

Unique Dielectric Behavior of $0.6\text{Pb}(\text{Ni}_{1/2}\text{W}_{1/2})\text{O}_3 \cdot 0.4\text{PbTiO}_3$ Derived from Mechanical Activation

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$0.6\text{Pb}(\text{Ni}_{1/2}\text{W}_{1/2})\text{O}_3 \cdot 0.4\text{PbTiO}_3$ (0.6PNW-0.4PT) of complex perovskite structure is successfully synthesized by mechanical activation of mixed oxide composition, followed by sintering at 950°C. It exhibits a considerably stable temperature dependence of dielectric constant over the wide temperature range of -120° to 20°C , although there occurs a dielectric peak at around 74°C . Raman spectroscopic studies show the coexistence of tetragonal and pseudocubic perovskite phases on sintering at 950°C, which are attributed to the inhomogeneous distribution of PbTiO_3 arising from mechanical activation. The dielectric behavior can be fine tuned by thermal annealing at 750°C , leading to phase redistribution in PNW-PT.

I. Introduction

$\text{Pb}(\text{Ni}_{1/2}\text{W}_{1/2})\text{O}_3$ (PNW) is an antiferroelectric of perovskite structure, which also exhibits an antiferromagnetic phase transition at relatively low temperature, rendering it a typical ferroelectromagnet.¹ It has attracted extensive investigation owing to its unique physical and ferroelectromagnetic properties that are required by a number of technologically demanding applications.² However, PNW of perovskite structure cannot be synthesized via the conventional ceramic processing routes, due to the occurrence of the unwanted pyrochlore phase. Hot pressing at a considerably high pressure is one of the very few synthesis routes that can lead to the retention of perovskite phase in PNW.¹ Doping with certain thermodynamically perovskite phases has also been attempted in order to stabilize the perovskite structure in PNW, however with a limited degree of success.^{3–5} It is therefore both scientifically interesting and technologically challenging to seek an alternative fabrication technique for PNW and PNW-based electroceramic materials, although there are a number of limitations of these Pb-based compositions for applications in certain components, such as capacitors and multilayer capacitors.

Mechanical activation, which was initially used for novel metallic alloys and composites,⁶ has recently been successfully applied to Pb-based relaxor ferroelectrics and piezoelectrics.^{7–10} Nanocrystallites of complex perovskite structure can be nucleated and grown in oxide matrixes by mechanical activation at room temperature, leading to formation of a single perovskite phase by skipping the unwanted pyrochlore phases. This therefore can give rise to a significant improvement in the ferroelectric properties of relaxors. Mechanical activation can also lead to formation of several complex perovskite structures that cannot be realized by

thermal activation at elevated temperatures.¹¹ In a recent study of $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$, we observed that mechanical activation generated a degree of compositional inhomogeneity, which causes an undesirable degradation in dielectric behavior.¹² On the other hand, compositional inhomogeneity and coexistence of two or more slightly different phases/structures are desirable for realization of certain ferroelectric and piezoelectric properties. The compositions near the morphotropic phase boundaries in $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT), where both the dielectric and piezoelectric properties can be maximized, are among the well-established examples.¹³ The compensation effect of multiple phases/structures can significantly improve the temperature stability of ferroelectric and dielectric behavior in both normal and relaxor ferroelectrics.^{14–15} The objective of this study is to investigate the feasibility of forming a multiphase structure in $0.6\text{Pb}(\text{Ni}_{1/2}\text{W}_{1/2})\text{O}_3 \cdot 0.4\text{PbTiO}_3$ by mechanical activation, and to investigate the dielectric behavior of the PNW-PT derived from mechanical activation.

II. Experimental Procedure

The starting materials used for this work are commercially available PbO (>99% in purity, J. T. Baker, Inc., Hayward, CA), NiO (>99% in purity, Fisher Scientific, Pittsburgh, PA), TiO_2 (>99% in purity, A Johnson Matthey Co., Jacksonville, FL), and WO_3 (>99.9% in purity, Aldrich Chemical Co., Inc., Milwaukee, WI). NiO and WO_3 were first mixed together by ball-mill and calcined at 1000°C for 4 h. The resulting oxide composition was then mixed with PbO and TiO_2 according to the stoichiometric composition of 0.6PNW-0.4PT. To adjust the resistance and dielectric loss of PNW-PT, 0.3 wt% MnO_2 was added into the mixed oxide composition. Mechanical activation of the mixed oxide composition was then conducted for 24 h in a shaker mill operated at ~ 900 rpm. The resulting nanocrystalline powder was subsequently pressed into pellets and sintered in air at 950°C for 2 h. Phase analysis using an X-ray diffractometer (XRD) (CuK α , X'pert Diffractometer, Philips Instruments, Eindhoven, Netherlands) confirmed that sintered PNW-PT exhibits a perovskite structure.

Both the nanocrystalline composition in powder form as derived from mechanical activation and the polycrystalline PNW-PT sintered at 950°C were examined using an XRD. They were also analyzed using a scanning electron microscope equipped with EDX mapping (Model XL30-FEG, Philips Instruments). Micro-Raman spectra were acquired at room temperature in the backscattering geometry using a single-grating Raman spectrometer (Model Spex T64000, Jobin Yvon, France). An LCR meter (Model HP 4284A, Hewlett Packard, USA) and an Impedance/Gain Phase Analyzer (Model S1 1260, Solartron Analytical, Houston, TX) were used to characterize the dielectric behavior of sintered PNW-PT over the temperature range -190° to 160°C , where the temperature range -190° to -50°C was measured using the

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Impedance/Gain Phase Analyzer and the temperature range -50° to 160°C was measured using the LCR meter.

III. Results and Discussion

XRD traces of 0.6PNW-0.4PT as derived from mechanical activation and subsequently sintered at 950°C are shown in Fig. 1. The conventional XRD detected a perovskite structure in the nanocrystalline PNW-PT powder composition, where the diffraction peaks exhibit a considerable degree of broadening. Calculation using the Sherrer equation suggested an average crystallite size of ~ 10 nm.¹⁶ On sintering at 950°C for 2 h, the diffraction peaks belonging to the perovskite phase are much sharpened, due to the growth in crystallite size at the sintering temperature. It was further observed that sintered PNW-PT exhibited a pseudocubic structure, where the splitting of (100) and (200) peaks cannot be detected. At the same time, a minor amount of impurity phases can also be observed (the diffraction peaks of these minor impurity phases are close to those of pyrochlore PbWO_4 and NiO , according to PDF file Nos. 29-0784 (International Centre for Diffraction Data, Newtown Square, PA, 1978) and 47-1049 (International Centre for Diffraction Data, 1991), respectively).

The temperature dependence of the dielectric constant and the dielectric loss for PNW-PT derived from mechanical activation over the temperature range of -190° to 160°C is shown in Fig. 2. A dielectric peak is observed at $\sim 74^{\circ}\text{C}$. Over the same temperature range, a relatively low dielectric loss of $<3\%$ was measured at 1 kHz, although there is a broad hump with increasing temperature. Over the temperature range of -120° to 20°C , a considerably stable temperature dependence of dielectric constant is demonstrated. Decreasing temperature at temperatures below -120°C led to a steady decrease in the dielectric constant, which exhibits a degree of frequency dispersion. This can be accounted for by the freezing behavior of dipole glass.¹⁷ At temperatures of around 0°C , a small anomaly in dielectric constant is observed, where a strong frequency dispersion is shown and is attributed to the space charge.¹⁸ Over the wide temperature range -120° to 50°C , the variation of dielectric constant is within $\pm 5\%$, and that from -55° to 125°C is within $\pm 17\%$ of the dielectric constant at 25°C , which is very close to the EIA's X7R specifications ($\Delta C/C \leq \pm 15\%$ over the temperature range -55° to $\sim 125^{\circ}\text{C}$, where C is the capacitance at 25°C).¹⁹

Figures 3(a) is an SEM micrograph showing a section of sintered 0.6PNW-0.4PT that was thermally etched at 750°C for

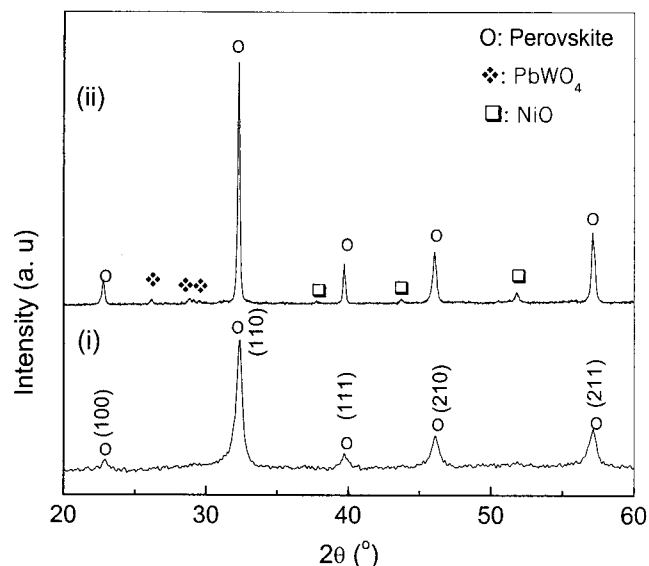


Fig. 1. XRD traces of 0.6PNW-0.4PT derived from (i) mechanical activation for 20 h, and (ii) subsequently sintered at 950°C for 2 h.

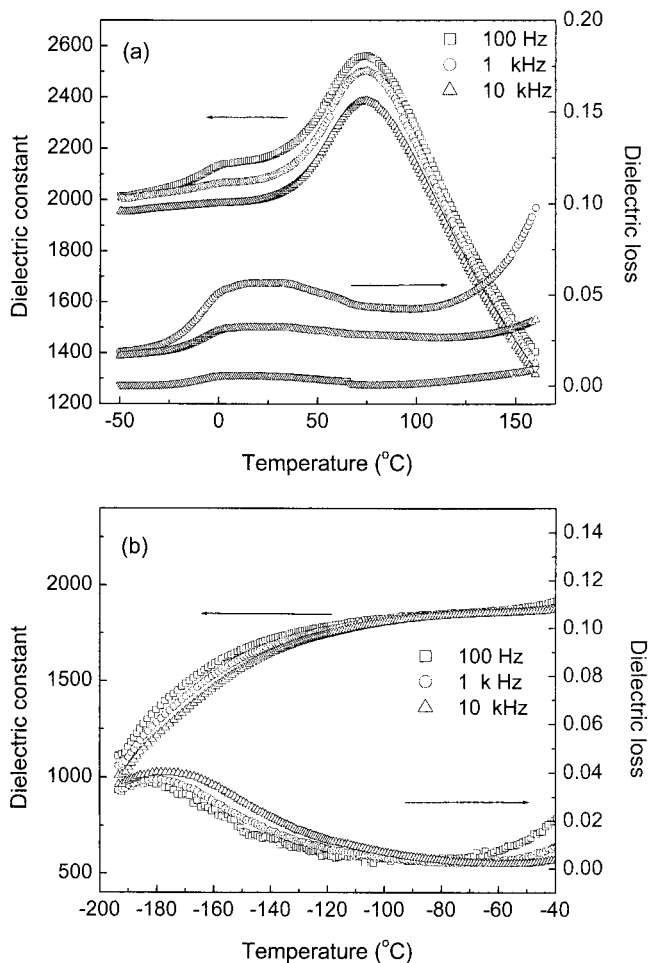


Fig. 2. Dielectric constant and dielectric loss of 0.6PNW-0.4PT as a function of testing temperature. The dielectric measurement over the temperature range of -190° to -50°C and -50° to 160°C was conducted using an impedance/gain phase analyzer and LCR meter, respectively, resulting in a discontinuity in both dielectric constant and dielectric loss at around -50°C .

0.5 h to reveal the grain boundaries, together with the elemental mappings for Ni, Ti, and W, respectively, on a selected area in the sintered electroceramic. The SEM micrograph shows that it consists of grains 2 to ~ 5 μm in size. The composition maps indicate that the distribution of Ni is largely homogeneous across different grains. However, this is not the case for Ti and W, as shown in Figs. 3(c) and (d). There is considerable variation in the concentration of Ti and W across different grains. In particular, Ti-deficient areas are those with W enrichment. Although there is no apparent Pb enrichment and deficiency in EDX analysis across spatial scales, the variation of Ti distribution shown in Fig. 3(c) clearly suggests that there is a strong differential distribution of PbTiO_3 in PNW. Further elemental analyses at numerous positions on the surface of 0.6PNW-0.4PT confirmed that the variation of PT phase in 0.6PNW-0.4PT was in the range of 30 to 60 mol%. It is therefore concluded that the dielectric peak observed at 74°C , shown in Fig. 2, is due to the existence of one or more PT-rich PNW phases, which agrees with what has been observed by Yasuyoshi.³

The composition of 0.6PNW-0.4PT selected in this study is close to the morphotropic phase boundary in PNW-PT, where tetragonal phase and pseudocubic phase can coexist.³ To further examine the phase constituents of 0.6PNW-0.4PT derived from mechanical activation in this work, Raman spectroscopic studies were used. As shown in Fig. 4, the Raman spectrum of the as-sintered 0.6PNW-0.4PT exhibits two distinctively different Raman-activated modes. The bands centered at 61, 382, and 745

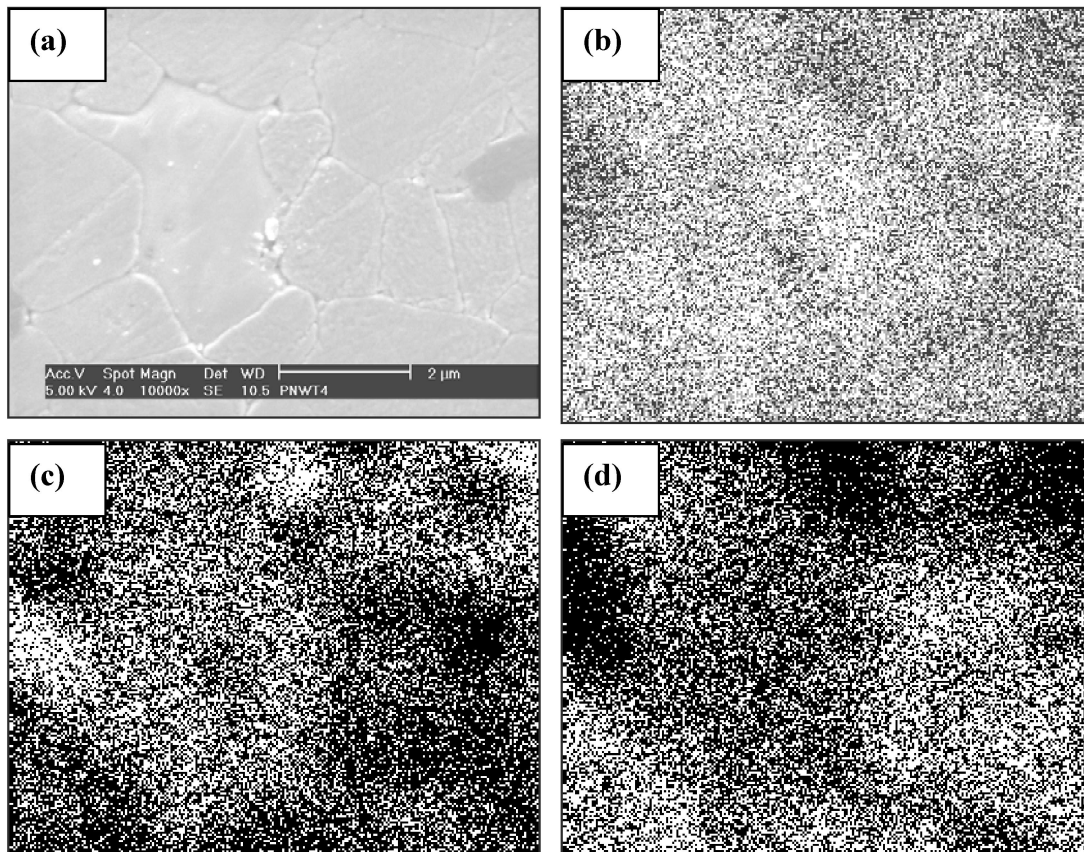


Fig. 3. SEM micrographs of 0.6PNW-0.4PT (polished specimen subjected to thermal etching at 700°C for 0.5 h), together with the EDX mappings: (a) SEM micrograph for the selected area, (b) mapping for Ni, (c) mapping for Ti, and (d) mapping for W.

cm^{-1} are attributed to the $F_{2g}(1)$, $F_{2g}(2)$, and A_{1g} modes in the $Fm3m$ space group, which are similar to those observed in pseudocubic $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, and $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$.^{20–22} The origin of 857 cm^{-1} can be traced to the B site order in complex perovskite structure, as has been observed in the Raman spectra of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 \cdot \text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$.²³ There is a sharp band around 901 cm^{-1} , which can be attributed to the minor impurity phase. More interesting are those Raman bands at

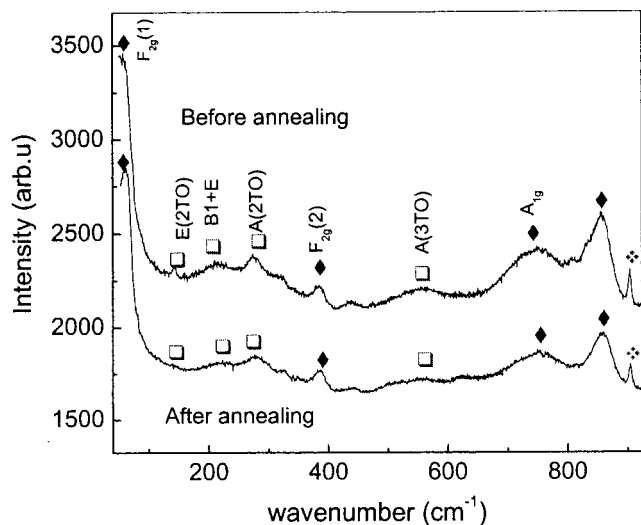


Fig. 4. Raman spectra of 0.6PNW-0.4PT before annealing and after annealing at 750°C for 10 h: (□) modes of tetragonal space group symmetry ($P4mm$), (◆) modes of pseudocubic types ($Fm3m$), (✦) impurity phase.

around 141, 214, 273, 433, and 562 cm^{-1} , which are very close to those of PbTiO_3 arising from the E(2TO), B1+E, E(2LO), A(3TO) excitations in the tetragonal $P4mm$ space group.²⁴ Therefore, these Raman spectroscopic studies confirmed the existence of PT-enriched tetragonal phases, which exhibit a higher Curie temperature than that of the pseudocubic phase. The dielectric peak at around 74°C in 0.6PNW-0.4PT, as shown in Fig. 2, can be ascribed to the phase transition of these tetragonal structures, while the temperature stability of dielectric behavior at low temperatures is related to the pseudocubic phase.

The Raman spectrum of sintered PNW-PT is strongly affected by further thermal annealing. As shown in Fig. 4, on annealing at 750°C for 10 h, the weak band centered at around 141 cm^{-1} had almost disappeared, and at the same time the band intensities of other Raman bands of tetragonal phase were also reduced simultaneously. This suggests that the thermal annealing at 750°C led to the redistribution of PT-rich tetragonal and pseudocubic phases. This will undoubtedly shift the temperature dependence of dielectric behavior. Accordingly, there is a significant change in the temperature dependence of the dielectric constant when measured at a frequency of 1 kHz on annealing at 750°C, as shown in Fig. 5. On annealing at 750°C for 20 h in air, the dielectric peak at $\sim 74^\circ\text{C}$ was dramatically flattened. At the same time, the broad dielectric peak observed at lower temperatures shifted upwards, the relaxor behavior strengthened, and the peak dielectric temperature centered at -82°C . When annealed at 750°C for 35 h, the low-temperature dielectric peak was further strengthened and the peak dielectric temperature was shifted to -98°C , while the dielectric peak at $\sim 74^\circ\text{C}$ had almost completely disappeared. This is consistent with what has been indicated by the Raman spectra, which clearly demonstrated that the amount of the tetragonal phase is depleted by annealing at 750°C, due to the redistribution of PT phase at the annealing temperature.

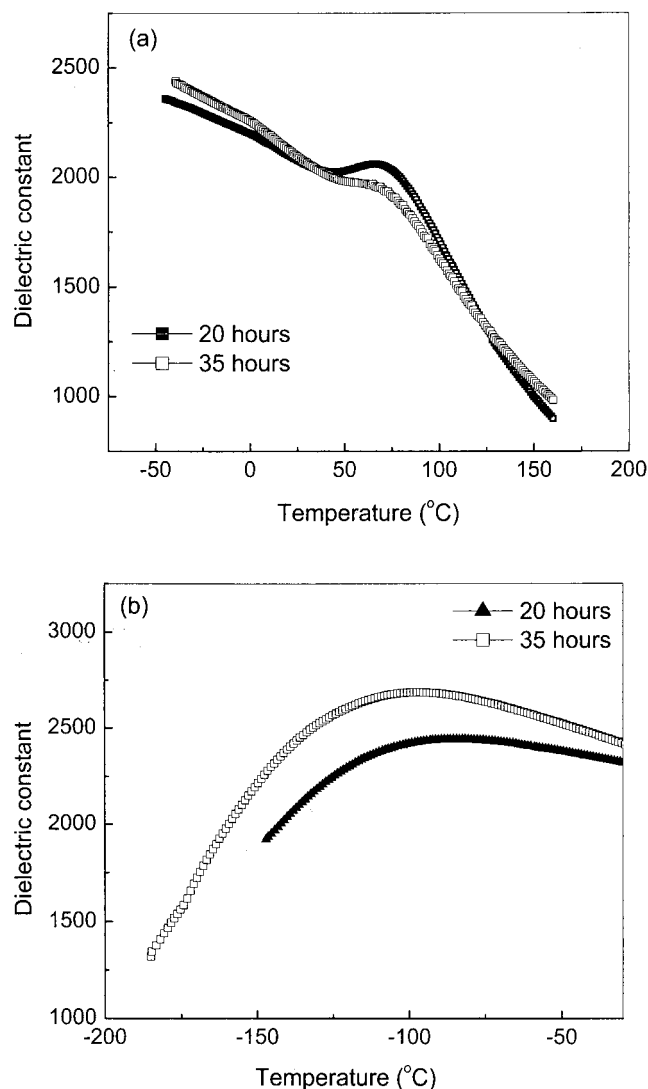


Fig. 5. Dielectric constant as a function of temperature at frequency of 1 kHz for 0.6PNW-0.4PT sintered at 950°C for 2 h and subsequently annealed at 750°C for 20 and 35 h, respectively. The dielectric measurement over temperature range of -190° to -50° C and -50° to -160° C was conducted using an impedance/gain phase analyzer and LCR meter, respectively, resulting in a discontinuity in dielectric constant at around -50° C.

Previous investigation by Yasuyoshi³ shows that the ferroelectric phase transition temperature increases monotonously with increasing PT content in PNW at PT \geq 50%. In the present work, a unique temperature stability of dielectric constant is observed with 0.6PNW-0.4PT derived from mechanical activation. As discussed above, there is a dielectric peak centered at around 74°C of 0.6PNW-0.4PT sintered at 950°C, which is very close to the Curie point for 0.5PNW-0.5PT. It is thus concluded that there is a PT-rich tetragonal phase with the composition close to the 0.5PNW-0.5PT in the PNW-PT sintered at 950°C. We also observed that, at low PT content ($<$ 40%), PNW-PT exhibits relaxor behavior, and the dielectric peak temperature shifts to lower temperatures with increasing PT content. For example, the dielectric peak temperature decreases from -78° C for 0.8PNW-0.2PT to -89° C for 0.7PNW-0.3PT. Therefore, the very diffusive phase transition observed at low temperatures (i.e., over the temperature range of -110° to -80° C) is due to the pseudocubic PNW-PT phase with PT deficiency, as confirmed by both the elemental mapping and Raman spectroscopic studies.

IV. Conclusions

Nanocrystalline 0.6PNW-0.4PT of perovskite structure was synthesized by mechanical activation of oxide composition at room temperature. On sintering at 950°C, the perovskite structure was retained in sintered PNW-PT. Sintered 0.6PNW-0.4PT demonstrated a well-established dielectric dispersion over a wide range of temperatures, which is close to EIA X7R capacitor specifications. The unique temperature stability of dielectric constant over the temperature range of -120° to 20° C arises from the compositional inhomogeneity in PNW-PT, where there is a variation of PT distribution in PNW ranging from 0.3 to 0.6, leading to the coexistence of PT-rich tetragonal and PT-deficient pseudocubic phases as confirmed by the elemental analyses and Raman spectroscopic studies. Accordingly, the dielectric behavior can be fine tuned by annealing at 750°C, which led to a redistribution of the tetragonal and pseudocubic phases.

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