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Dielectric behaviors and phase separation in $Pb(Ni_{1/2}W_{1/2})O_3$–$PbTiO_3$

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Abstract

Relaxor ferroelectric phases of $Pb(Ni_{1/2}W_{1/2})O_3$–$PbTiO_3$ (PNW–PT) near the morphotropic boundary composition (MPB) were synthesized by sintering of the perovskite nanocrystallites derived from mechanical activation of constituent oxides. They demonstrate unique temperature stability in dielectric behavior over the wide temperature range of −80 to 60 °C, when sintered at 970 °C. Their dielectric behavior is strongly dependent on the sintering schedule and subsequent annealing at relatively low temperatures, due to phase segregation and evolution of compositional inhomogeneity, as confirmed by Raman spectroscopy and compositional mapping.

Keywords: E. Capacitor; Mechanical activation; Relaxor ferroelectrics; X7R

1. Introduction

$Pb(Ni_{1/2}W_{1/2})O_3$ (PNW) exhibits both antiferroelectric and antiferromagnetic behaviors, rendering it a typical ferroelectromagnet [1,2]. In the ferroelectromagnet, magnetic and ferroelectric properties are coupled together, making it possible to alter the ferroelectric properties by applying a magnetic field, and also to modify the magnetic order via an electric field through the coupling effects. PNW also demonstrates a very broad dielectric peak and a low sintering temperature [2,3], which find applications in temperature stable capacitors, e.g. X7R specifications multiplayer capacitors [4,5].

In our previous study, an unexpected temperature stability was observed in $Pb(Ni_{1/2}W_{1/2})O_3$–$PbTiO_3$ (PNW–PT) near the morphotropic boundary (MPB) composition derived from mechanical activation [6]. The resulting dielectric behaviors were rather close to EAI X7R capacitor specifications [3]. The aim of the present study is to investigate the effects of sintering temperature, post-sinter thermal annealing, and composition variations on the dielectric properties and phase segregation in PNW–PT compositions near the MPB.

2. Experimental procedure

The detailed synthesizing processing procedures for PNW–PT via mechanical activation has been described elsewhere [6]. Briefly, NiO and WO_3 were first mixed together and calcined at 1000 °C for 4 h before mixing with PbO and TiO_2, and subsequently mechanical activation for 24 h in a shaker mill. The resulting nanocrystalline powders were subsequently pressed and sintered in air at 900–1050 °C for 2.0 h. To adjust their electrical properties, 0.3 wt.% MnO_2 was add into each PNW–PT composition. Phase analysis was carried out using X-ray diffractometer (Cu Kα, X'pert Diffractometer, Phillips). Elemental distributions in sintered PNW–PT were analyzed using a scanning electron microscope (SEM) equipped with EDX mapping (XL30-FEG, Philips). Micro-Raman spectra were acquired using a single-grating Raman spectrometer (Spex T64000, Jobin Yvon, France). A LCR Meter and an Impedance/Gain phase analyzer (Solartron S1 1260) were employed to characterize the dielectric behaviors of sintered PNW–PT.

3. Results and discussions

Our previous study have demonstrated an unique temperature stability in dielectric constant of 0.6PNW–0.4PT derived from mechanical activation [6] To explore whether

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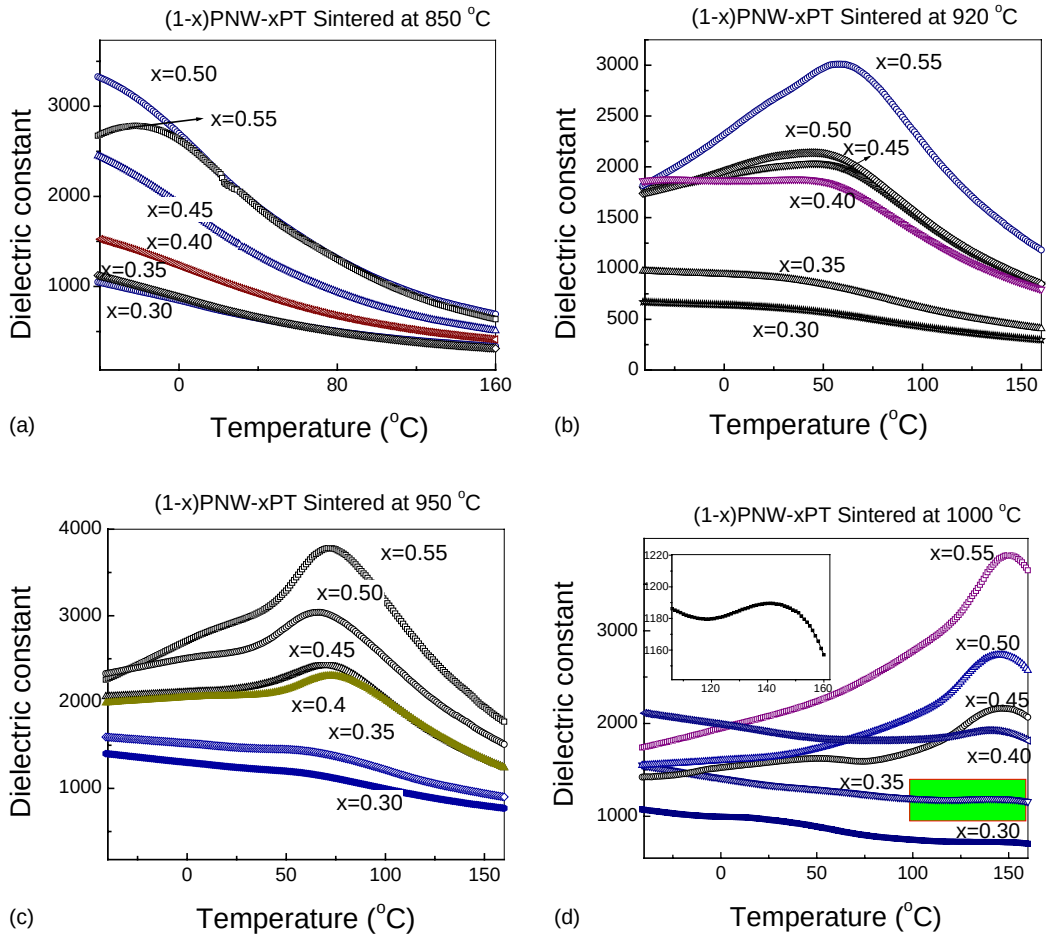

Fig. 1. Dielectric constant as a function of temperature for $(1-x)$PNW–xPT sintered at sintered at 850, 920, 950, and 1000 °C, respectively.

such a temperature stability phenomenon occur in other compositions $(1-x)$PNW–xPT ($x = 30$–55%) were synthesized and sintered at various temperatures. The dielectric constants of $(1-x)$PNW–xPT as a function of temperature in the range of −55 to 160 °C are shown in Fig. 1. When sintered at 850 °C (a), only one broad dielectric peak was observed in 0.45PNW–0.55PT, indicating the absence of any substantial phase segregation. For compositions content PT <0.50, there occurred a decline in dielectric constant with rising temperature, implying they were also of single-phase structure with a rather low Curie temperatures (<−55 °C). When the sintering temperature was raised to 920 °C (b), a newly formed second dielectric peak appeared at ∼50 °C in compositions with PT >40%. For the low PT compositions (<40%), a small anomaly could also be identified over the similar temperature range. These dielectric peaks and anomalies can be accounted for by the occurrence of tetragonal phase. With increasing sintering temperature (950 and 1000 °C), the peaks shifted upwards (c and d). Those PNW–PT with composition close to 45%PT and sintered at high temperature (>950 °C) demonstrated a rather stable dielectric constant over the temperature range of −55 to 100 °C. Therefore, 0.55PNW–0.45PT was selected as an example for further study the sintering and annealing effects.

Fig. 2 plots the dielectric constant of 0.55PNW–0.45PT sintered at 850 and 970 °C, together with the one sintered at 970 °C and subsequently annealed at 800 °C for 3 h. 0.55PNW–0.45PT sintered at 850 °C exhibits a single broadened dielectric peak of around −80 °C, suggesting a single phase transition. As the sintering temperature was raised to 970 °C, a newly formed second dielectric peak was obtained at around 108 °C. Simultaneously, the dielectric peak at around −80 °C has been greatly depressed into a broad hump, resulting rather stable dielectric spectrum over the wide temperature from −70 to 100 °C. Upon annealing, the low temperature dielectric peak recovered and shifted to −98 °C, while the dielectric peak at ∼108 °C had been greatly reduced in intensity and almost completely disappeared. These two dielectric peaks can be accounted for the occurrence of two different phases.

The phases present in 0.55PNW–0.45PT were further characterized by Raman spectroscopic studies (Fig. 3), which showed that it exhibited two space groups. The Raman bands at wavelength of around 53, 250, 389, 750, 857 cm^{-1} are due to the excitation modes of an $Fm3m$ space group, corresponding to a pesudocubic perovskite structure, while those bands at around 142, 214, 277, 433, 556, and 620 cm^{-1} are attributed to a tetragonal $P4mm$

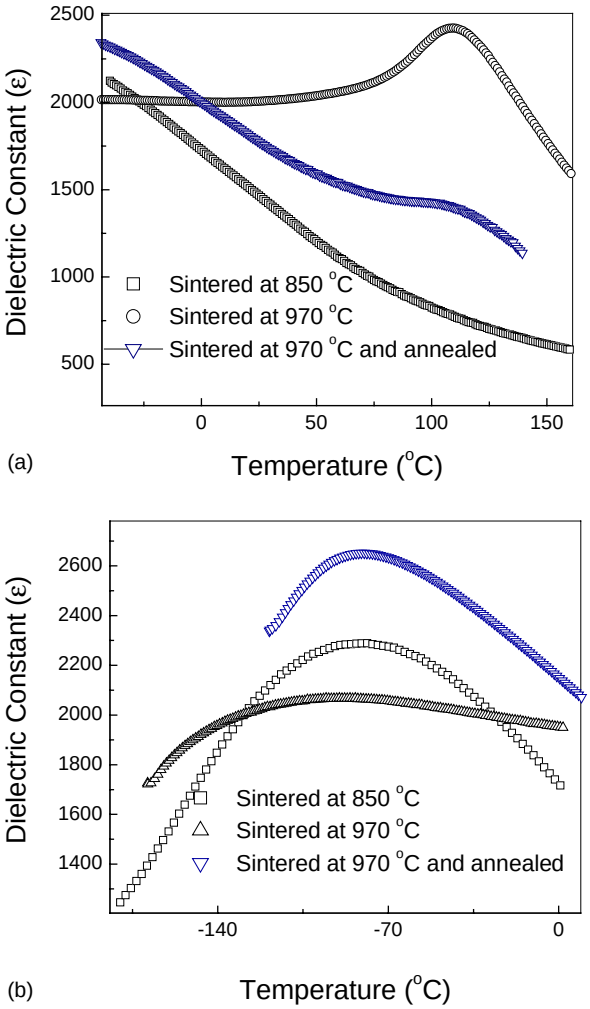

Fig. 2. Dielectric constant as a function of temperature for 0.55PNW–0.45PT sintered at 850 and 970 °C, respectively, and that sintered at 970 before annealing at 800 °C for 3 h (a) over the temperature range of −50 to 160 °C, and (b) over the temperature range of −190 to 10 °C.

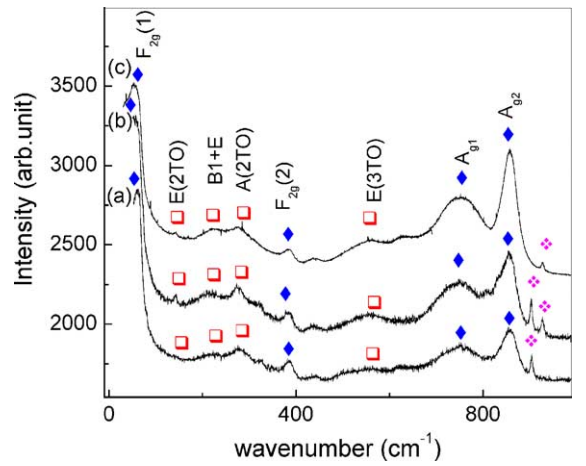

Fig. 3. Raman spectra of 0.55PNW–0.45PT: (a) sintered at 850 °C, (b) sintered at 970 °C, and (c) sintered at 970 °C and then annealed at 800 °C for 3 h. (❑) Modes of tetragonal space group symmetry (*P4mm*); (◆) modes of pseudocubic types (*Fm3m*); (❖) impurity phase.

space group [7–11]. The two sharp peaks at 901, and 927 cm^{-1} was ascribed to impunity phases [6]. The Raman spectra of 0.55PNW–0.45PT sintered at low temperatures did not demonstrate the present of tetragonal structure, which started to appear at the high sintering temperature (970 °C). Upon annealing, the weak band centered at around 141 cm^{-1}, which belongs to the tetragonal phase, has almost completely disappeared, and at the same time, the intensities of other tetragonal Raman bands are reduced. These Raman spectroscopic studies confirmed the coexistence of a tetragonal phase and a pesudocubic phase, the relative amount of which can further be tailored by the thermal annealing at low temperature.

The composition homogeneities in PNW–PT were also analyzed using EDX attached to SEM. Fig. 4(a–c) shows the elemental mappings of Ti in 0.55PNW–0.45PT sintered at 850 and 970 °C, respectively, together with that sintered at 970 °C and then annealed at 800 °C for 3 h. 0.55PNW–0.45PT sintered at the low temperature exhibited a rather homogeneous distribution in Ti elements. Compositional inhomogeneity appeared at the sintering temperature of 970 °C. Upon subsequently annealing at 800 °C for 3 h, the distribution homogeneity of Ti was largely recovered, confirming that the phase segregation involved a heterohomogeneity in PT distribution.

The tetragonal phase observed in 0.55PNW–0.45PT is attributed to the PT rich phase, which produces a dielectric peak over the high temperature range (∼108 °C), while the PT deficient phase is of pesudocubic phase corresponding to the broad dielectric hump at the low temperature. This demonstrated that the pesudocubic phase is stable at the low sintering temperature, but unstable at high sintering temperature leading to the formation of tetragonal phase. As a result, sintering at 970 °C triggered the occurrence of PT. Upon annealing at 800 °C, the PT rich tetragonal phase was partially transformed into the pesudocubic phase. For composition with high PT content in PNW (>50% PT), PT-rich tetragonal phase becomes dominating, leading to a strong dielectric peak over the temperature range of 50–150 °C. Low PT content (<40%) promoted the pseudocubic phase, resulting in the obvious dielectric hump at the lower temperature (<−50 °C), along with a small anomaly at the high temperatures. Increasing the sintering temperature can also enhance the concentration of PT in the tetragonal phase, leading to the shift of high temperature dielectric peak. In the compositions containing ∼45% PT sintered at ∼950 °C, there exist comparable amount of tetragonal phase and pseudocubic phase, and therefore temperature stability in dielectric behavior is demonstrated.

An appropriation combination of composition and sintering/annealing temperature can be used to adjust the temperature stability in dielectric behavior. For example, 0.55PNW–0.45PT sintered at 960 °C before annealing at 800 °C for 2 h exhibited a temperature stability that meets the X7R capacitor specification (variation of capacitance over the temperature range of −55 to 125 °C is within

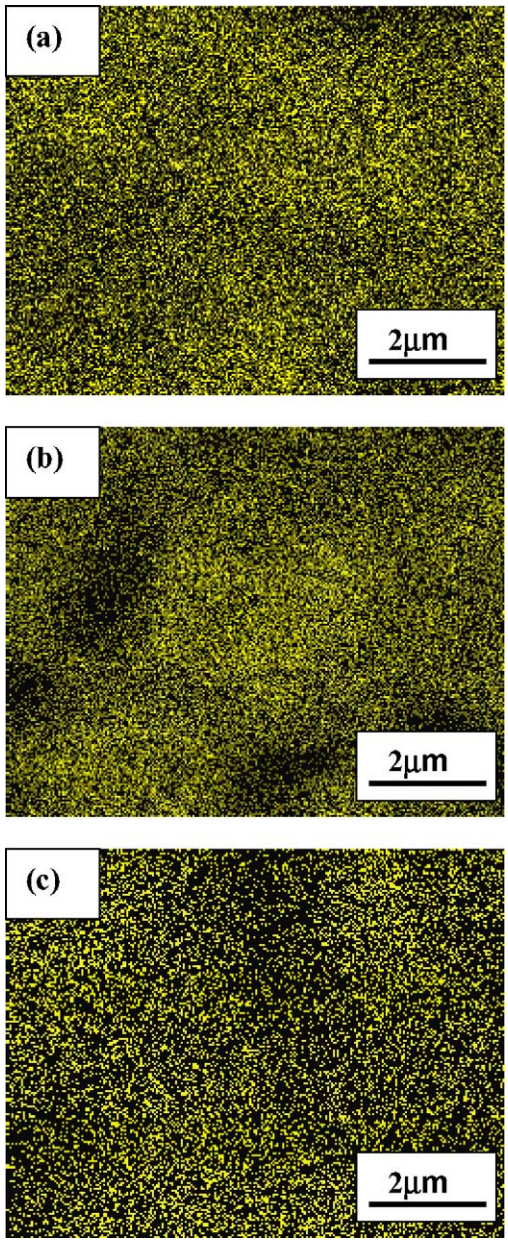

Fig. 4. Elemental mapping for Ti on the polished surfaces of 0.55PNW–0.45PT sintered at (a) 850 °C, (b) 970 °C, and (c) 970 °C and then annealed at 800 °C for 3 h, respectively.

15%), which was previous attempted by core-shell structure and careful control in processing [12].

4. Conclusions

A temperature stability in dielectric behavior was observed in 0.55PNW–0.45PT sintered at ~970 °C, which is related to the coexistence of PT-rich tetragonal and deficient pesudocubic phases. The phase segregation and dielectric behavior of PNW–PT were dependent on PT content, sintering temperature, and annealing temperature. Such temperature stability occurred with the compositions near the MPB composition (with ~45% of PT), when sintered at a temperature in the range of 950–1000 °C.

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