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Energy conversion with Zr-rich lead zirconate/titanate ceramics

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The conversion efficiency and power output to convert thermal energy to electrical energy by means of a ferroelectric–ferroelectric phase transition has been investigated. The material used was the ceramic mixed system lead zirconate/titanate (PZT) with a very Zr-enriched composition (Zr/Ti=97/3%). We have studied the performance dependence on sample thickness and working frequency, the main relevant parameters for a given PZT composition. The observed optimum values of efficiency and power output are analyzed in terms of the two main characteristic relaxation times of the process, the thermal time (sample thickness dependent) and the electric time (thickness independent). Possible ways of improving the overall performance are discussed. © 1997 American Institute of Physics. [S0003-6951(97)00239-8]

Direct thermal to electric energy conversion using Zr-rich lead zirconate/titanate (PZT) ferroelectric ceramic plates by thermal cycling at the phase transition between the two rhombohedral ferroelectric phases, F_{RL} (low-temperature phase) and F_{RH} (high-temperature phase), has been investigated by several authors.^{1–5} In these works, the advantages of using these kinds of phase transitions for energy conversion applications have been already pointed out, in comparison with other better known ferroelectric transitions.^{6–8} Ferroelectric energy conversion with poled PZT, through the F_{RL} – F_{RH} first-order transition occurs between two phases with nonzero polarization, and is the only demonstrated case in which no external fields are needed, unlike cases in which the ferroelectric–paraelectric (F–P)⁷ or the ferroelectric–antiferroelectric (F–AF)⁶ transitions are used, requiring external fields for cyclic operation. In these investigations, a polarized sample subject to thermal cycling is connected to an external load. By heating and cooling the sample around the F_{RL} – F_{RH} phase transition temperature (T_{LH}), positive and negative free charges are produced at the electrodes of the ceramic plate, due to the temperature induced change in spontaneous polarization, which is measured as a voltage signal through the load resistance.

It is well known that not all thermal energy transmitted to the ferroelectric plate is converted into electricity, apart from the thermodynamic limitation, $\eta \leq \eta_c = \Delta T/T_{max}$, because some of the thermal energy is wasted in mechanical expansion/contraction of the material, heating metallic plates in contact with the ceramic, and other processes.⁹ The actual efficiency and the power output could be, however, considerably improved in several ways, including the design of materials especially adequate for this purpose, combining a small dielectric constant and a large polarization change at the transition, and the so-called “multistage” operation.¹⁰ It consists in using a set of plates with changing composition and profiting from the wasted energy from one sample for heating the next sample with a slightly lower transition temperature. In this way, a set of PZT plates with gradually changing compositions ($x_1 < x_2 < \dots < x_n$), having transition

temperatures $T_{LH}(x_1) < T_{LH}(x_2) < \dots < T_{LH}(x_n)$, could be used. First, however, a better understanding of the process itself taking place during conversion in our system (PZT plate + experiment setup) is necessary.

In the present work, we have investigated the dependence with the sample thickness and the frequency of the output power and the efficiency of plates with a single Zr-rich PZT composition.

The experimental apparatus used is the same as in Ref. 4, but several improvements were made and the dynamic range was extended to lower frequencies. The heating source was an IR lamp and the temperature oscillations were created by a chopper. The center and the width of the temperature window could be reliably controlled by changing the lamp intensity as well as the frequency of the chopper, driven by a low-speed motor (range from 3 mHz to 0.11 Hz).

The composition of the thin plates used in the present work was PZT 97/3+3.9 mol % of Nb₂O₅, which has a transition temperature $T_{LH} \approx 49$ °C, with a polarization change of about $\Delta P \approx 2 \mu\text{C}/\text{cm}^2$.

The specific output power is given by

$$P_{out} = \frac{\text{energy/cycle}}{\text{volume}} f = \frac{IV}{v}, \quad (1)$$

where energy/cycle is the total output energy per cycle, f is the frequency, and v is the sample volume.

The efficiency of the conversion process can be obtained through

$$\eta = \frac{E_{out}}{E_{in}} = \frac{\int_0^{\Delta t} IV dt}{\int_{T_{min}}^{T_{max}} v \rho_v C_p dT} \approx \frac{\int_0^{\Delta t} IV dt}{v \rho_v C_p \Delta T}, \quad (2)$$

where ρ_v is the density, C_p the average specific heat per unit mass over the working temperature window, $\Delta T = T_{max} - T_{min}$, and $\Delta t = 1/f$ is the time for one cycle.

For a given lamp intensity, the temperature interval, ΔT , can be decreased by increasing the chopping frequency in such a way as to fix it to the place where the maximum change of polarization occurs, increasing, in this way, the efficiency [see Eq. (2)], which must be low enough to allow most of the charge to be, first, liberated at the electrodes after the heating/cooling period and, then, released through the

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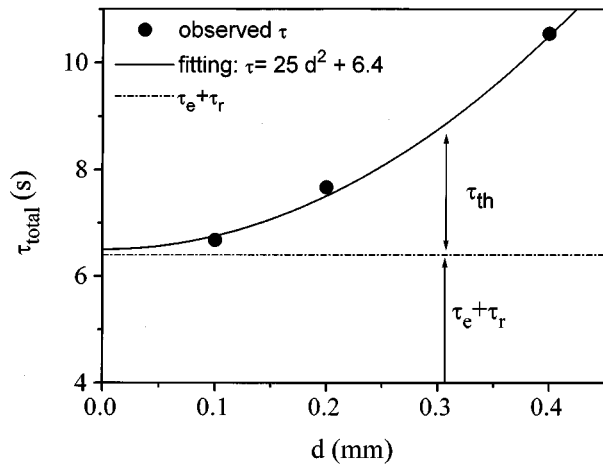


FIG. 1. Total optimum characteristic time observed vs. sample thickness. The full line represents the best fit $\tau_{\text{total}} = 6.4 + 25d^2$ (τ_{total} in seconds and d in mm) to the data. The dotted line marks the level of all other contributions to the characteristic time (independent of d), including the electrical characteristic time, τ_e .

load resistance. Here, the two characteristic times of the process¹⁰ are the electrical relaxation time ($\tau_e = \rho_e \varepsilon = RC$, where R is the optimized load resistance, equal to the sample resistance, and C is the sample capacitance), depending only on the material resistivity, ρ_e , and its dielectric constant, ε , and the thermal relaxation time ($\tau_{\text{th}} = \rho_v \bar{C}_p d^2 / k_{\text{th}}$), which depends on the density ρ_v , the average specific heat \bar{C}_p over the working temperature window, the thermal conductivity k_{th} , and the thickness of the sample d . Then, for a given material, the optimum working frequency can be tuned to the sample thickness. In principle, the lower the τ_{th} , the higher the working frequency and the efficiency. However, we know that $V_{\text{out}} = Q/C = \Delta P_s d / \varepsilon$, where Q is the charge liberated at the surface of the sample, C the capacitance of the sample, ΔP_s the change in spontaneous polarization, d the thickness, and ε the dielectric constant. Note that PZT around T_{LH} has a conveniently very low $\varepsilon(T)$ value in comparison with $\varepsilon(T)$ near the Curie point, contributing to a higher output voltage. We can expect, as it was found, that, for the same composition, V_{out} increases linearly with the sample thickness.

The total characteristic time of the process can be estimated from the full width at half-height of the voltage peak versus time obtained with a frequency low enough to observe the full peak real shape. These values are represented versus thickness in Fig. 1. The only expected thickness dependence comes through the contribution of the thermal characteristic time, proportional to the squared thickness ($\tau_{\text{th}} \propto d^2$). Then, we can easily extract from Fig. 1 the observed value of $\tau_{\text{tot}} - \tau_{\text{th}}$, fitting the experimental data to $\tau_{\text{tot}} = Ad^2 + B$ ($A = 25 \text{ s/mm}^2$, $B = 6.4 \text{ s}$), where the first term represents τ_{th} and the second term represents the contributions of the other characteristic times of the process (independent of d). This value (6.4 s) is much higher than the expected electrical time⁴ ($\tau_e = \rho \varepsilon \approx 0.8 \text{ s}$). We call residual time, τ_r , to the additional contributions to the total relaxation time, after discounting τ_e , which are mainly related to the indirect heating of the sample and to the thermal inertia of the whole system (setup + sample).

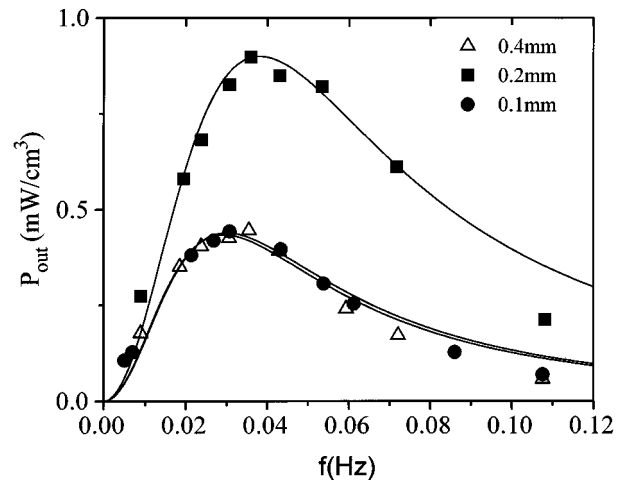


FIG. 2. Specific power output vs frequency for three different thicknesses.

Figure 2 gives the p_{out} as a function of frequency for three different thickness (0.1, 0.2, and 0.4 mm) in the range of $3 < f < 110 \text{ mHz}$. It is shown that the optimum p_{out} and efficiency correspond to a frequency of 0.04 Hz and a thickness of $(0.2 \pm 0.1) \text{ mm}$. Under these conditions, we have obtained a peak voltage of $\pm 83 \text{ V}$, an energy density per cycle of 7.5 mJ/cm^3 , a specific output power of 0.75 mW/cm^3 and an efficiency given by $m = \eta / \eta_c = 0.01$, being η_c the Carnot efficiency. From the fit in Fig. 1, we have obtained a $\tau_{\text{th}} = 25 d^2$, which gives a $\tau_{\text{th}} = 1 \text{ s}$ for a 0.2 mm thickness, of the same order as τ_e , as can be expected near optimum conditions.

There exists room for further improvement of the output power and the efficiency through a synchronized discharge operation. In it, charge is accumulated up to the maximum (in an open circuit), then the circuit is closed, and the charge is released through a proper load resistance, just before the chopper changes to another half cycle. Preliminary results show a maximum output voltage 1.6 times that of the value obtained by means of a spontaneous discharge operation. This figure can be improved varying the ratio open circuit time/short circuit time.

In conclusion, it is perhaps somewhat premature to make a final evaluation of ferroelectric materials as an energy converter, in view of the as yet relatively low efficiencies found. We note, however, that a better knowledge about the conversion process in Zr-rich PZT samples has improved by a factor of 10 the efficiency of the specific power output. This fact may be indicative that further improvements are possible by modifying the operation mode (multistage/multicomposition operation, synchronized discharge operation) and, perhaps more important, by identifying materials with a larger ΔP_s , accompanied by moderate ΔT and low $\varepsilon(T)$.

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