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# $F_{RL}$–$F_{RH}$ phase transition behavior in the stacked $Pb(Zr_{1-x}Ti_x)O_3$ perovskite ceramics

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***Abstract***

*Zirconium rich $Pb(Zr_{1-x}Ti_x)O_3$ (PZT in abbreviation) reveals a pronounced nonlinear pyroelectric effect at the temperature induced $F_{RL}$–$F_{RH}$ phase transition. This characteristic makes it a competitive candidate for the applications of the direct thermal-electric energy conversion and infrared detecting technology. However the narrow $F_{RL}$–$F_{RH}$ phase transition temperature range (about 2°C around the pyroelectric peak) restricts its wide applications. A stacked multi-layer PZT ceramics made by PZT 97/3 (Zr/Ti ratio) with different $Nb_2O_5$ dopants is expected to solve this problem. In the paper the $F_{RL}$–$F_{RH}$ phase transition behavior in a stacked three-layer PZT ceramics has been investigated. The results show that a smooth $F_{RL}$–$F_{RH}$ phase transition can take place in a certain temperature range. The XRD interface line analysis of the distribution of $Nb^{5+}$ content exhibits apparent $Nb^{5+}$ ion diffusion between each two layers. The $Nb^{5+}$ ion diffusion has significant effects on the behavior of the output pyroelectric current. A simple experiment has been explored to confirm this effect.* *© 1999 Elsevier Science Limited. All rights reserved*

*Keywords*: PZT, ferroelectric properties.

## 1 Introduction

Low temperature rhombohedral ($F_{RL}$) – high temperature rhombohedral ($F_{RH}$) ferroelectric phase transition takes place in the range of Zr/Ti ratio from 95/5 to 62/38 in the pure $PbZrO_3$–$PbTiO_3$ phase diagram.[1] When 1 wt% $Nb_2O_5$ is added, the $F_{RL}$–$F_{RH}$ and $AF_O$–$F_{RH}$ phase boundaries shift to the higher Zr content end, around 97/3.[2] The $F_{RL}$–$F_{RH}$ phase transition can be induced by stress, electric field and temperature. In particular, temperature induced $F_{RL}$–$F_{RH}$ displacive phase transformation is accompanied with the change of spontaneous polarization in a narrow transition temperature range. Thus large pyroelectric coefficient $p$ is obtained, while the dielectric constant $\varepsilon$ stays low. This character favors the application for infrared detector, where high figure of merit, proportional to ($p/\varepsilon$), is required. The spontaneous polarization change ($\Delta P_s$) is attributed to the cation shifts along $\langle 111 \rangle$ and oxygen octahedral tilt and their coupling. When Ti content increases, $\Delta P_s$ decreases and vanishes around 80/20 due to the change of coupling type.[3] Composition dependence of the change in spontaneous polarization ($\Delta P_s$) shows that $\Delta P_s$ reaches maximum in the PZT 97/3 with 1wt% Nb dopant.[4] Nb is believed to be an excellent dopant to increase the resistivity $\rho$ of the material, which is in favor of the application of energy conversion with high specific power output and efficiency.[5]

Consequently, PZT 97/3 with $Nb_2O_5$ dopant is chosen as the optimal working media for the applications stressed above due to its large $\Delta P_s$ and $p/\varepsilon$ and high $\rho$. The sharp transition temperature range of this material, however, restricts its applications in a wide temperature region. Therefore a novel material design is taken into consideration. Previously, the pyroelectric $F_{RL}$–$F_{RH}$ phase transition behavior of PZT 97/3 with different $Nb_2O_5$ contents has been studied for the parallel configuration, where wide but discontinuous transition temperature is obtained.[6] In this paper, we investigate the pyroelectric behavior of the stacked configuration with the same compositions.

## 2 Experimental

PZT 97/3 with 0·8, 1·0, and 1·3 wt% $Nb_2O_5$ contents is chosen for the multi-composition composite.

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Conventional solid state reaction synthesis is used for the material preparation. More details can be found in Ref. 7. Calcined powders with different compositions are laminated one by one to form a stacked configuration as shown in Fig. 1 and sintered at 1260–1360°C for 2 h. Then the sample is cut and polished in dimension $10\times10\times2{\cdot}5$ mm and polarized with an electric field 20 kV $cm^{-1}$ for 10 min. Pyroelectric current output measurement is made by 'charge integrated method'.[7]

## 3 Results

Figure 2 presents the output pyroelectric current for each single composition. It is clear that the $F_{RL}$–$F_{RH}$ transition temperature increases while the output pyroelectric current decreases with the Nb content as expected.

Figure 3 shows the output pyroelectric current for three different cases, that is, for compositions placed in order of the content of $Nb^{5+}$ (denoted as I) and for the composition with least or most $Nb_2O_5$ content placed in the middle of the other two compositions (denoted as II and III, respectively). It is clear that all three combination configurations show broad or diffuse transition temperature compared with the single composition sample in Fig. 2. Moreover it may be seen that the output pyroelectric current behavior through the transition for the three different cases is similar.

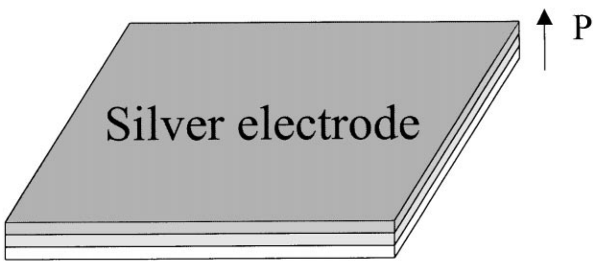


**Fig. 1.** Scheme of the stacked sample.

## 4 Discussions

The output pyroelectric current behavior of the stacked multi-composition sample can be understood by its equivalent circuit in Fig. 4. Each single composition sample can be equivalent to a parallel circuit of a resistor and a capacitor. The effect of the inductance and the conductivity on the pyroelectric current measurement can be neglected under the low $F_{RL}$–$F_{RH}$ phase transition temperature.

In each case of stacked configuration when the temperature is up to the transition temperature of one of the components, the corresponding phase transition takes place. The charges accumulated on the sides of this component will be released through the other two components. Thus the pyroelectric behavior for three cases is similar. From the equivalent circuit it is obvious that the charge through the circuit is independent on the order of the sample.

However we can still find some minor differences between I and II or III. There shows not much difference for the behavior of the output pyroelectric current in cases II and III. In case I higher $F_{RL}$–$F_{RH}$ phase transition temperature and lower output pyroelectric current is found. We think that

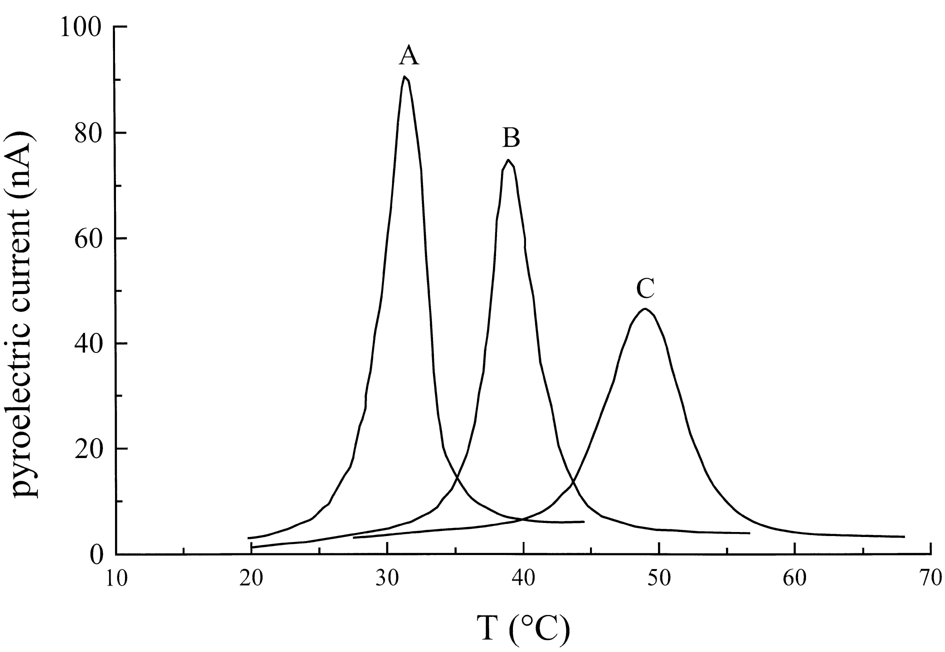


**Fig. 2.** Pyroelectric current in $Pb(Zr_{0{\cdot}97}Ti_{0{\cdot}03})O_3$ with various contents of $Nb_2O_5$ doping. A: 0·8; B: 1·0; and C: 1·3 in weight percentage.

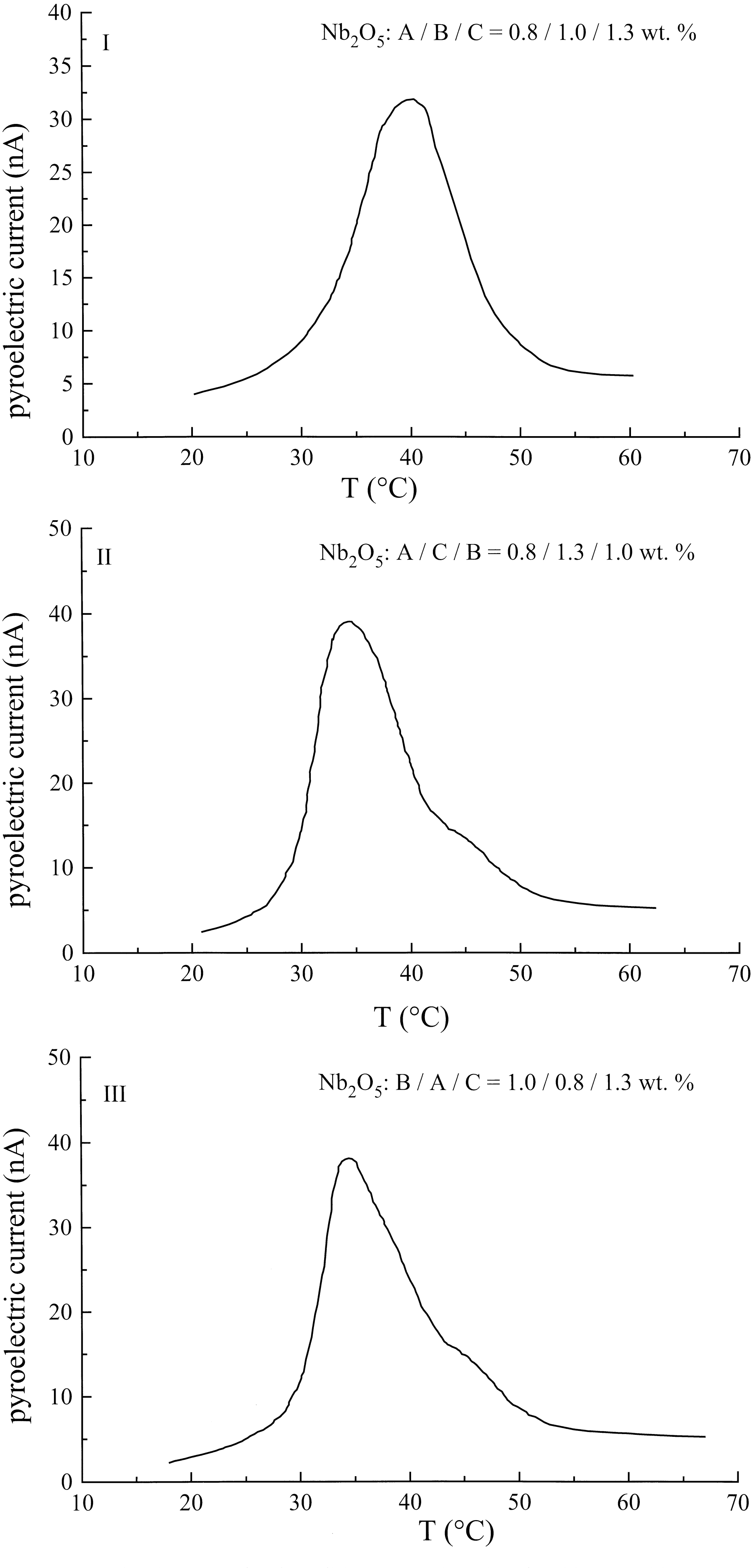


**Fig. 3.** Output pyroelectric current for three different cases in series of multi-composition PZT samples.

this is due to the varying strength of $Nb^{5+}$ ion diffusion. In previous work[8] it has been shown from the XRD interface line analysis that the $Nb^{5+}$ ion diffusion interface increases on the difference of Nb concentration in the sample. The thickness of each composition in a stacked multi-composition configuration is relatively small comparing with that of the parallel type configuration[6] and the effect of the ion diffusion on the output pyroelectric current becomes much larger. It is known that $Nb^{5+}$ ions diffuse from the high concentration side towards the low concentration one. In the case of I the distribution of $Nb^{5+}$ ions is probably more homogenous and relatively higher Nb concentration than that of the other two cases. This is why in the case of I we get higher and much smoother transition temperature, while in the other two cases we get an additional shoulder at high temperature.

On the other hand since the $Nb^{5+}$ ion diffusion is limited during the sintering process, the $Nb^{5+}$ ion concentration cannot become exactly homogenous in the whole ceramic. Therefore the phase transition can take place in some temperature range. Because of the small $Nb^{5+}$ difference, the transition temperature window is narrow in these case compared with the parallel type configuration case.[6]

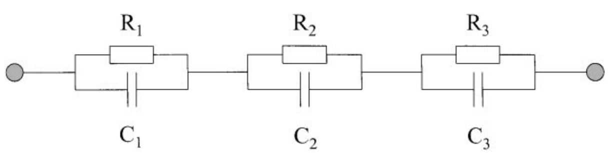


**Fig. 4.** Equivalent circuit diagram. Each pair of $R_i$ and $C_i$ represents one composition in the multi-composition sample.

To confirm the effect of ion diffusion on the output pyroelectric current we use a simple way to test it. Three single composition samples, with silver electrode on both sides of sample, are connected in series in the same way as in the above three cases.

Under this condition there is no ion diffusion between samples. The output pyroelectric current for all three cases has been measured. It seems that there is no apparent difference between these cases. One of the output pyroelectric current patterns for three serial samples is shown in Fig. 5, where three peaks correspond to each single composition. This further shows that ion diffusion in series multi-composition ceramics has pronounced effects on the behavior at the $F_{RL}$–$F_{RH}$ phase transition. If the ion diffusion is properly controlled by adjusting the sintering conditions or Nb concentration difference, it is possible to obtain a smooth and broad $F_{RL}$–$F_{RH}$ phase transition. More work is needed in this direction.

## 5 Conclusions

In conclusion, in the stacked configuration the $Nb^{5+}$ ion diffusion has pronounced effects on the behavior of the output pyroelectric current. A smooth phase transition can take place in a certain temperature range, because of the $Nb^{5+}$ ion diffusion interface which cannot be ignored, but the transition temperature window is relatively narrow compared with that of the parallel type configuration. In

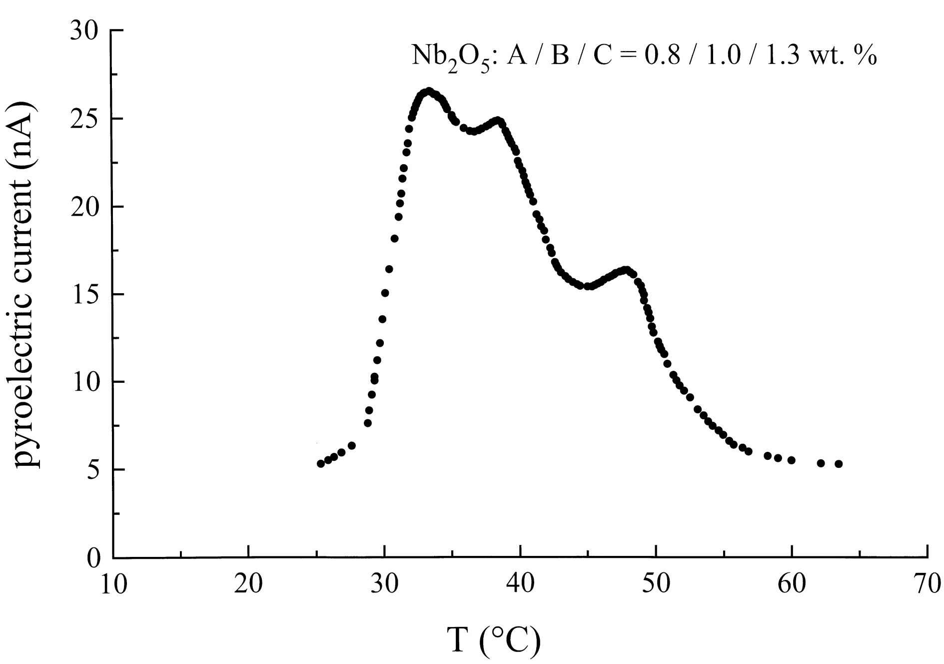


**Fig. 5.** Output pyroelectric current patterns for three single composition samples, with silver electrode on both sides of sample, connected in series in the same way as in the above three cases shown in Fig. 3.

theory, the order of different composition for an array in series has no effect on the pyroelectric behavior of a series multi-composition ceramic plate. However small differences exist between various cases investigated, which can be attributed to the effect of changes in Nb ion diffusion.

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