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Temperature Dependence of Material Constants of PLZT Ceramics

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Abstract

The piezoelectric resonance and the ferroelectric hysteresis loop were simultaneously measured in bulk 8/65/35 PLZT ceramics in the temperature range from 20 to 140°C. From the piezoelectric resonance data temperature dependences of several material constants in the vicinity of the transition from the relaxor to the induced ferroelectric state were extracted. It is shown, that the second order smeared continuous transition, through which the long-range ferroelectric state is established, reflects itself mostly in changes of the real part of the piezoelectric constant, the electromechanical coupling factor, and the electromechanical quality factor. © 1999 Elsevier Science Limited. All rights reserved

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1 Introduction

Ferroelectric $Pb_{1-x}La_x(Zr_yTi_{1-y})_{1-x/4}O_3$ (PLZT) ceramics has attracted continuous attention in recent years due to its possible applications in memory elements.[1] The early measurements of the dielectric, pyroelectric, and electrooptic response in relaxor PLZT ceramics[2] were followed by several more studies.[3–6] The rhombohedral $x=0{\cdot}08$ and $y=0{\cdot}65$ (8/65/35) PLZT ceramics show typical relaxor characteristics. The temperature of the dielectric constant maximum (T_m) depends strongly on the frequency and it is particularly interesting to note that the local polarization exists in the material even above T_m, which reflects itself in a slim ferroelectric hysteresis loop.[3] It was shown that in zero electric field no transition to long-range ferroelectric state occurs in 9/65/35 PLZT ceramics,[4] while the application of a bias electric field above a threshold field of 5 kV/cm, induces long-range ferroelectric state at temperatures somewhat lower than the temperature of a dielectric maximum.[5] The transition from the long-range ferroelectric to relaxor state—structurally, this is normal micron-sized ferroelectric domain to polar clusters transformation—has already been identified in a tetragonal 12/40/60 PLZT ceramics by TEM.[6]

In the material with the diffuse transition to the ferroelectric state, the piezoelectric constant is expected to decay slowly with the increasing temperature. Such dependence of the piezoelectric constant has already been observed by piezoelectric current measurements in 8/65/35 PLZT ceramics[7] and by the resonance technique in relaxor SBN60.[8] The complex piezoelectric and dielectric constants, and the complex elastic compliance can all be extracted from the piezoelectric resonance data. The electromechanical properties have already been studied by this technique in several ceramic materials,[9–11] however, the complete set of complex material constants in the vicinity of the smeared ferroelectric to relaxor phase transition in PLZT ceramics has not yet been reported.

In this work we present simultaneous measurement of the piezoelectric resonance and the ferroelectric hysteresis loop in 8/65/35 PLZT ceramics in the temperature range from 20 to 140°C. Temperature dependences of the remanent polarization and the coercive field were obtained from the ferroelectric hysteresis loops, while temperature dependences of the complex piezoelectric and dielectric constants, the complex elastic compliance, the electromechanical coupling factor, and various quality factors were determined from the piezoelectric resonance data.

2 Experimental Procedure

Bulk 8/65/35 PLZT ceramics used in these studies was prepared as described elsewhere.[12] The

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temperature dependences of piezoelectric resonance and ferroelectric hysteresis loop were measured simultaneously on samples having typical dimensions of $5{\cdot}21\times1{\cdot}72\times0{\cdot}30\,mm^3$ during the heating run. The ferroelectric hysteresis loop was measured by Sawyer–Tower technique and sampled by digital oscilloscope Nicolet Pro30. During measurement the ac electric field at the frequency of 50 Hz and of the amplitude of $15\,kV\,cm^{-1}$ was applied to the sample. After the measurement of the ferroelectric hysteresis loop the sample was poled by a dc electric field of $15\,kV\,cm^{-1}$, and the piezoelectric resonance was then studied by measurements of admittance $|Y|$ and phase angle θ in the frequency range 1 kHz–1 MHz by using a HP 4192A Impedance Analyzer.

From the piezoelectric resonance data, the complex dielectric and piezoelectric constants and the complex elastic compliance can be determined. An equivalent circuit simplifying the treatment of a piezoelectric ceramic bar with a large piezoelectric phase angle was introduced by Damjanović.[11] Following his approach and defining $Y = G + iB$, the equations for conductance G and susceptance B can be in the vicinity of the resonant frequency written explicitly in terms of the equivalent circuit components

$$G = \frac{\omega^2 RC^2 - x(\omega C - \omega^3 LC^2)}{(1-\omega^2 LC)^2 + \omega^2 R^2 C^2} + \frac{1}{R_2} \tag{1}$$

$$B = \frac{\omega C - \omega^3 LC^2 + x\omega^2 RC^2}{(1-\omega^2 LC)^2 \omega^2 R^2 C^2} + \omega C_0 \tag{2}$$

Here l, w, and t are length, width, and thickness of a piezoelectric bar resonator, respectively. The parameters of the equivalent circuit C, L, R, C_0, R_2 and x are connected to the material constants via $R = s''_{11}/s'_{11}\omega C$, $C = 8lwRe(d^{*2}_{31}/s^*_{11})/t\pi^2$, $LC = l^2\rho s'_{11}/\pi^2$, $1/R_2 = \omega[\varepsilon''_{33} + Im(d^{*2}_{31}/s^*_{11})]lw/t$, $C_0 = [\varepsilon'_{33} - Re(d^{*2}_{31}/s^*_{11})]lw/t$, and $x = Im(d^{*2}_{31}/s^*_{11})/Re(d^{*2}_{31}/s^*_{11})$. Real and imaginary parts of the dielectric $\varepsilon^*_{33} = \varepsilon'_{33} - i\varepsilon''_{33}$, elastic $s^*_{11} = s'_{11} - is''_{11}$, and piezoelectric $d^*_{31} = d'_{31} - id''_{31}$ constant can so be evaluated from the set of parameters of the equivalent circuit, which were determined by fitting the experimental data to eqns (1) and (2).

3 Results and Discussion

Figure 1 shows susceptance B versus conductance G in the vicinity of the piezoelectric resonance at room temperature. Solid lines represent fits by using eqns (1) and (2) in the frequency range 295–325 kHz. With increasing temperature the resonance amplitude was suppressed, and the frequency range, in which the resonance can be described by eqns (1) and (2), was shrinking. This can be clearly seen in Fig. 2, which shows susceptance versus conductance at the temperature of 71·53°C.

Temperature dependences of real and imaginary parts of complex material constants determined from piezoelectric resonance data are shown in Fig. 3. While ε'_{33} reaches peak value at ~130°C, ε''_{33} reaches maximum value at ~90°C indicating slowing dynamics. d''_{31} exhibits local peak value at ~80°C, while d'_{31} is decreasing in the temperature range from 50 to 90°C. Since d'_{31} becomes saturated below 50°C, it is possible to conclude that the long-range ferroelectric order is completely established

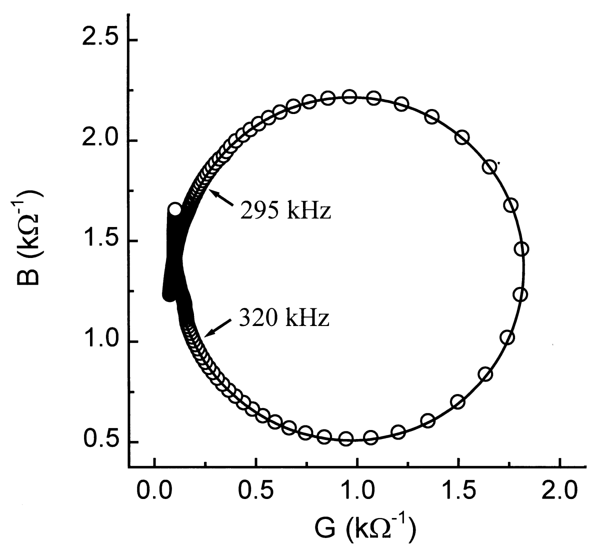

Fig. 1. Susceptance B as a function of conductance G at $T = 23{\cdot}88$°C. Solid lines represent fits to eqns (1) and (2).

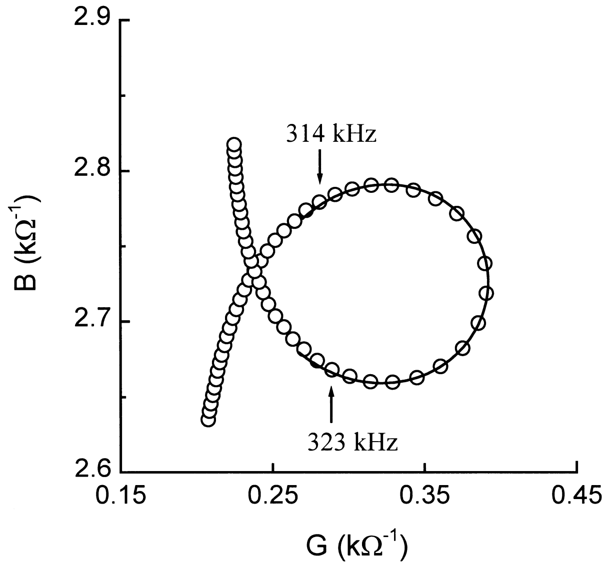

Fig. 2. Susceptance B as a function of conductance G at $T = 71{\cdot}53$°C. Solid lines represent fits to eqns (1) and (2).

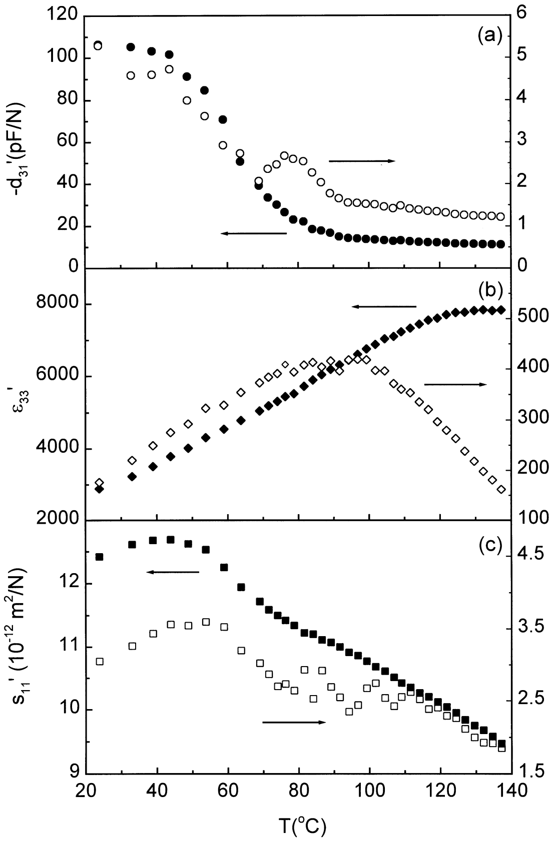

Fig. 3. Temperature dependences of the real and imaginary parts of the (a) piezoelectric constant d_{31}, (b) dielectric constant ε_{33}, and (c) elastic compliance s_{11}, determined from piezoelectric resonance data.

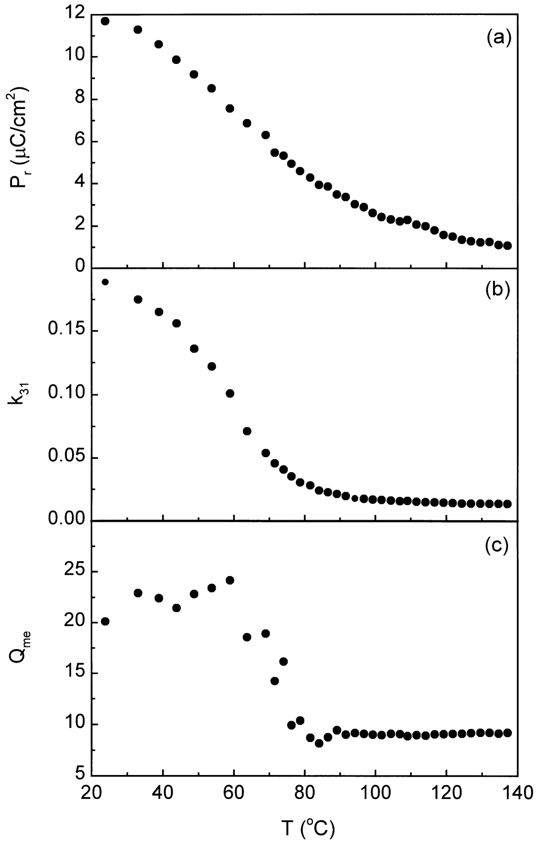

Fig. 4. Temperature dependences of the (a) remanent polarization P_r, (b) electromechanical coupling factor k_{31}, and (c) electromechanical quality factor Q_{me}.

below this temperature. Both quantities, s'_{11} and s''_{11}, exhibit a peak value in the vicinity of T = 50°C. It should be stressed, however, that only absolute values of the real and the imaginary part of the complex piezoelectric constant and their product can be determined from the piezoelectric resonance data. Since we found that the above product is negative and since it is known that the real part of the piezoelectric constant is negative in 8/65/35 PLZT ceramics,[7] we assign the negative sign to the real and positive sign to the imaginary part of the complex piezoelectric constant.

As mentioned before, the amplitude of the resonance is becoming smaller and at temperatures from 90 to 140°C only the piezoelectric resonance peak can be observed. In addition, the slim ferroelectric hysteresis loop can also be observed at temperatures above 90°C. This indicates that in the temperature range from 90°C up to at least 140°C the long-range ferroelectric state is replaced by short-range polar clusters oriented in the dc bias electric field.[6]

Figure 4 shows temperature dependences of several other material properties. In the temperature range of 50–90°C, variations in remanent polarization [Fig. 4(a)] are not so distinctive in comparison to the temperature variation in the real part of the piezoelectric constant. Temperature dependence of electromechanical coupling factor k_{31} [Fig. 4(b)], which can be calculated from

$$\frac{k_{31}^2}{1-k_{31}^2} = \frac{\pi}{2}\sqrt{1+\frac{C}{C_0}}\tan\left[\frac{\pi}{2}\left(\sqrt{1+\frac{C}{C_0}}-1\right)\right] \quad (3)$$

is very similar to the dependence of the real part of the piezoelectric constant. At 90°C, its value becomes only one tenth of its room temperature value, but due to slower variations at higher temperatures it remains non-zero up to 140°C. The electromechanical quality factor $Q_{me} = d'_{31}/d''_{31}$ [Fig. 4(c)] undergoes smeared step-like transition from one constant value below 50°C to another constant but smaller value above 90°C. This variation in the electromechanical quality factor is reminiscent to the onset of the long-range ferroelectric order with decreasing temperature in the presence of the bias electric field.

It is also interesting to note that the smeared step-like temperature behaviour in d'_{31} and k_{31} is actually in accordance with the theoretical predictions for the electromechanical response near paraelectric-ferroelectric phase transition. Comparison of the temperature behaviour in d'_{31} and k_{31} to the theoretical results based on Landau–Devonshire theory[13] indicates that the field induced ferroelectric order is established in 8/65/35 PLZT ceramics through rather smeared second order phase transition.

4 Conclusions

Saturation of the piezoelectric constant and electromechanical coupling factor indicates that below 50°C the ferroelectric order is established in 8/65/35 PLZT ceramics in the presence of a dc electric field. On the other hand, it is possible to conclude, that above 90°C both the piezoelectric resonance peak and the slim ferroelectric hysteresis loop originate from the existence of polar clusters. The smeared second order phase transition between these two states reflects itself mostly in the changes of the real part of the complex piezoelectric constant, the electromechanical coupling factor and the electromechanical quality factor.

Acknowledgements

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