrystalline PCN were performed within the temperature range 173–723 K. Two processes were observed (Fig. 4): a low-temperature (weak) one at ~240 K and a second, much stronger, one at ~660 K.

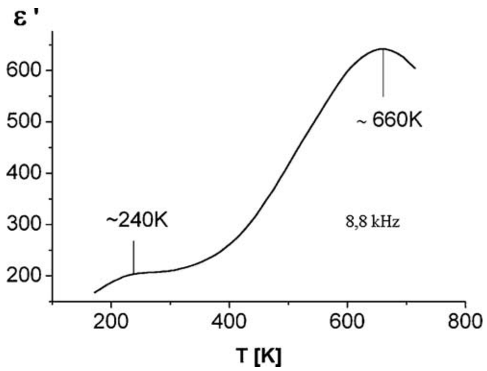

Fig. 4. Relative dielectric permittivity ε' PCN as the temperature function.

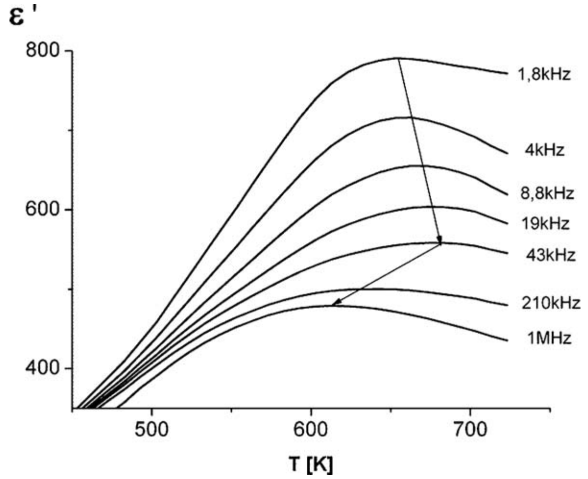

Fig. 5. The dielectric permittivity dependence on temperature T for diffuse type of polarization transition in polycrystalline PCN.

Both transitions are characterized by frequency-dependent temperature, $T_m(\nu)$. In typical ferroelectric relaxors, as ν increases ε_m values fall while T_m grows. In PCN, an increase of ν above 43 kHz (up to 1 MHz in these measurements) is accompanied by a rapid drop of T_m (Fig. 5).

The dielectric permittivity dependence on temperature, as in Fig. 5, can be described for DPT as following:

$$\varepsilon^{-1} = \varepsilon_m^{-1} + A(T - T_m)^{\gamma}, \tag{2}$$

where ε_m is the maximum value of the dielectric permittivity, T_m as before, A, γ are constants for the chosen frequency.

In the diffuse transition of polarization the γ value is close to 2, as can be seen from Fig. 6, where the (2) dependence was linearized by means of the following abbreviations:

$$y = \varepsilon^{-1} - \varepsilon_m^{-1} \tag{3}$$

$$x = T - T_m \tag{4}$$

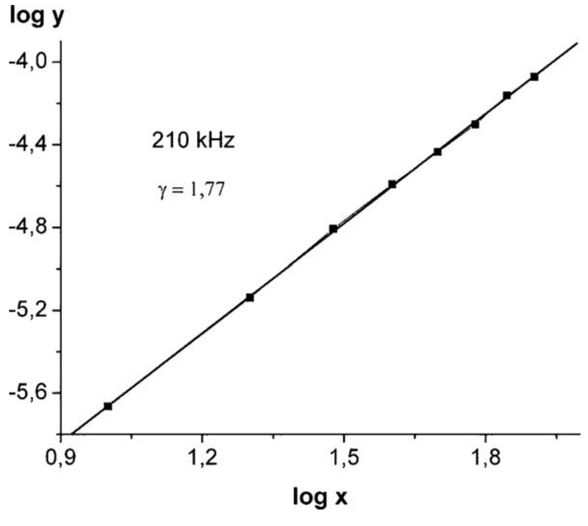

Fig. 6. The dependence of log(y) on log(x) for PCN sample (for abbreviations see text).

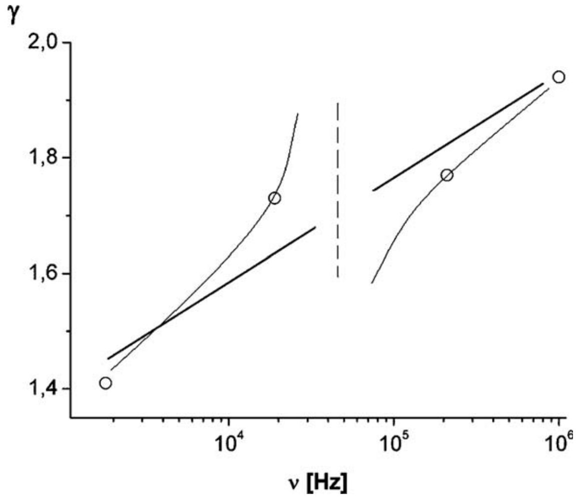

Fig. 7. The γ parameter dependence on frequency ν for PCN sample at 210 kHz.

The dependence shown in Fig. 6 is presented in the form of $\log(y) = f(\log(x))$ for a frequency of 210 kHz. The dependence $\gamma = \gamma(\nu)$ for frequencies applied in the measurements is shown in Fig. 7. It follows from Fig. 7 that, along with the frequency increase, the value of γ rises up to a value of 2. Thus, it can be concluded that PCN polarization undergoes diffusive transition at $\nu \sim 10^6$ Hz. The rapid increase of γ at about 43 kHz could suggest local $\gamma(\nu)$ frequency instability of the polarization response. This response probably originates from a population of polar regions present within the sample structure. At high temperatures these regions may involve dynamic complexes of dipoles with a small correlation range. At these high temperatures, the external electric field may disturb the dynamic equilibrium of these complexes. This, in turn, may disturb the local distribution of B ions in the $A(B'B'')O_3$ system.

From the glass model [16] one can write down the following equation involving $T_{m,\nu}$ values for low frequencies:

$$\nu = \nu_0 \exp\left(\frac{E_a}{k_b\left(T_{m,\nu} - T_f\right)}\right) \tag{5}$$

where ν and ν_0 are the relaxation frequency at temperature T and temperature high enough, E_a is the activation energy of polar region, k_b is the Boltzman constant and T_f is the freezing temperature of polar regions.

The dependence of $\ln(\nu_m)$ on $10^3/T$ for $T_f \sim 600$ K is shown in Fig. 8.

Additional information about PCN electric structure behaviour within the investigated temperature range can be obtained from the phase angle (Φ) dependence on temperature and frequency (see Figs. 9 and 10), as follows.

Low-temperature measurements taken in the 173–473 K range, with a frequency range of 20 Hz–1 MHz, show that Φ takes values of about -90°, characteristic for dielectric behaviour. Above ~500 K, the $\Phi(T, \nu)$ dependence is presented in Figs. 9 and 10. Within this temperature range, for low frequencies Φ increases up to about 0°.

From this result it can be assumed that, together with an increase of temperature (up to 723 K), the dipole component of

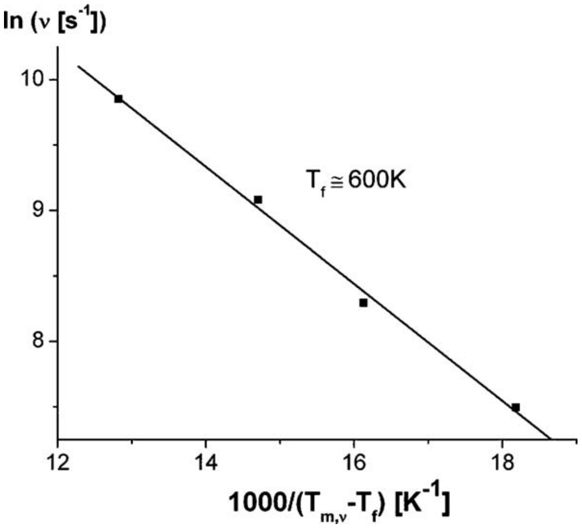

Fig. 8. The $\ln(\nu_m)$ dependence on $10^3/T$ for PCN sample at the high temperature transition.

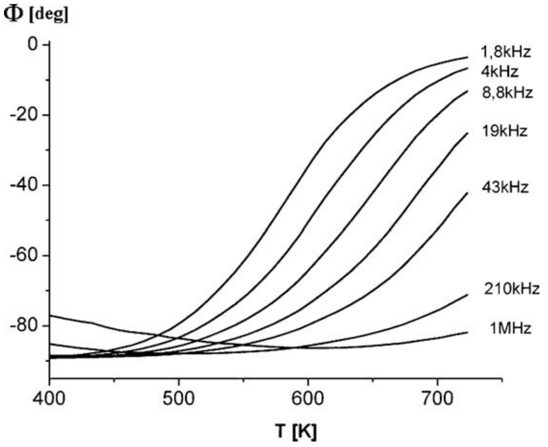

Fig. 9. Phase angle as a function of temperature for PCN sample.

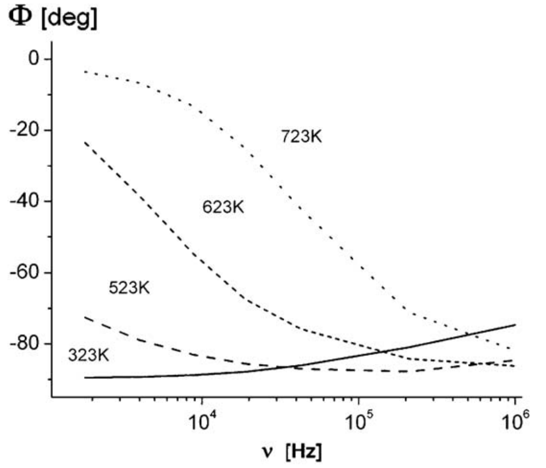

Fig. 10. Phase angle as a function of frequency for PCN sample.

ac conductivity becomes less intensive, and electronic or ionic components prevail. One can assume that electric dipoles and polar regions (clusters) can be formed at temperatures close to and exceeding 700 K.

The distribution of Cd^{2+} and Nb^{5+} in sub-lattice B can be considered as one of the reasons of their formation. When the sample is cooled, deformation of Nb^{5+} (4p6) orbitals can be arranged as dipoles in the (1 1 1) direction [17]. Local network deformation and its complexing interactions with similar deformations within neighbouring cells leads to formation of clusters. That possess polar properties and contribute to macroscopic polarization during the cooling process. This is why the value of Φ falls to -90°.

Lack of long-range ordering and high temperatures does not allow formation of bigger polar objects. Temperature lowering induces coordination of the deformation of adjacent cells, and therefore cluster growth takes place. A model of clusters coexisting within a very broad temperature range, with different grain-size and collectivization, can also explain the anomalous behaviour of relaxors within the high temperature region. PCN can be classified as quasi-ferroelectric material with a mixed (diffuse-relaxor-glass-like) character of the PT.

3. Conclusions

Dilatometric measurements of polycrystalline PCN reveal a change of thermal coefficient of linear expansion occuring within a broad temperature range, with a glass-like character. Fitting to experimental outcomes of ε' frequency and temperature dependences show a diffused and relaxational type of dielectric phase transition. This transition is dielectrically active and has a mixed character; it is not a structural PT. Low values of the phase angle suggest the occurence of dipolar polarization, originating from the creation of polar regions. These regions are not able to create ferroelectric domains at low-temperatures because of the statistical distribution of Cd and Nb ions within the sample structure. Lack of long-range correlation is also connected to the lack of structural phase transition. It follows that PCN should be classified as a dipolic glass material, with mixed, diffuse-relaxor-glass-like dielectrically active phase transition.

References

[1] L.E. Cross, Relaxor ferroelectrics: an overview, Ferroelectrics 151 (1994) 305–320.

[2] K. Uchino, Relaxor ferroelectrics devices, Ferroelectrics 151 (1994) 321–330.

[3] C. Kajtoch, K. Wójcik, Diffuse phase transition in $Pb(Cd_{1/3}Nb_{2/3})O_3$, Acta Universitatis Wratislaviensis 1084 (1988) 155–158.

[4] C. Kajtoch, Electric properties of polycrystalline $Pb(Cd_{1/3}Nb_{2/3})O_3$, Ferroelectrics Letters 25 (1999) 81–84.

[5] C. Kajtoch, H. Arndt, J. Cieminski, A. Rost, Dielectric, electric and dilatometric investigation of $Pb(Cd_{1/3}Nb_{2/3})O_3$, Ferroelectrizitaet 87 (1987) 148–151.

[6] X. Wei, Y. Feng, X. Wan, X. Yao, Evolvement of dielectric relaxation of barium stannate titanate ceramics, Ceramics International 30 (2004) 1397–1400.

[7] M. Adamczyk, Z. Ujma, L. Szymczak, J. Koperski, Influence of post-sintering annealing on relaxor behaviour of $(Pb_{0.75}Ba_{0.25})(Zr_{0.70}Ti_{0.30})O_3$ ceramics, Ceramics International 31 (2005) 791–794.

[8] J. Ravez, A. Simon, Some solid state chemistry aspects of lead-free relaxor ferroelectrics, Journal of Solid State Chemistry 162 (2001) 260–265.

[9] C. Kajtoch, W. Bąk, F. Starzyk, M. Gabryś, Study of phase transition specific in polycrystalline $Pb(Cd_{1/3}Nb_{1/3})O_3$, Archives of Materials Science and Engineering 29/1 (2008) 20–23.

[10] W. Bąk, C. Kajtoch, K. Mroczka, K. Wójcik, Structure and AC conductivity of polycrystalline $Pb(Cd_{1/3}Nb_{1/3})O_3$, Archives of Materials Science and Engineering 33/2 (2008) 75–78.

[11] N. Ichinose, Y. Yokomizo, T. Takahashi, The behavior of the micro domains on the diffuse phase transition ferroelectrics, Acta Crystallographica A28/4 (1972) 187–190.

[12] G. Burns, Crystalline ferroelectrics with a glassy polarization phase, Phase Transition 5/4 (1985) 261–275.

[13] G. Burns, F.H. Dacol, Ferroelectrics with a glassy polarization phase, Ferroelectrics 104 (1990) 25–31.

[14] C. Kajtoch, Dilatometric and dielectric investigations of phase transitions in $Ba(Ti_{1-x}Sn_x)O_3$, Annalen der Physik 2 (1993) 335–338.

[15] G. Schmidt, Diffusive phase transitions, Ferroelectrics 78 (1988) 199–206.

[16] D. Viehland, S.J. Jang, L.E. Cross, Freezing of the polarizations in lead magnesium niobate relaxors, Journal of Applied Physics 68 (1990) 2916–2922.

[17] R. Comes, M. Lambert, A. Guinier, The chain structure of $BaTiO_3$ and $KNbO_3$, Solid State Communication 6 (1968) 715–719.