



# Structure and AC conductivity of polycrystalline $\text{Pb}(\text{Cd}_{1/3}\text{Nb}_{2/3})\text{O}_3$

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Received 19.06.2008; published in revised form 01.10.2008

## ABSTRACT

**Purpose:** Purpose of this work was to determine crystalline structure and ac electric conductivity of polycrystalline sample  $\text{Pb}(\text{Cd}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PCN) in paraelectric phase. Controversies involving uncertainties of phase transition character were the motivation of our experimental investigation: roentgenostructural, electron microscopy (SEM) and dielectric ( $\epsilon'$ ) as well as electric ( $\sigma'$ ) spectroscopy.

**Design/methodology/approach:** Polycrystalline PCN samples were prepared using hot pressing method. X-ray measurements had been performed with use of DRON3 apparatus (Cu  $K_{\alpha}$ , monochromator: monocrystal LiF, at detector NaI side) with jump of  $2\theta$  angle accounting for 0.02deg within a range 10-120deg. Structure images were made at room temperature with a use of electron microscope Philips SEM 525M. Dielectric measurements were made with a use of automatic measuring system Quatro Cryosystem 4.0 and Agilent Precision LCR meter HP4284A equipped with WinDETA 5.62 software Novocontrol. Before measurements, polycrystalline PCN samples were refreshed by annealing at 700 K. Next, electric measurements were carried out under cooling with 2 K/min speed.

**Findings:** It was established that cubic phase is present within the whole range of temperatures (173 K-723 K) applied in our measurements. The polar component of the electric conductivity was dominate below the  $T_m$  temperature ( $T_m$  – temperature at which the maximal value of dielectric permittivity takes place). Above this temperature, activation energy ( $\phi$ ) is falling down, along increasing frequency of measuring field.

**Research limitations/implications:** Changes of AC conductivity of PCN were interpreted in terms of polar regions properties evolution.

**Originality/value:** Results obtained have broad the knowledge about phase transitions occurring without crystal structure change, but involving freezing of polar regions under cooling.

**Keywords:** Ferroelectrics; Phase transition; Polarization; Electrical properties

## MATERIALS

### 1. Introduction

According to literature [1], PCN is classified as a ferroelectric material of perovskite structure with relaxor type of polarization. Among others, it is applied as capacitor ceramic as well as piezoelectric component in actuators [2, 3]. At room temperature PCN has cubic structure. Its dielectric permittivity ( $\epsilon'$ ) behaves

anomaly within the wide temperature range [4]. Temperature of dielectric permittivity maximum ( $T_m$ ) strongly depends on frequency. It is found as typical feature for relaxors [5-7]. For PCN,  $T_m$  shifts towards lower values as the frequencies increase above  $10^5$  Hz [4, 8]. It is in contradiction to classical relaxor behaviour. For polycrystalline samples, the  $T_m$  value (~ 600 K) exceeds that for monocrystals (~ 550 K). Ichinose et al [7] suggested existence of polar regions (clusters) in PCN structure.

The cluster presence and behaviour may be a source of effective polarization discrepancies reported in the literature. Possessing high symmetry, the cubic PCN structure at low temperatures (the lack of structural phase change) is not typical for ferroelectric behaviour. Ferroelectrics show coexistence of paraelectric and ferroelectric phases in the  $T_m$  region. This coexistence evolves into long – range correlation of ferroelectric domains in ferroelectric phase. In the PCN case, at the  $T_m$  temperature, the structural transition is not observed. Additionally, PCN polar properties (phase angle  $\Phi \sim 90^\circ$ ) are still present at high frequencies of measuring electric field even above 700 K (readily higher than  $T_m$ ). These controversies involving uncertainties concerning phase transition character of PCN was motivation of our experimental studies based on roentgenographic, electron SEM microscopy as well as dielectric spectroscopy.

## 2. Experimental

Polycrystalline PCN samples were prepared using hot pressing method. X-ray measurements had been performed with use of DRON3 apparatus (Cu  $K_\alpha$ , monochromator: monocrystal LiF, at detector NaI side) with jump of  $2\theta$  angle accounting for  $0.02^\circ$  within a range  $10\text{--}120^\circ$ . Structure images were made at room temperature with a use of electron microscope Philips SEM 525M. Dielectric measurements were made with a use of automatic measuring system Quatro Cryosystem 4.0 and Agilent Precision LCR meter HP4284A equipped with WinDETA 5.62 software Novocontrol. Before measurements, polycrystalline PCN samples were refreshed by annealing at 700 K. Next, electric measurements were carried out under cooling with 2 K/min speed.

## 3. Results and discussion

A roentgenogram of the PCN sample is shown in Fig. 1. Sharp peaks and Miller's indicators for cubic structure are seen. Lattice constant of PCN cubic cell equals about 0.414 nm (at room temperature).

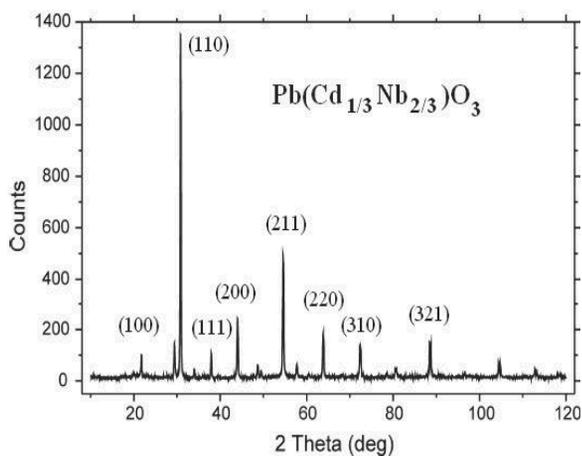


Fig. 1. Roentgenogram of polycrystalline PCN prepared by hot pressing at room temperature

The domination of cubic structure together with very small contribution of the structures with lower symmetry confirm the lack of connection between observed dielectric anomalies and crystal PCN structure changes [9]. In Fig. 2, (110) line profile is shown. Such line is characteristic for cubic phase of many ferroelectric perovskites.

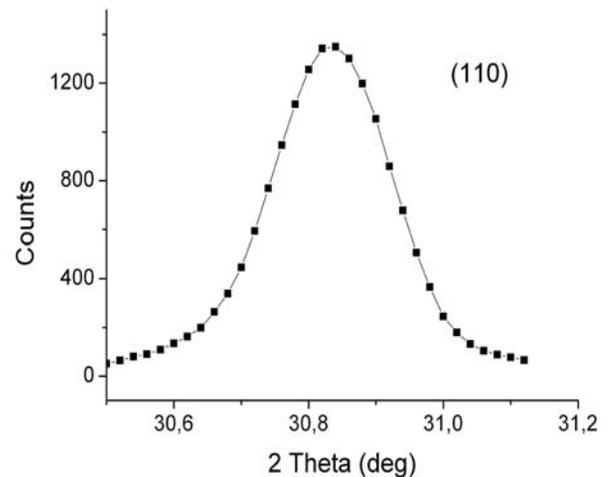


Fig. 2. Profile of (110) line of roentgenogram for PCN sample at room temperature

Electron microscopy image (SEM) shows nonhomogeneous morphology of polycrystalline samples. At magnification of  $12000\times$ , well shaped crystallites are visible (Fig. 3).

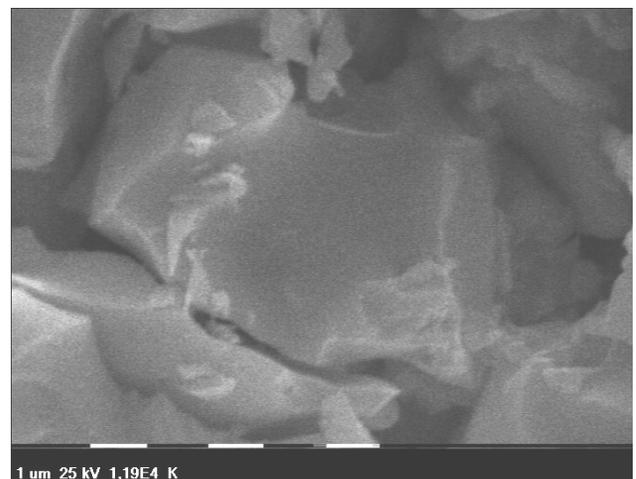


Fig. 3. PCN crystallites at  $1,2 \times 10^4$  magnification

Dilatometric measurements show occurrence of a glass – like phase transition (PT). It takes place at glass – point temperature  $T_g \sim 560$  K. It involves so called glassy polarization or dipolar polarization  $P_d$ . Similar anomaly of glassy type was observed for polycrystalline sample of  $\text{Ba}(\text{Ti}_{0.90}\text{Sn}_{0.10})\text{O}_3$ . The dielectric measurements for polycrystalline PCN were carried out within the temperature range 173 K–723 K (Fig. 4). The  $\epsilon'$  has two maxims:

low temperature one (PT1) at  $\sim 240$  K and high temperature (PT2) at about 660 K. Both these transitions have a features of relaxational behavior [10]. Both of them are characterized by a dependence of  $\epsilon'(T_m) = \epsilon'_{m,f}$  on the frequency. For typical ferroelectric relaxors the lowering of  $\epsilon'_m$  and elevation of  $T_m$  values  $T_{m,f}$  is observed when frequency (f) increases.

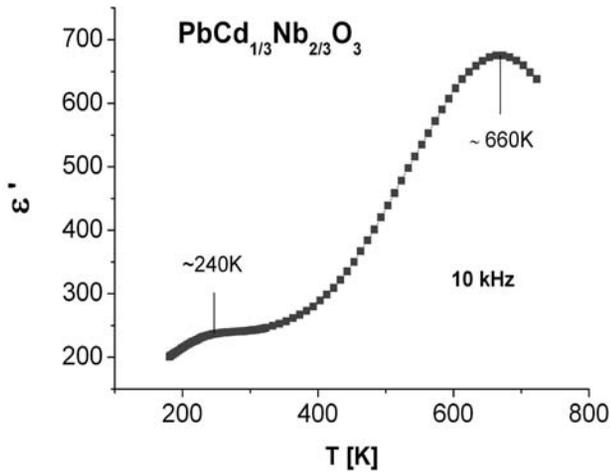


Fig. 4. Relative dielectric permittivity  $\epsilon'(T)$  dependence on temperature for polycrystalline PCN sample

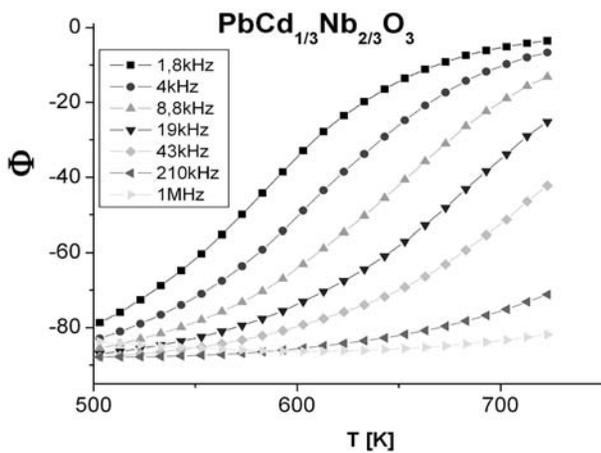


Fig. 5. Phase angle ( $\Phi$ ) dependence on temperature for polycrystalline PCN sample

Such changes were observed in both cases. But in the second anomaly case only up to frequency  $f = 43$  kHz. The further frequency increase (to 1 MHz) was followed by rapid decrease of  $T_{m,f}$  [9]. The phase angle ( $\Phi$ ) measurements, carried out for low temperatures have about  $\sim -90$ deg within the frequency range 20 Hz-1 MHz. Within the temperature range 500 K-700 K,  $\Phi$  values rise up to about 0deg at low frequencies (Fig. 5). It points on the shift of the equilibrium of electric conductivity processes towards electronic conduction.

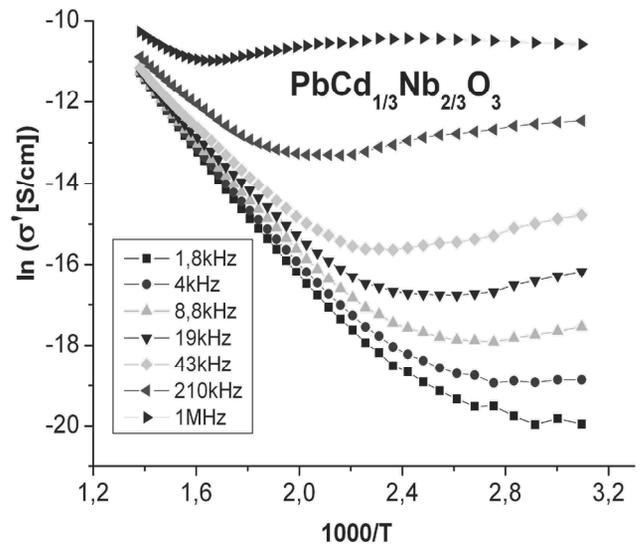


Fig. 6. AC electric conductivity: real part of  $\sigma'$  versus reciprocal temperature for polycrystalline PCN

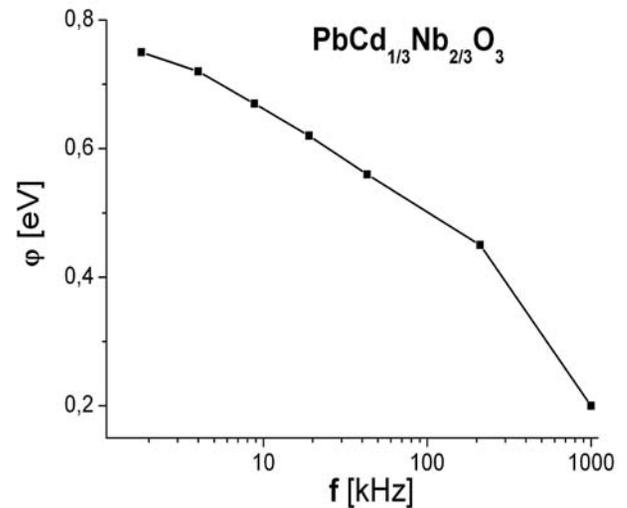


Fig. 7. Dependence of activation energy ( $\phi$ ) of ac conductivity on the frequency for polycrystalline PCN for temperatures above 500 K (data collected from the Fig. 6)

In the Fig.6, the electric ac conductivity ( $\sigma'$ ) dependence on the reciprocal temperature is shown for  $T > T_m$ . The increase of the frequency of 3 orders of magnitude at low temperatures is followed by  $\sigma'$  increase within 9 – orders of magnitude. The frequency increase is connected with appropriate increase of the temperature related to the conductivity maximum. It is also correlated to the positive temperature coefficient value of thermal expansion within this temperature range. The frequency increase leads to energy activation lowering at high temperatures (Fig. 7).

## 4. Conclusions

Typical paraelectric – ferroelectric phase transition involving the lowering of the symmetry of crystalline structure does not occur for PCN at temperatures 173 K-723 K. This behaviour can be classified as glassy dipolar system. A deformation of elementary cell of PCN originates from the differences of Cd and Nb ions distribution. Different ions sizes deform local net structure. It leads to cluster's formalism [11]. These clusters are growing with temperature lowering. Electric dipoles and polar regions are created at the temperatures above 700 K. Local structure deformations and their complexing lead to deformations of T, O, R types taking place in vicinal cells and it can be termed as cluster formation. These clusters have polar properties and effective dipolar polarization. The lowering of temperature forces a coordination of vicinal cells. The growth of the clusters occurs. The coexistence of the clusters with different sizes within wide temperature range explains anomaly dielectric and electric behaviour in the PT2 range. Considering only the spontaneous polarization in ferroelectric materials turns out to be limited to one part of polarization, called cooperative and occurring in the ferroelectric phase. Taking into consideration a primary polarization type i.e. dipolar one (free dipoles) can make easier the interpretation of dielectric properties for paraelectric phase of ferroelectric materials. Measurements taken within wider temperature range enable the evaluation of polarization components values (free, dipolar  $P_d$ , cooperative  $P_k$ , spontaneous  $P_s$ ) taking place in paraelectric phase as well as at paraelectric – ferroelectric phase transition. Similarities and differences of dielectric behaviour in “cross – over” region of ferroelectrics to those of nanocomposites (microcomposites) can make easier understanding of their specific physical properties. The respective discussion can be useful in designing these properties for practical applications [12-15].

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