

Effect of tungsten doping on the dielectric response of PZN–PT–BT ceramics with the morphotropic phase boundary composition

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Abstract

In this paper, effect of tungsten doping on the dielectric property of the $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--BaTiO}_3\text{--PbTiO}_3$ system around morphotropic phase boundary (MPB) composition is presented. Samples were prepared according to the formula $\text{Pb}_{0.85-x}\text{Ba}_{0.15}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.7}\text{Ti}_{0.3}]_{1-x}\text{W}_x\text{O}_3$ assuming the compensation for W is achieved via the appearance of the lead vacancies. X-ray diffraction results show that a nearly complete perovskite phase was maintained as W was progressively added up to 5 wt.%. Introduction of W stabilizes the tetragonal phase against the rhombohedral one, resulting in the displacement of MPB composition region towards relaxor end. Moreover, lattice distortion of the tetragonal phase is enlarged, that of the rhombohedral phase is lowered. W-doping leads to an increase in the dielectric permittivity maximum and a decrease in the phase transition temperature (T_m). The frequency dispersion of T_m is successively weakened as W ions are gradually incorporated, reflecting the strengthened couplings among ferroactive oxygen octahedra. A maximum on the degree of diffuse phase transition is observed at 1 mol% WO_3 , which can be interpreted in terms of competing effects of chemical inhomogeneity and ferroelectric couplings. W-doping also induces an increase in the tendency towards Curie–Weiss behavior above T_m , which is associated with the growth of ferroelectric domains. © 2001 Published by Elsevier Science Ltd. All rights reserved.

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1. Introduction

Last several decades have witnessed extensive study on the relaxor ferroelectrics since their discovery by Smolenskii et al.,¹ owing to their significant technical importance on the application of electromechanical devices such as multilayer ceramic capacitors, electrostrictive transducers, micro-displacement positioners. Like $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN), $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZN) is a member of lead-based relaxor ferroelectric family with different cations on the B-site of perovskite lattice. Unlike normal ferroelectric, relaxor ferroelectric displays rounded paraelectric to ferroelectric transition, frequency-dependence of the dielectric permittivity as well as negligible remnant polarization in the absence of bias. Microscopically, relaxor can be viewed as an ensemble of nanometer-sized polar regions with spontaneous

polarization fluctuating among the crystallographically equivalent orientations.²

Pure PZN is scarcely available due to its inherently low tolerance factor leading to the impossibility of fabrication of perovskite PZN under atmospheric condition. Addition of small amount of BaTiO₃ (BT) is a problem-solving practice and, as a result, the PZN–BT solid solution system has been widely investigated.^{3–6} Incorporation of PbTiO₃ (PT) into this system has been shown to reduce the diffuseness of the phase transition and weaken the frequency-dispersion of the dielectric response.⁷ Furthermore, a morphotropic phase boundary (MPB) composition region from 12 to 18 mol% PT, where the tetragonal and rhombohedral phases coexist, has been identified.⁸ In close analogy with $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT), MPB compositions exhibit both enhanced dielectric, ferroelectric,⁴ and piezoelectric properties evidencing the potential of PZN–BT–PT system for electronic applications.

Doping at either the A or B-site of the perovskite structure with isovalent or aliovalent cations is a very

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useful approach to modify the ferroelectric and piezoelectric properties of the host material for practical applications. The underlying mechanism for the property alteration is also of theoretical significance. For instance, La-doping at A-site of MPB composition in the PZN–BT–PT system has been revealed to make the phase transition more diffuse, enhance the relaxor characteristics as well as shift the MPB region towards PT-rich end.⁹ Donor doping of PMN–PT with tungsten has also been experimentally confirmed to significantly improve the electromechanical property providing the doping level is optimally identified.¹⁰

The aim of the present paper was to investigate the effect of W-doping on the phase constituent and dielectric response of MPB composition in the PZN–BT–PT system. To this end, composition containing 15 mol% PT was chosen since it lies in the middle of the MPB composition range and exhibits peak dielectric permittivity. Tungsten was intended to substitute for B-site cations and charge compensation was assumed to be achieved by Pb-vacancies.

2. Experimental procedure

Ceramic samples of various compositions of the W-modified $\text{Pb}_{0.85}\text{Ba}_{0.15}[(\text{Zn}_{1/3}\text{Nb}_{1/3})_{0.7}\text{Ti}_{0.3}]_x\text{O}_3$ system were prepared. The raw powders were weighed according to the formula $\text{Pb}_{0.85-x}\text{Ba}_{0.15}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.7}\text{Ti}_{0.3}]_{1-x}\text{W}_x\text{O}_3$ ($0 < x < 0.05$) where the charge neutrality is maintained by the presence of the negatively charged A-site vacancies. Columbite precursor method¹¹ was used where ZnO and Nb_2O_5 were pre-reacted to form ZnNb_2O_6 . Then powders of WO_3 (>99.9% pure), PbCO_3 (>99%), BaTiO_3 (>99.5%), TiO_2 (>99%) and ZnNb_2O_6 , were weighed in a mole percentage according to the above formula. To compensate for the PbO loss during the calcination and sintering, 5 wt.% of excess PbCO_3 was added. The milled and dried powders were calcined at 900°C for 5 h in a covered alumina crucible with heating and cooling rates of 10°C/min. The calcined product was milled again for 6 h to decrease the particle size. Pellets of 10 mm diameter were obtained by uniaxial pressing at 100 MPa, followed by cold isostatic pressing at 300 MPa. Sintering was performed at 1150°C for 1 h with heating and cooling rates of 15°C/min. To minimize the lead loss, an inverted crucible method developed by Arkas et al.¹² was adopted. Weight loss was less than 0.5 wt.% after sintering and the relative density of the sintered samples measured by Archimedes' method was above 98%.

Phase identification and lattice calculation of the sintered samples crushed into powders were performed by X-ray diffraction using $\text{CuK}\alpha$ radiation. The relative fraction of the pyrochlore phase was calculated using the formula proposed by Swartz et al.¹¹ For the com-

positions containing both rhombohedral and tetragonal phases, partial overlapping of peaks belonging to two different phases at $2\theta = 45^\circ$ on X-ray diffractograms often occurs. In order to calculate the relative fraction and lattice parameters of the two phases, the deconvolution of the ensembles of the peaks was performed to determine the angular position and integrated intensities of each peak. This was accomplished by fitting the parameters of the pseudo-Voigt functions to simulate the individual peaks in the diffraction patterns.¹³ The relative fraction of rhombohedral phase was calculated using the following formula:

$$R(\%) = \frac{I_{r(200)}}{I_{r(200)} + I_{t(002)} + I_{t(200)}} \times 100\%, \quad (1)$$

where $I_{r(200)}$, $I_{t(002)}$, and $I_{t(200)}$ refer to integrated intensity of the (200) plane of the rhombohedral phase, (002) and (200) planes of the tetragonal phase, respectively. Calculation of the lattice parameters was done by the least square approach using the angular position of each peak determined for two phases.

Samples for dielectric measurements were polished and sputtered with gold electrodes. Finally, the electrodes were covered with silver paste to improve electric contact. Dielectric measurements were performed in a tube furnace using HP 4284A LCR meter. Dielectric permittivities and dissipation factors were measured at various temperatures in the frequency range 0.1–100 kHz, as the samples were heated or cooled at a rate of 1°C/min. Measurements showed no obvious differences between heating and cooling.

3. Results and discussion

3.1. Solid solution of WO_3 in $\text{Pb}_{0.85}\text{Ba}_{0.15}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.7}\text{Ti}_{0.3}]_x\text{O}_3$

XRD profiles of sintered ceramics with different amounts of WO_3 are illustrated in Fig. 1(a). All the peaks can be identified as perovskite phase with exception of trace amount of pyrochlore phase for the doped specimens. Increasing the doping level doesn't inevitably bring about more pyrochlore phase (compare 3 and 5 mol% doping). Most of the W added enters into the host lattice rather than precipitates in the form of pyrochlore phase. This point can be further verified by examining the effect of W^{6+} -doping on the relative amounts of rhombohedral and tetragonal phases using profile fitting. In the fitting process, it is assumed that the integrated intensity ratio between (200) and (002) planes is 2:1 for tetragonal phase, and the (200) plane of rhombohedral phase usually overlaps with the same plane of tetragonal phase, leading to the broadening of diffraction profiles around $2\theta = 45^\circ$ for the specimens

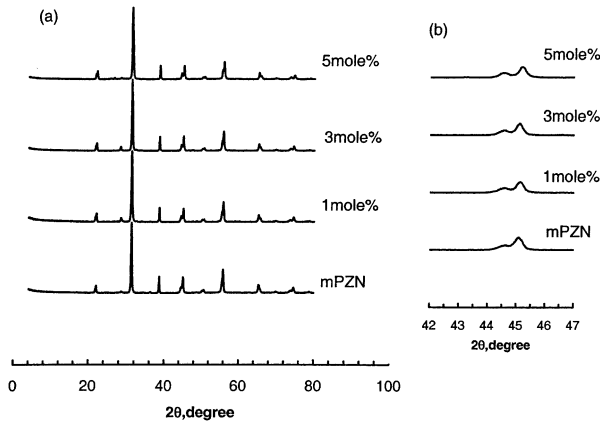


Fig. 1. (a) XRD profiles of undoped and W-doped specimens of the morphotropic phase boundary composition, (b) the magnified portion around peak (200) to highlight the enhanced splitting with doping.

containing both phases. Fig. 1(b) highlights the ever-increasing splitting of these peaks with increasing doping. Presented in Fig. 2 is the variation of the relative amounts of each phase with W addition. Incorporation of W obviously favors the formation of the tetragonal phase against the rhombohedral one. Actually, the 5 mol% doped sample is composed entirely of tetragonal phase. Stabilization of the tetragonal phase against the rhombohedral one subsequently leads to the shift of MPB region at room temperature towards PZN-rich end. In a previous paper,⁹ La³⁺ doping at A-site of the same base material has been revealed to stabilize the rhombohedral phase and move the MPB region to the PT-rich end. Therefore, it appears that the position of MPB region in the PZN–BT–PT system can be adjusted in either direction via appropriate doping.

Not only the amount of the tetragonal phase, but also the tetragonality which characterizes the degree of lattice

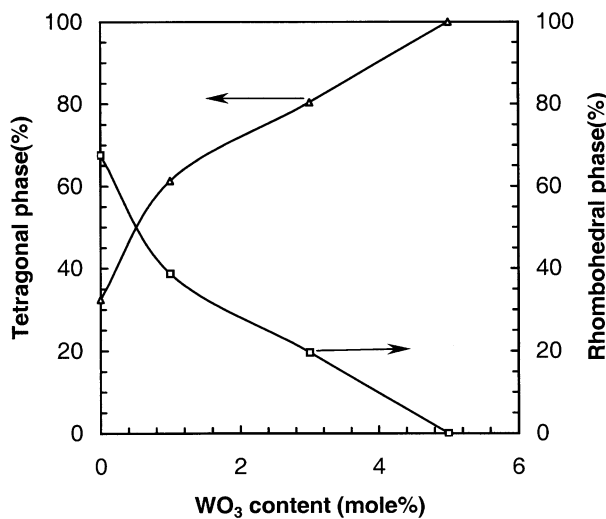


Fig. 2. Variations of the relative amounts of the rhombohedral (or tetragonal) phase with WO₃ content.

distortion, is promoted by W addition, which is shown in Fig. 3. By the same token, both the amount and rhombohedrality (inversely proportional to the rhombohedral angle) of the rhombohedral phase is reduced by W doping. Hence, doping increases overall lattice distortion of the perovskite structure.

3.2. Effect of W doping on the dielectric response

Dielectric permittivity behavior for the base and doped compositions is illustrated in Fig. 4(a–d). One of salient features of doping is the enhanced frequency-dependence of dielectric permittivity, which might be related to the widening of size distribution of polar microregions. As shown in Fig. 5, the value of permittivity maximum is substantially increased by W addition. However, the temperature of permittivity maximum (T_m) is lowered as illustrated in Fig. 6. These observations are fairly consistent with the results of W-doping in PMN–PT ceramics.¹⁰ Another noteworthy trend is the induced weakening of frequency-dispersion of T_m as shown in Fig. 6 where ΔT_1 indicates the temperature difference of T_m at 1 and 100 kHz ($\Delta T_1 = T_m^{100 \text{ kHz}} - T_m^1 \text{ kHz}$) and can be used to evaluate the degree of frequency dispersion for relaxors. This implies the strengthened ferroelectric couplings among ferroactive oxygen octahedra as a result of W-doping.

It is well established that maximization of both dielectric and piezoelectric properties of the MPB composition is attributed to the enhanced domain mobility

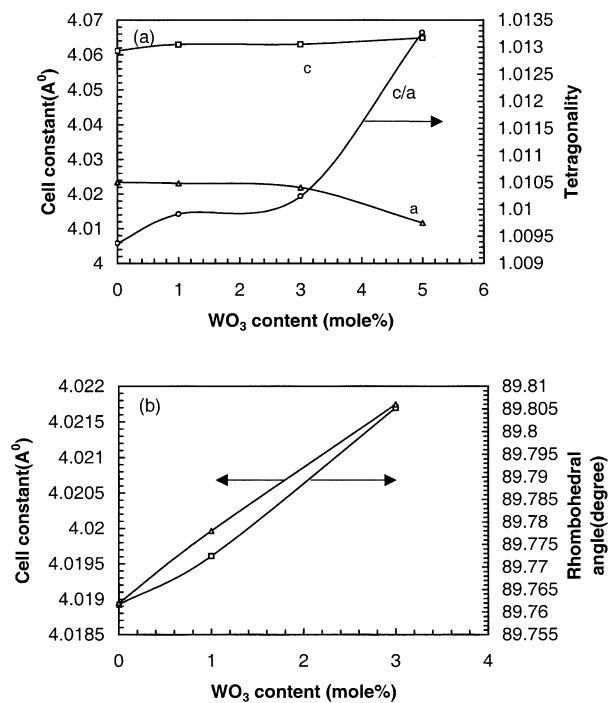


Fig. 3. Effect of W-doping on the lattice parameters of the (a) tetragonal and (b) rhombohedral phases.

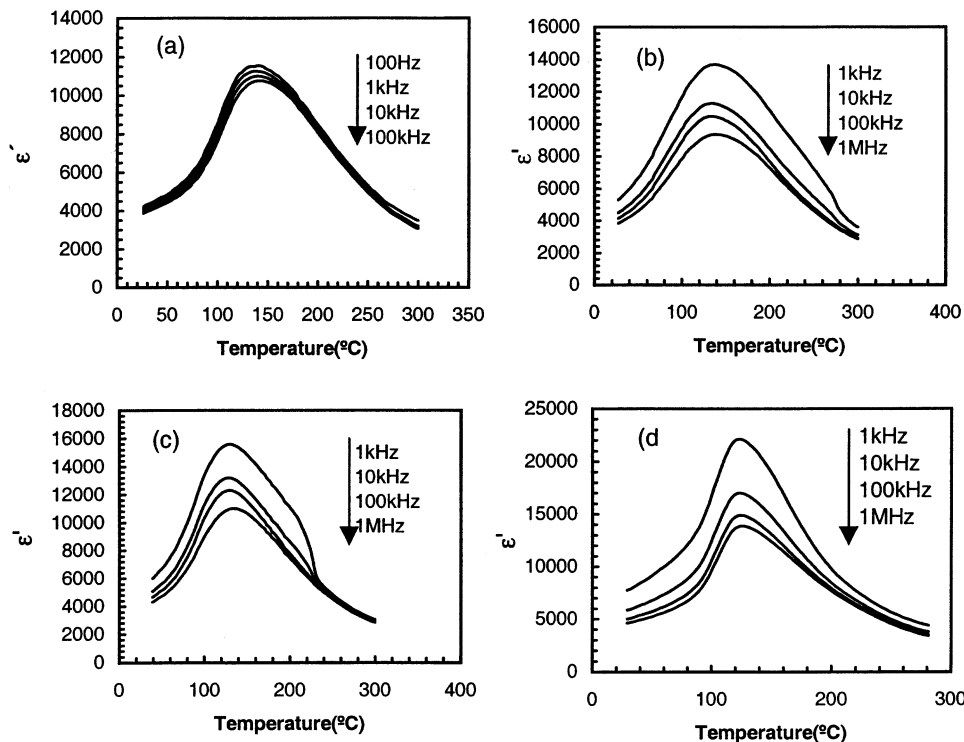


Fig. 4. Dielectric permittivity vs temperature at various frequencies for the undoped and doped compositions: (a) base material; (b) 1 mol% WO_3 ; (c) 3 mol% WO_3 ; (d) 5 mol% WO_3 .

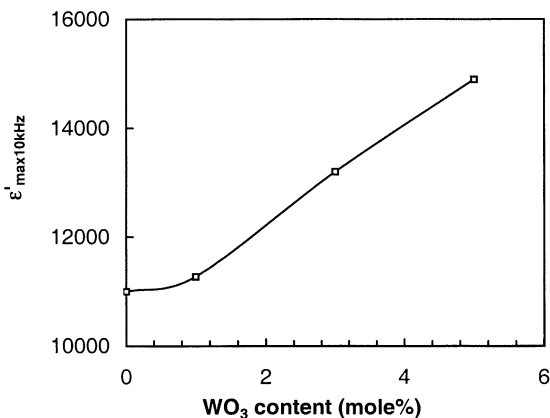


Fig. 5. Effect of doping level on the dielectric permittivity maximum at 10 kHz.

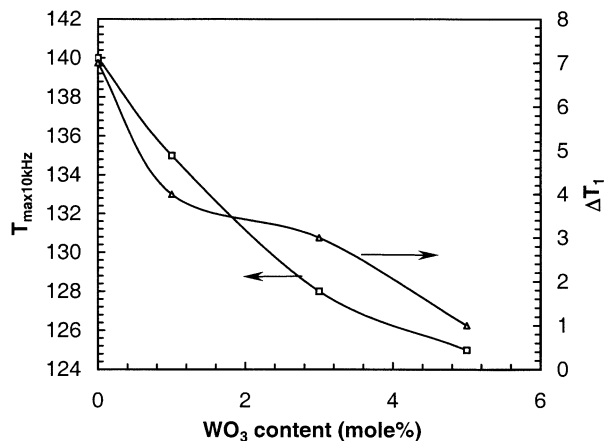


Fig. 6. Effect of dopant concentration on the phase transition temperature at 10 kHz and the frequency-dispersion of T_{max} .

arising from the presence of multiple polarization directions inherent to two phases. W addition can further improve the dielectric property despite the appearance of a single tetragonal phase at relatively higher doping content. This suggests that the enhanced polar moment associated with the spontaneous polarization of W ions outweighs the negative effect of reduced polarization orientations. Based on the composition with the highest doping level, it is expected that dielectric permittivity can be further improved by introduction of a normal ferroelectric with rhombohedralsuch

symmetry such as PbZrO_3 (PZ), thus pushing the composition back into the MPB region.

The role of W is somewhat similar to that of PT: shifting the phase structure to the tetragonal side, increasing the tetragonality as well as weakening the frequency dispersion of T_m . It is equally noticed that the reduced frequency-dependence of T_m does not entail the reduced frequency-dependence of ϵ' , as demonstrated by the response of 1 mol% doped sample. This phenomenon is opposite to the influence of PT addition in that frequency-dependence of both T_m and ϵ' is simultaneously

weakened. However, as WO_3 concentration is further increased, the frequency-dispersion of ϵ' is slightly weakened, as confirmed by the frequency spectroscopy of the normalized permittivity shown in Fig. 7. This indicates that slight doping with W is likely to broaden the size distribution of the polar microregions. Further addition of WO_3 beyond 1 mol% leads to the narrowing of the size distribution of the polar nanodomains, which is believed to stem from the strengthened ferroelectric couplings among polar vectors of spontaneous polarization.

3.3. Effect of W-doping on the diffuseness of phase transition

Illustrated in Fig. 8 are plots of normalized permittivity ($\epsilon'/\epsilon'_{\text{max}}$) against reduced temperature ($\tau = (T - T_m)/T_m$) at 10 kHz for various compositions. These curves explicitly reflect the influence of W-doping on the broadness of phase transition around T_m . A maximum in half width is observed for the 1 mol% doping. A

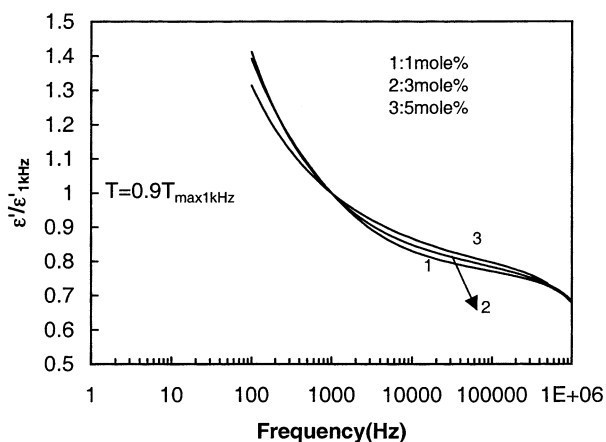


Fig. 7. Normalized dielectric permittivity as a function of frequency for the doped compositions.

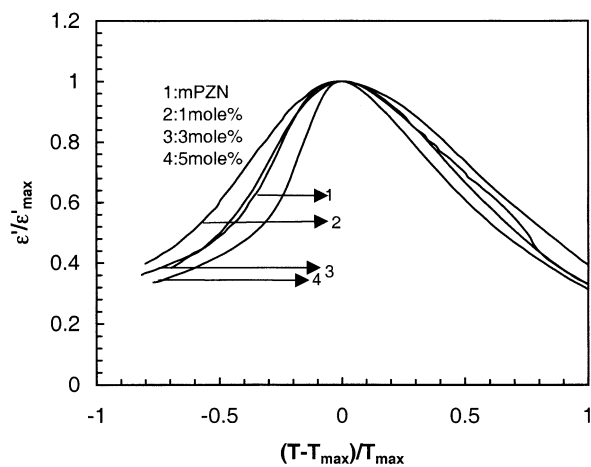
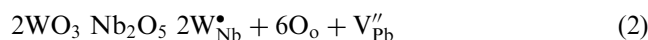


Fig. 8. Normalized dielectric permittivity vs the reduced temperature at 10 kHz for the undoped and doped compositions.

lower or higher level of doping results in the reduced diffuseness. For relaxors, smearing-out of paraelectric to ferroelectric phase transition has been attributed to the presence of local compositional fluctuation on a microscopic scale, giving rise to a distribution of phase transition temperatures. Some microstructural studies reveal that the compositional inhomogeneity in $\text{Pb}(\text{B}'_{1/3}\text{B}''_{2/3})\text{O}_3$ -type perovskites, in particular, originates from the existence of B-site 1:1 short-range ordered nanodomains.¹⁴ These nonstoichiometric domains are rich in B' cations and embedded in B''-rich matrix. Moreover, strong charge imbalance develops where the ordered domains carry a net negative charge as opposed to the disordered matrix.

In the present case, W is intended to substitute for B-site cations and chemical neutrality is achieved by the appearance of Pb-vacancies. Previous investigation¹⁵ on Na-doped PMN indicates that Na cations prefer to replace Mg cations owing to the valence proximity. W ions are most likely to occupy Nb-sites from both size and valence point of view (the ionic radii of W^{6+} and Nb^{5+} are 0.68 Å and 0.70 Å, respectively). Hence, the defect chemistry reaction can be supposed to take place via following equation, which is actually an ionic compensation process:



Where the presence of positively charged $\text{W}_{\text{Nb}}^{\bullet}$ is accompanied by the generation of negatively charged Pb-vacancies. At small doping level (less than 1 mol%), the enhanced broadness of the phase transition can be ascribed to the increased chemical heterogeneity of B-site ions. Both the increased number of B-site cation type and the promoted 1:1 nonstoichiometric short-range ordering are the contributors. The enhanced chemical ordering is chiefly due to the existence of $\text{W}_{\text{Nb}}^{\bullet}$ defects which facilitates the growth of the negatively charged nanodomains.

As WO_3 concentration is increased larger than 1 mol%, the effect of strengthened ferroelectric couplings among oxygen octahedra predominates, the half width characterizing the extent of diffuse phase transition correspondingly falls off. Besides, the defect dipole pairs in the form of $\text{W}_{\text{Nb}}^{\bullet} - \text{V}_{\text{Pb}}^{\prime\prime}$ couple with the polar vectors of spontaneous polarization of B-site cations, especially those of W ions. This also contributes to the enhanced correlation between the lattice dipole moments, and consequently leads to the observed decrease in diffuseness.

Deviation from Curie–Weiss law within a certain temperature interval above T_m is one of salient features of relaxor ferroelectrics.¹⁶ Temperature-dependence of the dielectric reciprocal at 10 kHz for several typical compositions is illustrated in Fig. 9, where the onset temperature (T_{cw}) for the departure from Curie–Weiss

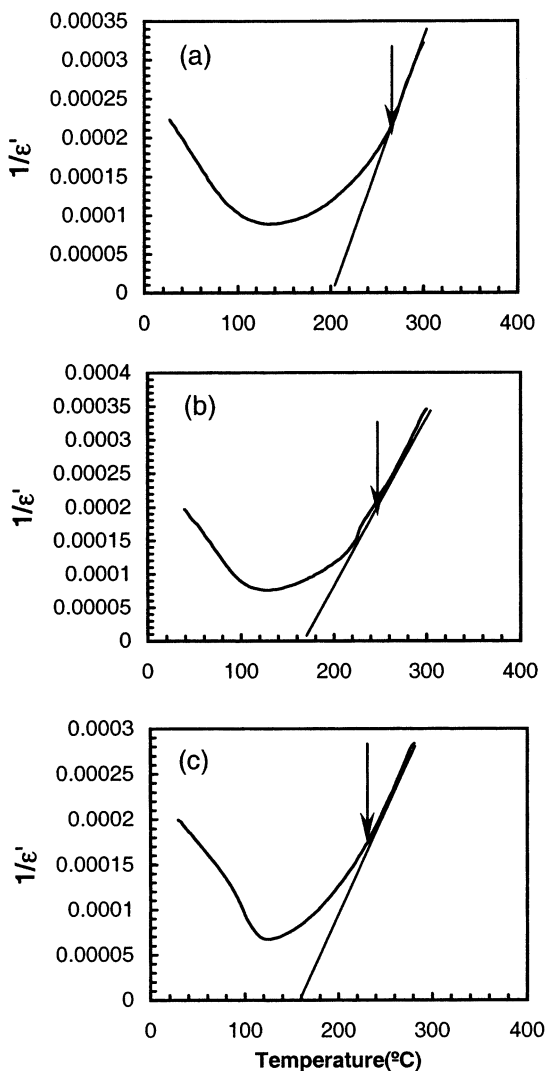


Fig. 9. Temperature dependence of the permittivity reciprocal at 10 kHz for the doped compositions: (a) 1 mol% WO_3 ; (b) 3 mol% WO_3 ; (c) 5 mol% WO_3 .

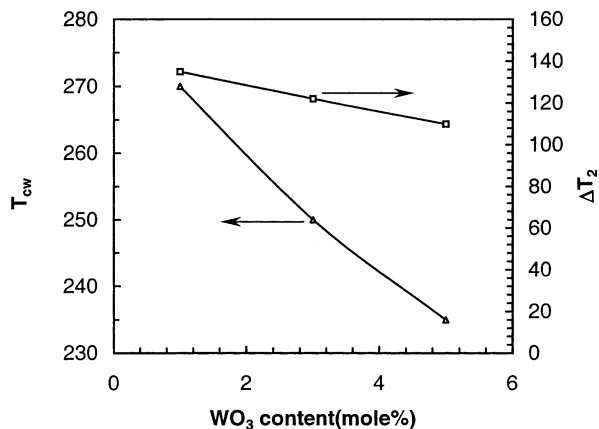


Fig. 10. Effect of dopant concentration on the onset temperature for the departure of Curie–Weiss behaviour (T_{cw}) and the temperature difference between T_{cw} and T_{m} .

phenomenon (linear behavior) is indicated. The temperature gap (ΔT_2) between T_{m} and T_{cw} can be used to assess the degree of this departure. Fig. 10 shows the trends of these two parameters as a function of WO_3 content. Evidently, W-doping leads to the reduction of both T_{cw} and ΔT_2 which implies the enhanced stability of ferroelectric phase as well as enlarged scale of polar domains.

4. Conclusions

1. Using columbite precursor approach, only insignificant amount of pyrochlore phase was encountered with perovskite phase being predominant one even at the highest doping level of 5 mol% WO_3 . Incorporation of W ions into MPB composition of PZN–BT–PT system stabilizes tetragonal phase against rhombohedral one, contributing to the shift of MPB region towards PZN-rich end at room temperature.
2. Increase in W content considerably improves the dielectric permittivity, and moves the phase transition down to room temperature. Doping leads to the successive weakening of the frequency-dispersion of T_{m} . However, the frequency-dispersion of ϵ increases at small doping level, then slightly weakens as the WO_3 concentration is further increased.
3. In close analogy with frequency behavior of ϵ , a maximum on the diffuseness of phase transition occurs at 1 mol% doping level, which can be rationalized in terms of opposing effects between chemical inhomogeneity and ferroelectric couplings. The proximity of dielectric response above T_{m} towards Curie–Weiss behavior also suggests the enhanced stability of ferroelectric phase induced by WO_3 doping.

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