



Study of phase transition specific in polycrystalline $\text{Pb}(\text{Cd}_{1/3}\text{Nb}_{1/3})\text{O}_3$

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ABSTRACT

Purpose: of this paper was to isolate and attempt to identify experimentally specific features of paraelectric diffused phase of $\text{Pb}(\text{Cd}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PCN) not reported yet in the literature.

Design/methodology/approach: we used to measure and analyse the temperature and frequency dependence of polarization, energy loss, phase angle and ac-conductivity components.

Findings: we have isolated four specific processes visible as specific behaviour of $\epsilon''(T, \nu)$; on ϵ'' and phase angle also temperature and frequency dependences and three contributions to ac-conductivity.

Practical implications: processes isolated will be used to construct a model of polarizability and energy loss as well as ac-conductivity in diffused paraelectric phase of PCN.

Originality/value: of the paper rely on the possibility of experimental verification of temperature induced evolution of polar regions structure and dynamics created in high temperature region of paraelectric phase of PCN.

Keywords: Ceramics; Electrical properties; Phase transition; Relaxor; Dielectric relaxation spectroscopy

MATERIALS

1. Introduction

Investigations of basic physical properties of polycrystalline materials are stimulating a knowledge development about new materials structures – properties correlations. They enables designing of new practical applications of these materials [1-4].

PCN is a ferroelectric material and have perovskite structure. It is classified as member of relaxor containing lead as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN), $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZN). It is applied among others as capacitor ceramic and as piezoelectric in actuators [5, 6]. PCN investigated in this work is polycrystalline and was prepared by method of hot pressing. Lattice constant in the paraelectric phase equals 0.41 nm. At the room temperature it forms cubic and quasicubic structure. Phase transition occurs within wide range of temperature [7]. Temperature (T_m) of maximum of dielectric permittivity (ϵ) strongly depends on frequency. It is typical for relaxors [8-11]. In PCN with frequency of measuring field increase the T_m shift towards lower temperatures is observed [12]. Values of T_m for polycrystalline

materials (~600K) exceed that one for monocrystals (~550K). The linear expansion coefficient dependence on temperature for PCN is typical as for glassy materials behavior [13-15]. Ichinose et al [10] suggested existence of polar regions (clusters) in PCN structure. This possibility may be a source of discrepancies reported in literature. This controversies involving uncertainties of phase transition character was motivation of our experimental study based on dielectric spectroscopy method.

2. Measurement of complex dielectric permittivity and ac conductivity

Sample of PCN ceramic of 8mm diameter and 1mm thickness with silver paint electrodes were placed within measuring chamber. Measuring chamber was designed symmetrically and involves two parts: one for measured ceramic sample and the second fully symmetrical dummy part in order to precise

measurement of sample temperature. The sample temperature was measured by PT100 sensor connected to RE15 Lumel temperature regulator and PC with LUMEL REGULACJA program. This system enables us to stabilize temperature (T), with 0.1K accuracy, or to programme T linearly with the $\pm 1\text{K}/\text{min}$. speed. All measurement were carried out within the temperature range (723÷323)K (cooling with 1K/min.). Prior to dielectric properties measurements, sample was heated up to 723K and kept at this temperature for 1h in order to eliminate the thermal history of the sample. Next, the cooling was initiated and at every 10K step down the fast frequency scan was performed within the range 20Hz÷1MHz. The frequency (ν) scan was performed by means of Agilent 4284A Precise LCR meter equipped by PC with WinData (Novocontrol–Germany) program. Both components of complex dielectric permittivity $\epsilon^*(\nu)=\epsilon'-i\epsilon''=\epsilon^*$ were calculated and recorded together with ac complex conductivity ($\sigma^*(\nu)=\sigma'-i\sigma''$) as well as phase angle $\Phi(\nu)=90^\circ-\arctg(\epsilon''/\epsilon')$.

3. Results and discussion

The relative thermal expansion of PCN on temperature with the glassy transition temperature $T_g \approx 560\text{K}$ is presented in the Fig.1. Thermal expansion coefficient within the lower (α_1) and higher (α_2) temperatures ranges equal appropriately $8 \times 10^{-6}\text{K}^{-1}$ and $14 \times 10^{-6}\text{K}^{-1}$. Real part of dielectric permittivity (ϵ') dependence on temperature (T) and frequency (ν) for polycrystalline PCN ceramic is presented in the Fig.2. The two characteristic features of $\epsilon'=(T, \nu)$ dependence can be pointed out. The first one is maximum of ϵ' , ranging from (~ 480) to (~ 800) and taking place within the temperature range $\Delta T \approx (600 \div 675)\text{K}$. The maximum of ϵ' depends on frequency. Positions of $\epsilon'_{\text{max}}(T)$ at given frequency are pointed by (O)-signs in the Fig.2. The highest ϵ' value (~ 800) occurs for 1.8 kHz. The lowest one is taking place for 1MHz. The whole high temperature process (ϵ'_{max}) of elevated polarizability is taking place within the temperature range specified above and the second one feature is ϵ'_{max} dependence on frequency. Along the temperature lowering an additional process is visible. It can be described as loosing of ϵ' dependence on frequency. All curves in the Fig.2 are approaching the $\epsilon(T_r)$ value about 360 and it is taking place of the temperature region of $T_r \approx 475\text{K}$ value. This process is of diffuse character and one can claim that it is distributed within the range of $\Delta T_r \approx 60\text{K}$. The dependence of imaginary part of dielectric permittivity (ϵ'') on temperature and frequency for polycrystalline PCN ceramic is shown in the Fig.3. It represents energy losses taking place in the sample under the external electric field (EEF) influence at given temperature and EEF frequency. The whole ϵ'' dependence on T consists generally of two parts: C – nonlinear decrease (assigned by arrow with symbol C in the Fig.3) with T lowering and further weak increase of ϵ'' value along T lowering advance. This process is assigned by arrow with symbol D in the Fig.3. The energy losses are also generally frequency dependent and they got maximum at high temperature and low frequency. The minimum of each run is shallow but the whole process, starting from minimum of ϵ'' points (assigned by (O) in the Fig.3) undergoes inversion in its frequency dependence and at the lowest temperature recorded in the experiment (323K), max of ϵ'' occurs for 1MHz. The points of min of ϵ'' monotonically decreases with T – lowering and as well as with frequency change from 1MHz to 1.8 kHz.

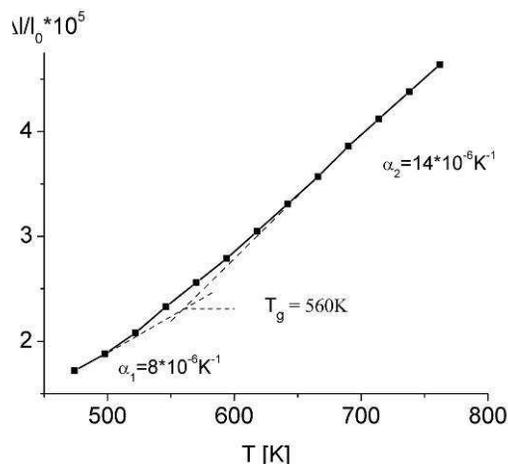


Fig. 1. Dependence of relative thermal expansion on temperature for polycrystalline PCN

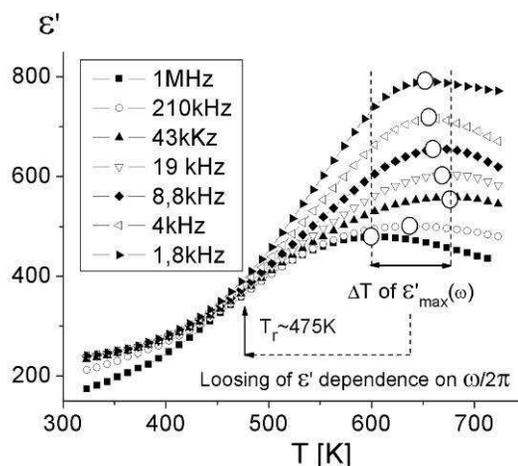


Fig. 2. Real part of dielectric permittivity (ϵ') of polycrystalline PCN ceramics as a function of temperature (T) for 6 selected frequencies. Measurement was performed on cooling with $-1\text{K}/\text{min}$

The phase angle (Φ) dependence on frequency (ν) and temperature (T) for polycrystalline PCN ceramic is demonstrated in the Fig.4. Generally, the whole dependence is geometrically similar to that of ϵ'' . At high temperature (650K÷700K), measuring voltage is almost in phase with resulting current $\Phi \sim (0 \div -10)\text{deg}$ but only for low frequencies. For higher frequencies ($\sim 1\text{MHz}$) the $\Phi(T)$ dependence is weak and Φ values are close to $(-80 \div -90)\text{deg}$ (dielectric type of behaviour).

With T coming down, to about $\sim 450\text{K}$ the frequency dependence of Φ vanishes (process assigned by arrow with c symbol). This seems to be correlated with T_r region in the Fig.2. The further lowering of T makes a split of $\Phi(T, \nu)$ dependence. One part (assigned as arrow with d symbol in the Fig.4) involves a weak elevation of Φ (from -85deg to -75deg) and the second one remains rather unchanged by T (for low frequencies). It is assigned by symbol b in the Fig.4. In the Fig.5 there are values of $|\sigma^*|$ (ac conductivity modulus) prescribed to a given (T, ν) point in S/cm for pointing out the correlation of $\Phi(T, \nu)$ dependence with $\sigma^*=\sigma'-i\sigma''$, which will be described next (Fig.5).

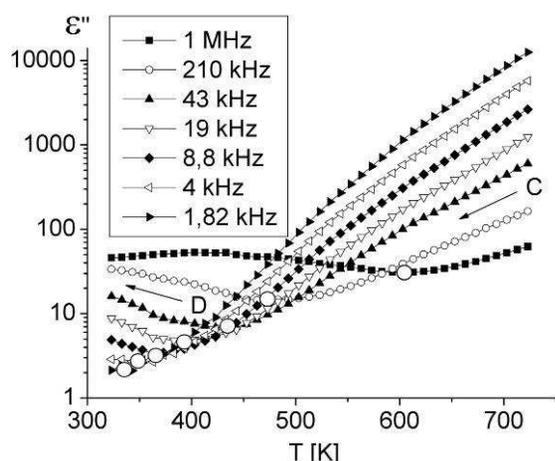


Fig. 3. Imaginary part of dielectric permittivity (ϵ'') of polycrystalline PCN ceramics as a function of temperature (T) for 6 selected frequencies. Measurement was performed on cooling with -1 K/min

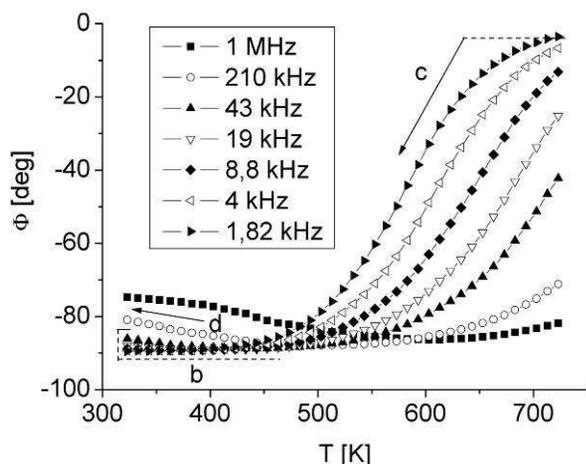


Fig. 4. Phase angle (Φ) dependence on frequency (ν) and temperature (T) for polycrystalline ceramic PCN. Measurement was performed on cooling with -1 K/min. d: low T weak decrease of Φ for high frequency, b: decay of frequency and T dependence of Φ – dielectric type of behaviour, c: increase of Φ to 90deg with T lowering

The absolute value of ac conductivity ($|\sigma^*|$) dependence on temperature (T) and frequency of polycrystalline PCN ceramic is demonstrated in the Fig.5. As it is indicated by symbols A, B and C, one can postulate that the mechanism of ac conductivity absolute value consists of three processes. The A process dominates at high T region ($T \geq 550$ K) and for high frequency ($\nu \geq 50$ kHz). It's temperature dependence is very weak. Within the same temperature region but for low frequencies ($\nu \leq 50$ kHz), one can identify process C which have thermally activated character and is dominating for low frequencies. For temperatures lower than ~ 550 K, process assigned as B is taking place. For all frequencies involved in the experiment the temperature dependence of $\log|\sigma^*|=f(T)$ seems to differ only by preexponential factor.

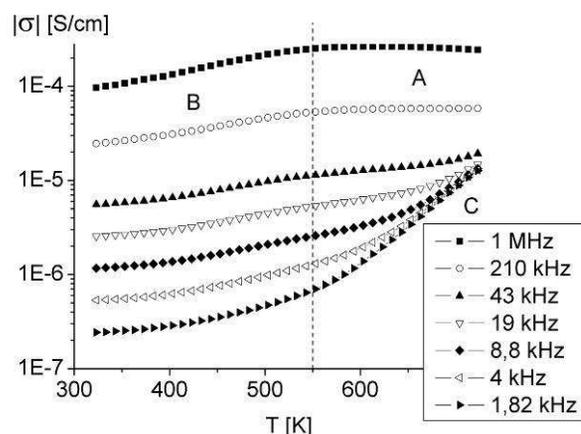


Fig. 5. The absolute value of ac conductivity dependence on temperature (T) and frequency (ν) of polycrystalline PCN ceramic. A: $|\sigma^*| \neq f(\nu)$ for high frequencies, B: low T similarity of $|\sigma^*|=f(T)$ for all frequencies, C: high T and low ν elevation of $|\sigma^*|$

The dependence of real part of ac conductivity (σ') on temperature and frequency for investigated PCN ceramic is shown in the Fig.6. σ' represents the ac current flowing under measuring generator voltage applied to the sample and maintaining in the same phase ($\Phi=0$). As it is easy seen in the Fig.6 σ' strongly depends on T and ν . For 1MHz $\sigma'(T)$ is almost independent on T but for 1.82kHz σ' is changing about 5 orders of magnitude (from $\sim 10^{-5}$ S/cm at 723K to $2 \cdot 10^{-9}$ S/cm at 323K for cooling experiment). It is nonlinear function of the shape $\log\sigma'=f(T, \nu)$. All records have a minimum value for every frequency at different temperature. The min σ' points are assigned by (O) symbols in the Fig.6. These points undergo monotonically but nonlinear shift towards lower T with simultaneous lowering of σ' and frequency. Conductivity σ' consist of two processes assigned as E (increase of σ' with T lowering after passing through minimum point for a given frequency) and assigned as F (lowering of σ' with T coming down to minimum). Process F gives a main contribution to that assigned as C in the Fig.5. The evolution of σ'_{\min} with T and ν reflexes probably the evolution of complex electric structure occurring within ceramic polycrystalline relaxor. It is open the question whether the border line connecting σ'_{\min} points can be used to characterize the changes of dynamic polar structures evolution within the sample.

The temperature and frequency dependence of σ'' for investigated ceramic is presented in the Fig.7. The σ'' represents the capacitive current ($\Phi \approx -90$ deg). The observed dependence of σ'' on T and ν should be treated as strongly correlated with to processes indicated in the Fig.5 as A and B. It is composed of two parts: one assigned as A1 with weak dependence on T for $T \geq 550$ K and the second one below that temperature. This dependence on T is universal for all frequencies used within experiment.

4. Conclusions

Dilatometric data shows that phase transition has relaxor and/or a glass-like character. Also the $\epsilon'_{\max}(T)$ is frequency dependent and scattered into two regions above and below $\sim 10^5$ Hz. The ΔT of ϵ'_{\max} (Fig.2) can be used to characterize extend of transition dispersion. Within one region values of ϵ'_{\max} are falling down with frequency increase and undergoes shifting towards higher temperatures.

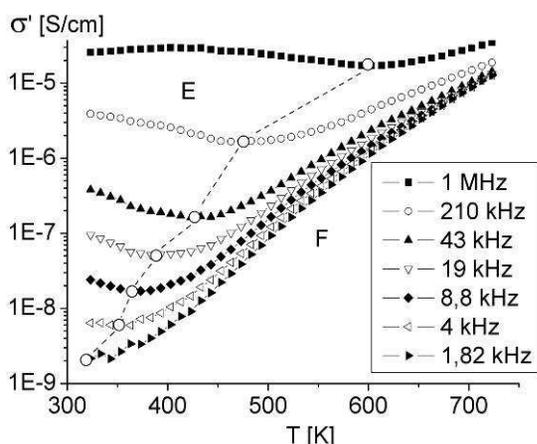


Fig. 6. The real part of ac conductivity dependence on temperature (T) and frequency (ν) for PCN polycrystalline ceramic. It is been correlated with process C assigned as C on Fig. 5

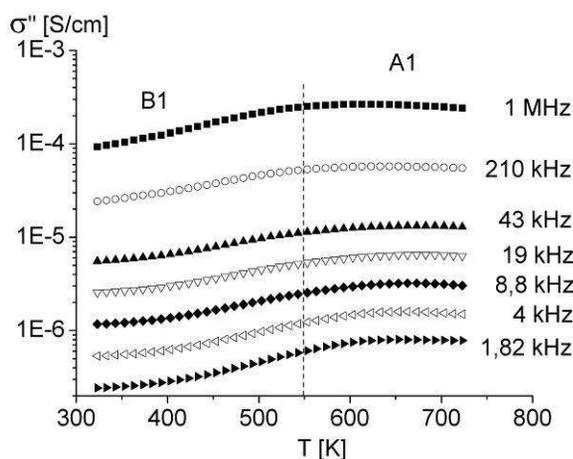


Fig. 7. The imaginary part of ac conductivity dependence on temperature (T) and frequency (ν) for polycrystalline PCN ceramic. It is been correlated with process A and B in Fig. 5

But above $\sim 10^5$ Hz ϵ'_{\max} temperature is shifted oppositely. It is not typical for relaxor behavior. Along temperature lowering, the process of losing frequency dependence of ϵ' is taking place and terminating about $T_r \sim 475$ K. At this temperature polarization (or energy storage) of the sample is not dependent on frequency. The origin of this process should be a matter of closer investigation. It has to be correlated with the evolution of sample polar species structure (clusters). Energy loss dependence on temperature (Fig. 3) consists of two processes: Process C is thermally activated process and D is another origin. Both these processes strongly depend on frequency and transition of temperature from ~ 600 K to ~ 330 K is connected with frequency dependence inversion. Very similar behavior can be observed on phase angle dependence on frequency and temperature. The postulated temperature evolution of polar structure of the PCN sample manifest itself by ac-conductivity dependence on temperature and frequency. The first noticeable correlation involves points $\epsilon''_{\min}(T, \nu)$ (assigned as (O) in the Fig. 3) and $\sigma'_{\min}(T, \nu)$ in the Fig. 6. This correlation is two dimensional: in temperature and in frequency. Generally 3 types/regions of T and ν

dependence of ac-conductivity can be considered. Within the range of $T \leq 550$ K and above 550 K. Imaginary component of ac-conductivity (σ''), representing the capacitive current depends on the temperature in universal manner for all used frequencies (Fig. 7). The $\sigma''(T, \nu)$ dependence on T for temperatures higher than T_r (O) has thermally activated character for all frequencies. The lower temperature region, inside which the lowering of T induces σ' increase have to be correlated with analogical character of $\epsilon''(T, \nu)$ function. The detailed investigation of all above specified processes will be performed in order to prepare the base of proper model of polarized structures/clusters models together with their dynamics. As far as we know there is a lack in the literature of such models of polar regions behavior in paraelectric phase of ferroelectric relaxors.

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