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Piezoelectric and ferroelectric properties of new $Pb_9Ce_2Ti_{12}O_{36}$ and lead-free $Ba_2NdTi_2Nb_3O_{15}$ ceramics

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Abstract In this paper, measurements of the nonlinear ferroelectric, piezoelectric and dielectric properties of $Pb_9Ce_2Ti_{12}O_{36}$ (Pb_9CTO) and $Ba_2NdTi_2Nb_3O_{15}$ (BNTN) ferroelectric ceramics are presented. Hysteresis *P(E)* loops were measured as a function of applied electric field, frequency and temperature. The coercive field (E_c) and remnant polarization (P_r) displayed temperature and frequency dependence. Lead-free BNTN ceramics exhibited a coercive field E_c>2.4 kV mm^{-1} and a piezoelectric coefficient d_{33}=2 pC N^{-1}. The hysteresis loop was pinched above 110°C and a linear response was observed at 155°C, typical of a paraelectric material. Pb_9CTO was shown to be ferroelectric with coercive field E_c=1.2 kV mm^{-1} and a d_{33}=65 pC N^{-1}. The frequency dependences of the impedance of the Pb_9CTO discs were analyzed.

Keywords Ferroelectric properties · Piezoelectric properties · $Pb_9Ce_2Ti_{12}O_{36}$ · Pb free ferroelectric ceramics

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1 Introduction

The present applications of actuators and sensors require maximum piezoelectric response. That is nowadays fulfilled for classical piezoceramics and relaxor monocrystals. But these ones have high content of lead or are technologically demanding. We looked therefore for other materials with lower content of lead, possibly lead-free materials and of technological availability as well. The starting points of our contribution were two completely new piezoelectric ceramics: lead-free $Ba_2NdTi_2Nb_3O_{15}$ (BNTN) and $Pb_9Ce_2Ti_{12}O_{36}$ (Pb_9CTO). Although these materials have different compositions and symmetries, with regards to possibilities of applications, electromechanical (piezoelectric) properties were the points to compare.

Recent investigations have focused on finding new low-lead or lead-free piezoelectric materials as alternatives to lead based ferroelectric perovskites such as $Pb(Zr_xTi_{1-x})O_3$ (PZT) [1–4]. The reason behind the interest is an increased drive for the removal of lead from electrical components. Most of the materials that have been considered as potential replacements of classical Pb containing piezoelectric materials exhibit small piezoelectric coefficients. An overview and comparison of piezoelectric and dielectric properties of lead-free and lead containing piezoelectric ceramics was reported [1]. The most promising lead-free materials were grouped into three distinct families: 1) $BaTiO_3$, 2) (Na,Bi)Ti-$BaTiO_3$-(K,Bi)TiO_3 (BNBK) and 3) (K,Na)NbO_3 (KNN). Although enhanced properties were observed for compositions at the morphotropic phase boundary (MPB) between the ferroelectric rhombohedral and tetragonal phases in the BNBK system, they were still inferior to those observed in PZT. The presence of a ferroelectric to antiferroelectric transition well below T_C, and their relatively high coercive field, E_c>3 kV mm^{-1}, further limit their usefulness [1]. Piezoelectric properties comparable to that of PZT were reported for compositions in the KNN system where the polymorphic phase transition was shifted downward towards room temperature. Coercive fields approximately 5 kV mm^{-1} were reported [2]. The effect of Ba^{2+} as donor dopant on the piezoelectric properties of compositions in the $K_{1/2}Na_{1/2}NbO_3$-$LiTaO_3$-$LiSbO_3$ (KNN-LT-LS) system and an evaluation of the performance of ceramics for ultrasonic transducer application were studied [2]. Piezoelectric and dielectric properties of KNN ceramics modified by Li-substitution and CuO addition have also been investigated [4]. An enhanced mechanical quality factor, Q_m, of 414 and piezoelectric coefficient, d_{33}, of 100 pC N^{-1} was reported. Anomalous anti-ferroelectric-like hysteresis curves were observed in 2 mol% CuO-doped KNN ceramics. The dielectric and ferroelectric properties of ceramics belonging to the $Na_{0.5}Bi_{0.5}TiO_3$-$K_{0.5}Bi_{0.5}TiO_3$ (NBT-KBT) systems were studied as a function of temperature and frequency [5].

Our contribution concerns the measurement of the piezoelectric and ferroelectric properties of two completely new ferroelectric systems $Pb_9Ce_2Ti_{12}O_{36}$ (Pb_9CTO) and lead-free $Ba_2NdTi_2Nb_3O_{15}$ (BNTN). The temperature and frequency dependence of the complex permittivity of BNTN ceramics in the low- and high-frequency range were reported [6] and the dielectric and structural data of Pb_9CTO were summarized [7]. At room temperature tetragonal BNTN and monoclinic Pb_9CTO ceramics were assigned the non centrosymmetric space groups *P4bm* and *Cc*, respectively. Here we present the experimental results of our studies on the ferroelectric and piezoelectric properties of lead-free $Ba_2NdTi_2Nb_3O_{15}$ (BNTN) in comparison with $Pb_9Ce_2Ti_{12}O_{36}$ (Pb_9CTO) ceramics. Until now, the piezoelectric properties of these new materials were not studied or published.

2 Experiment

2.1 Experimental methods

Polarization measurements were performed using a modified Sawyer-Tower circuit. The experiment setup consisted of a signal generator (GX1010, Metrix Instrument), a high voltage amplifier (10/40A, Trek Inc.) and an AD/DA card (PCA-7428, Tedia). Non-linear characteristics, such as the dependence of polarization on electric field were measured. Sinusoidal electric fields of amplitude ±3.5 kV mm^{-1} for Pb_9CTO, and ±6 kV mm^{-1} for BNTN were applied at a frequency of 2 Hz. The small harmonic signals were amplified by high voltage amplifier. Ferroelectric hysteresis loops were measured in the temperature range from room temperature to 120°C (Pb_9CTO) and 155°C (BNTN), respectively. To prevent dielectric breakdown during testing, the samples were immersed in silicon oil. The ferroelectric hysteresis loops were also measured for various frequencies from 0.5 to 50 Hz at room temperature.

Permittivity values, ε_{33}^{T}, were obtained from the measurement of the capacitance of the samples at a frequency of 1 kHz and an electric field of 1 V mm^{-1}. The influence of DC electric field on the permittivity of BNTN and Pb_9CTO ceramics was also investigated. The measurement set-up for application of high bias electric fields is described [8]. A blocking circuit was used to separate the high- and low voltage signals to protect the inputs of the impedance analyzer (HP 4192A, Agilent). The impedance analyzer, signal generator and high voltage amplifier (610D, Trek Inc.) were controlled by a PC, using the GPIB bus. Special electric circuit and calibration procedures were used to compensate for the parasite capacitance and resistance of the sample holder.

Piezoelectric coefficients, d_{33}, of BNTN and Pb_9CTO ceramics were measured using a d_{33}-meter (ZJ-3C, Academia Sinica, China).

The frequency dependence of the impedance was measured using the impedance analyzer (HP 4192A, Agilent). Both the fundamental resonance frequencies, f_r and f_a, were determined by the phase method. The resonance was indicated by a zero value of the impedance phase (zero value of the imaginary part of the resonator impedance).

2.2 Devices under test

The nonlinear properties of $Pb_9Ce_2Ti_{12}O_{36}$ (Pb_9CTO) and $Ba_2NdTi_2Nb_3O_{15}$ (BNTN) ferroelectric ceramics have been investigated. Lead-free BNTN ceramic samples were provided by the Dept. of Engineering of Materials, University of Sheffield, UK. The synthesis of the BNTN samples was described [6]. The measurements of the hysteresis loops were conducted on semi-circular sections of samples with a diameter of 10 mm and a thickness of 1 mm. The electrode area on the segment was 26 mm^2. Discs with a diameter of 10 mm and a thickness of 1 mm were used for the resonance measurements. Silver electrodes were applied using a Ag-suspension. Pb_9CTO samples were provided by the Inst. of Materials and Minerals Division, National Institute for Interdisciplinary Science and Technology Trivandrum, India. The synthesis procedure and properties characterizations were described [7]. Disc shaped samples with a diameter of 9 mm and a thickness of 0.5 mm or 1 mm were used for the hysteresis measurements and for the resonance measurements discs with a diameter of 15 mm and a thickness of 1 mm were used. Pt electrodes were applied by sputtering to the samples and they were poled in the thickest direction.

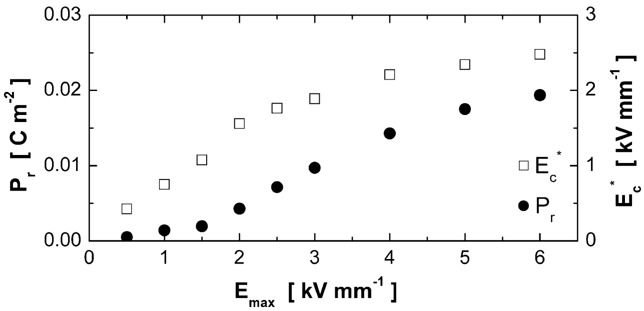

Fig. 1 Remnant polarization, P_r, and coercive field, E_c^*, vs. electric field amplitude of BNTN, measured at 2 Hz

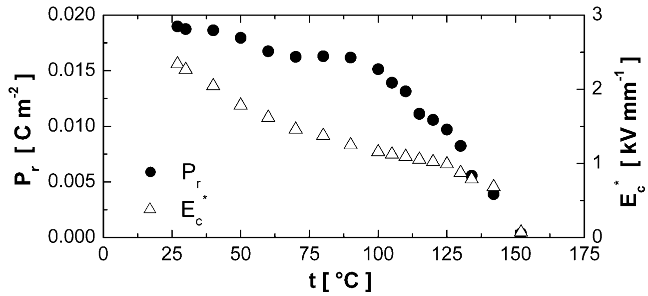

Fig. 3 Temperature dependence of the remnant polarization, P_r, and the coercive field, E_c^*, of BNTN, measured at 2 Hz

3 Results and discussion

Using a modified Sawyer-Tower circuit, the room temperature ferroelectric hysteresis loops, *P*(E), were measured at various electric field amplitudes. The hysteresis loops, *P*(E), of lead-free $Ba_2NdTi_2Nb_3O_{15}$ (BNTN) measured up to electric field of ±6 kV mm^{-1} still did not saturate. The maximum electric field for P(E) hysteresis loops was 6 kV mm^{-1} in respect to electric breakdown at higher electric field amplitudes. BNTN ceramics was shown to be ferroelectric with coercive field, $E_c > 2.4$ kV mm^{-1}. Figure 1 shows the remnant polarization, P_r, and the coercive field, E_c^*, vs. electric field amplitude for the BNTN ceramics measured at 2 Hz. The coercive field of non-saturated hysteresis loops was assigned, E_c^*. The remnant polarization of BNTN ceramics rapidly increased for applied electric field >1.5 kV mm^{-1}.

The polarization measurements were performed in the temperature range between room temperature and 155°C (Fig. 2). *P*(E) hysteresis loops were measured at various temperatures using an applied electric field of 5.75 kV mm^{-1} and a frequency of 2 Hz. The polarization hysteresis loops became less pronounced with increasing temperature. BNTN ceramics exhibit a first order ferroelectric phase transition at 116°C (on cooling) and a temperature hysteresis of 26°C [6]. The shape of hysteresis loops of BNTN changed on heating. First the hysteresis loop was pinched above 110°C and finally a linear response was observed at 155°C, typical of a paraelectric material (see Fig. 2). The coercive field, E_c^*, decreased with increasing temperature. The decrease of coercive field, E_c^*, with increasing temperature in the temperature range from 25°C to 70°C was 38% (Fig. 3). A rapid decrease of coercive field, E_c^*, of BNTN with increasing temperature in the range just below the Curie temperature was also observed (Fig. 3).

The room temperature hysteresis loops were measured over frequencies in the range of 0.5 to 50 Hz. The increase of the coercive field, E_c^*, with increasing frequency was 19% in this range. Significant frequency dependence of the coercive field, E_c^*, was observed in the frequency range between 0.5 and 2 Hz (Fig. 4). No dependence was observed at higher frequencies in the range from 10 Hz up to 50 Hz.

The density of BNTN ceramics was 5,580 kg m^{-3}. The density was compared with the theoretical XRD density.

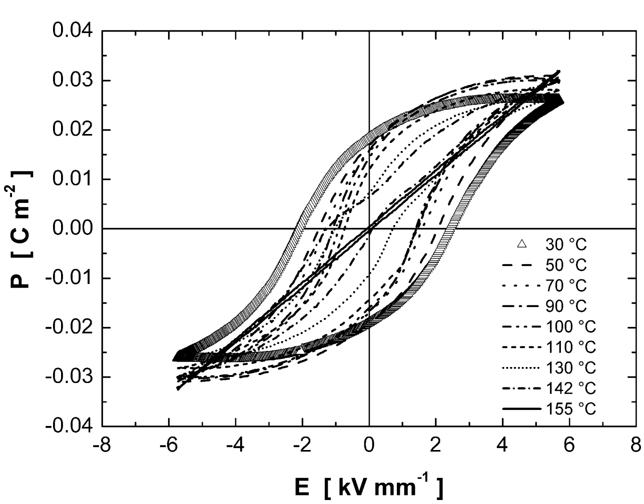

Fig. 2 Polarization hysteresis loops of BNTN at various temperatures, measured at 2 Hz, and 5.75 kV mm^{-1}

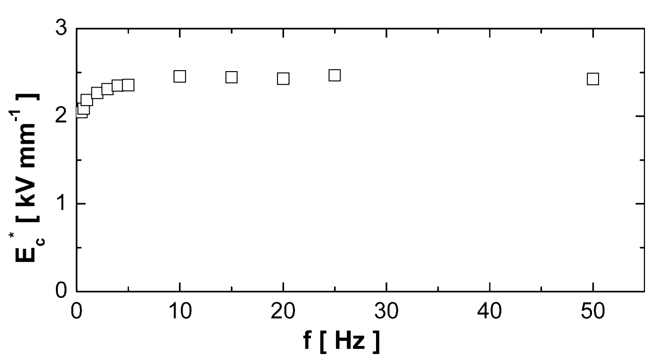

Fig. 4 Frequency dependence of coercive field, E_c^*, of BNTN at room temperature

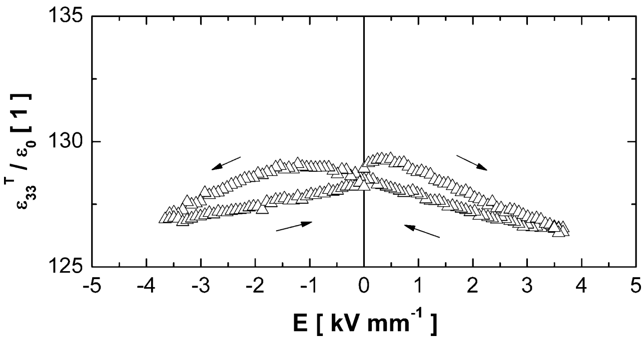

Fig. 5 Permittivity, $\varepsilon_{33}^{\mathrm{T}}/\varepsilon_0$, of BNTN vs. bias field at room temperature, measured at 1 kHz

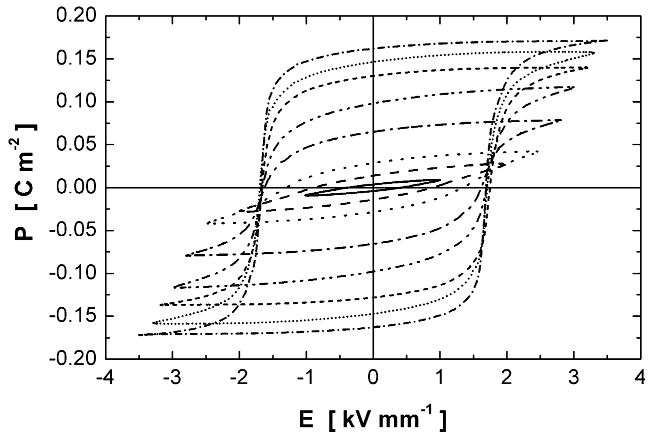

Fig. 6 Polarization hysteresis loops of Pb_9CTO at various amplitudes of electric field, measured at 2 Hz

The samples had the high relative density of 98%. The measured room temperature permittivity of BNTN was relatively low, $\varepsilon_{33}^{\mathrm{T}}/\varepsilon_0 = 130$, at 1 kHz. The influence of DC electric field on the permittivity of BNTN was investigated and the typical butterfly shape was observed (Fig. 5).

BNTN samples were poled at room temperature using two methods: by application of a DC electric field and by application of a pulsed electric field. The piezoelectric coefficient, d_{33}, was measured using a d_{33}-meter. The values of the observed piezoelectric coefficients were slightly higher when the pulsed electric field method was used. Electric field was applied in the form of unipolar rectangular pulses for 5 min. Pulse shape was applied as follows: DC field 3 kV mm^{-1} for 0.5 s, zero field for 2.5 s (this repeated for the period of 5 min). The piezoelectric coefficient, d_{33}, was 2×10^{-12} C N^{-1} at room temperature (see Table 1). The samples were also poled at room temperature by the DC electric field 3 kV mm^{-1} for 10 min in silicon oil bath. In this case the piezoelectric coefficient, d_{33}, was 1.5×10^{-12} C N^{-1} at room temperature (see Table 1). In our experiment at poling temperature 130°C the effect of poling temperature on the piezoelectric activity wasn't proven. The selection of the room temperature for poling was influenced by increased conductivity of the sample and possibility of breakdown at higher temperatures. Values of piezoelectric coefficient, $d_{33,}$ don't represent intrinsic values, but we don't expect significant increase of d_{33} by optimalization of poling process. Disc shape sample of BNTN ceramics did not show any undamped modes of vibration.

The room temperature hysteresis loops, P(E) of $Pb_9Ce_2Ti_{12}O_{36}$ (Pb_9CTO) samples were measured at varying electric field amplitude and a frequency of 2 Hz (Fig. 6). We found, that the hysteresis loops, P(E), for applied electric field 3.5 kV mm^{-1} were saturated. Pb_9CTO was shown to be ferroelectric and also exhibited piezoelectric properties. The room temperature remnant polarization rapidly increased for applied electric field >2.5 kV mm^{-1} (Fig. 7). A remnant polarization, P_r, of 0.17 C m^{-2} and coercive field, E_c, of 1.62 kV mm^{-1} were obtained at 2 Hz. A lower coercive field and a higher remnant polarization were observed for the Pb_9CTO in relation to the BNTN ceramics (Table 1). The P(E) hysteresis loops of Pb_9CTO ceramics measured at different temperatures are shown in Fig. 8. The P(E) loops were measured at an applied electric field of 3.5 kV mm^{-1} and a frequency of 2 Hz. At higher

Table 1 Comparison of coercive field, E_c, remnant polarization, P_r, measured at 2 Hz, and piezoelectric coefficient, d_{33}, of BNTN and Pb_9CTO.

Sample	BNTN	Pb_9CTO
E_c [kV mm^{-1}]	>2.4	1.62
P_r [C m^{-2}]	0.02	0.17
d_{33} [10^{-12} C N^{-1}][a]	1.5	65
d_{33} [10^{-12} C N^{-1}][b]	2.0	60

[a] DC poling

[b] Pulse poling

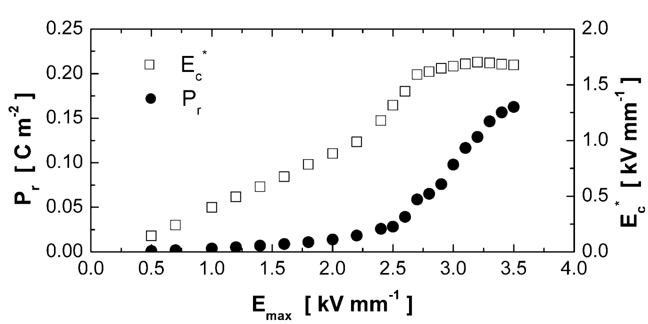

Fig. 7 Remnant polarization, P_r, and coercive field, E_c^*, vs. electric field amplitude of Pb_9CTO, measured at 2 Hz

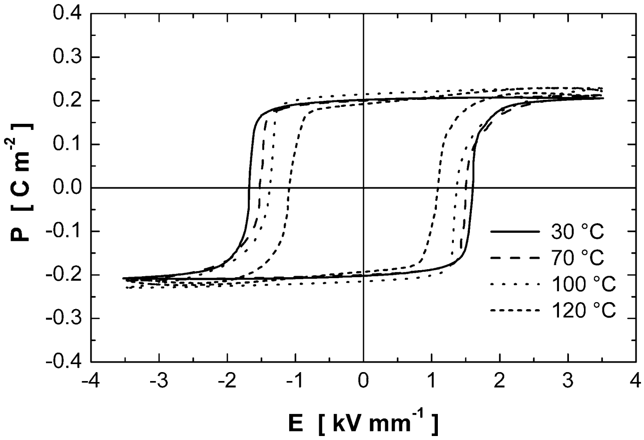

Fig. 8 Polarization hysteresis loops of Pb_9CTO at various temperatures, measured at 2 Hz

temperatures the influence of conductivity was observed requiring conductivity compensation to be performed. To avoid the generation of the pyroelectric charge, the sample was short-circuited during the heating stage. The measured temperature range was well below the ferroelectric phase transition temperature (T_C=277°C). The temperature dependence of the dielectric response and critical temperature T_C=277°C was determined elsewhere [7]. The decrease in the coercive field with increasing temperature in the temperature range between 25°C and 70°C was lower than 8% (Fig. 9).

The room temperature hysteresis loops were measured in the frequency range between 0.5 and 50 Hz. A decrease in the coercive field, E_c, and an increase in the remnant polarization, P_r, with increasing frequency was observed. A remnant polarization, P_r, of 0.2 C m^{-2} and a coercive field of 1.2 kV mm^{-1} were measured at 50 Hz at room temperature.

The density of Pb_9CTO ceramics samples was 7,230 kg m^{-3}. This density was compared with the theoretical XRD density. The samples had the relative density of 79%. The lower relative density of the ceramics may be due to the presence of irregularities, such as

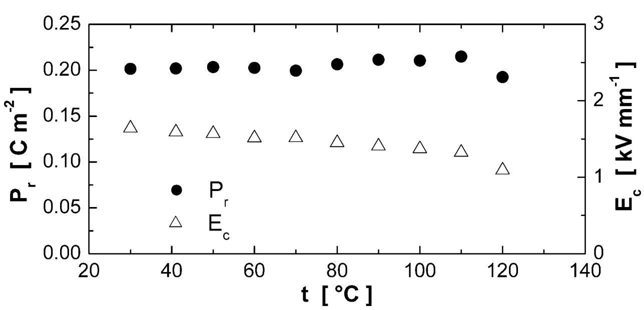

Fig. 9 Temperature dependence of the remnant polarization, P_r, and coercive field, E_c, of Pb_9CTO, measured at 2 Hz

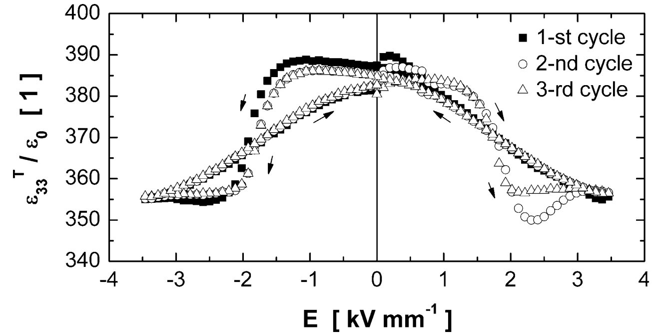

Fig. 10 Permittivity, $\varepsilon_{33}^{T}/\varepsilon_0$, of Pb_9CTO vs. bias field at room temperature, measured at 1 kHz

vacancies, porosity or micro-cracks. This probably causes, together with presence of dislocations and grain boundaries, the breakdown fields lowering. Pb_9CTO ceramics shows a bias in the electric field dependence of the relative permittivity $\varepsilon_{33}^{T}/\varepsilon_0$ (Fig. 10). The permittivity decreased with the application of a positive bias and increased with a negative bias, before depoling occurred. The relative permittivity of Pb_9CTO, $\varepsilon_{33}^{T}/\varepsilon_0$, was 385 at 1 kHz under zero bias was obtained.

Pb_9CTO samples were poled at room temperature by application of a DC electric field and by application of a pulsed electric field. The conditions of the both poling processes were the same as for BNTN ceramics. The piezoelectric coefficient, d_{33}, of Pb_9CTO, measured using a d_{33}-meter, was 60×10^{-12} C N^{-1} at room temperature for pulse poling, and 65×10^{-12} C N^{-1} for DC poling (see Table 1).

The impedance analyzer was used to measure the frequency dependence of the impedance, Z, and phase, φ, of the Pb_9CTO sample (Fig. 11). The maximum phase in the inductive region was still low and far from π/2. An

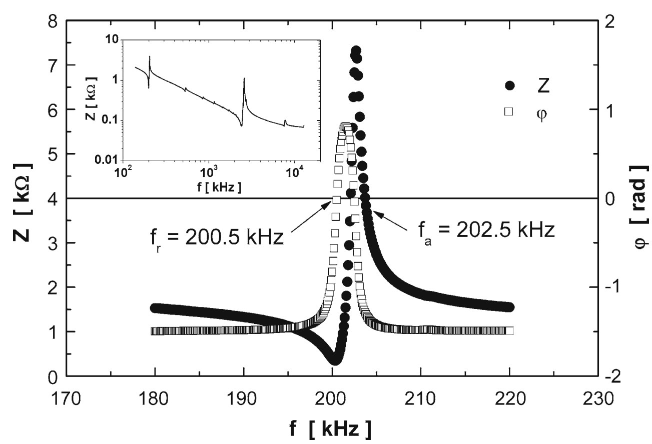

Fig. 11 Frequency dependences of the impedance and impedance phase of the first harmonic mode of the radial vibrations of a Pb_9CTO disc

improvement would be possible by optimalization of poling process and dimensions of the sample. We found that the planar frequency constant, N_p, of Pb_9CTO was 2,910 Hz·m and the thickness frequency constant, N_t, was 2,420 Hz·m. The frequency constant allows to calculate the required dimensions of a piezoelectric resonator to obtain resonance at a desired frequency. The electromechanical planar coupling factor, $k_p \sim 0.16$, and the electromechanical coupling factor, k_t, of 0.37 were determined according to the CENELEC European Standard EN 503224-2 (2002), Piezoelectric properties of ceramic materials and components. Part 2: Methods of measurement—Low power [9].

Comparison of two new piezoelectric ceramics lead-free $Ba_2NdTi_2Nb_3O_{15}$ (BNTN) and $Pb_9Ce_2Ti_{12}O_{36}$ (Pb_9CTO) from point of view of properties for actuators and sensors applications shows, that in the immediate future, materials with low content of lead will come more useful. The low piezoelectric coefficient of lead-free piezoelectric ceramics (Table 1) is significant limitation, namely for actuator applications.

4 Conclusion

Both Pb_9CTO and lead-free BNTN ceramics are piezoelectric, but piezoelectric response of the BNTN ceramics is low. Hysteresis loops, P(E) in Pb_9CTO and lead-free BNTN ceramics have been shown to increase and widen with increasing applied electric field. For BNTN, a noticeable influence of temperature on coercive field value was observed. The polarization hysteresis loops narrowed with increasing temperature, and a pinched loop in BNTN was seen near the Curie temperature. The area of the hysteresis loops decreased with increasing temperature. Pb_9CTO ceramics are suitable for use in the temperature range from 25°C to 70°C, where the polarization is reasonably stable. In both systems a decrease of the coercive field with increasing temperature was observed. At room temperature, piezoelectric coefficients, d_{33}, of 2×10^{-12} C N^{-1} for BNTN and 65×10^{-12} C N^{-1} for Pb_9CTO were obtained. The Pb_9CTO resonator samples exhibited radial and thickness extensional modes of vibration.

We have found that a promising way in the next studies of the new materials will be decreasing of the Pb in the Pb_9CTO. We suppose that a new low-lead system $Sr_{9-x}Pb_xCe_2Ti_{12}O_{36}$ (x=8,7) will be equipped by larger piezoelectric response.

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