Preparation of PZN-BT-PZT ceramics using A-site element sequential mixing columbite method

Chen-Liang Li[a)], Chen-Chia Chou[a)] and Dah-Shyang Tsai[b)]

[a)]Department of Mechanical Engineering, [b)]Department of Chemical Engineering, National

Taiwan University of Science and Technology, Taipei 106, Taiwan.

Complex $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN)-based ceramics have been prepared by three different columbite methods: individual columbite (IC), modified columbite (MC) and A-site elements sequential mixing columbite (ASMC). The sintered ceramics via the IC method, their pyrochlore ratio were always higher than those prepared from the other two methods. Addition of a perovskite phase, such as $BaTiO_3$ and $PbZrTiO_3$, to effectively reduce the pyrochlore content of PZN has been a criterion in evaluating various preparation methods. The perovskite/pyrochlore ratio was decreased effectively by MC process. However, the pyrochlore was not removed completely by MC process to PZN-rich compositions. The presence of a substantial amount of pyrochlore phase in PZN-base ceramics causes a decreasing in the dielectric properties. The transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) observation of the MC samples show that the BaO was segregated at triple junctions, implying that stabilization of the perovskite structure of the specimens was not completely achieved due to element segregation. The full perovskite phase was obtained by ASMC method for all compositions, and the dielectric constant of ASMC ceramics was higher than those of IC and MC. Even thought the pyrochlore phase can be removed by all three processes at the same composition, and the dielectric behavior of PZN-base ceramics was markedly affected by processing procedures.

Keywords: Electron microscopy, Ferroelectric, Dielectric properties, Perovskite,

Sintering.

Introduction

Lead zinc niobate, $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN), is a relaxor type of ferroelectric material.[1] The solid solution between PZN with rhombohedral symmetry and $PbTiO_3$ (PT) with tetragonal symmetry has a morphotropic phase boundary (MPB) near 10 mol % PT.[1] Single crystals with composition near MPB shows extremely large dielectric constant (k>>22,000) and piezoelectric coefficients Kp~92%, d_{33}~1500pC/N.[2] However, it has been reported that perovskite PZN or 0.9PZN-0.1PT crystals are thermodynamically unstable over a wide range of temperatures (600-1400) rapidly yielding a pyrochlore phase and PbO and ZnO as it decomposes.[3-5] To date, the most useful method to stabilize the perovskite structure includes additives such as $BaTiO_3$ (BT) and $SrTiO_3$ and so on.[6-7] The bond valence method was an effective way to estimate how many additives could stabilize the PZN perovskite structure.[8] However, formation of the pyrochlore phase has been frequently observed in lead-based $Pb(B_1,B_2)O_3$ type ferroelectric compounds which are supposed to possess perovskite structure. Yet the columbite method was effective in decreasing the pyrochlore phase in $Pb(B_1,B_2)O_3$ ceramics system. The columbite method can be employed to prepare pyrochlore free for the $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramic system, but it was difficult to use in a PZN ceramic system, indicating that atomic arrangement and phase formation in PZN ceramics may be correlated with preparation procedures or sequences, even if a columbite method was adopted.

In the present study, we attempted to find the best processing sequences to synthesize a perovskite PZN ceramic system. We believed that there are various reaction routes when one uses different processing procedures. Therefore we modified the mixing sequences during material processing, was based upon the structural and microstructural analysis, in order to obtain PZN ceramics with appropriate electric properties.

Experimental Procedure

According to the formulas $x(0.94 \, Pb(Zn_{1/3}Nb_{2/3})O_3 + 0.06 \, BaTiO_3) + (1-x)PbZr_{0.52}Ti_{0.48}O_3$, $x(PZN+BT)+(1-x)PZT$, the specimens studied in this investigation were fabricated. The compounds were prepared using three preparation sequences: (a) individual columbite (IC), (b) columbite method (MC) and (c) sequential mixing columbite method (ASMC), as shown in Fig. 1.

The structure of samples was investigated by using powder X-ray diffraction (XRD). Percentage of the perovskite phase can be calculated from the X-ray peak intensities by using the following equation: $\% \, perovskite = I_{perovskite \, (110)} / (I_{perovskite \, (110)} + I_{pyrochlore \, (222)})$. The microchemical homogeneity of the specimens was examined by using an Energy Dispersive X-Ray Spectrometer (EDS) on a Field Emission Gun Transmission Electron Microscope (FEG-TEM) (Philips Tecnai F30). The electron beam was contracted to 10 nm during EDS analysis of FEG-TEM.

After the pellets were polished, gold sputtered, painted with silver paste as electrodes, and fired at 600   for 30 mins. Dielectric measurements were conducted to an HP4194A automated system which with a temperature controlled chamber to measure the dielectric constant of the specimens as a function of temperature between 100 Hz and 1 MHz. The samples were heated at a rate of 2   /min.

Results and Discussion

The ferroelectric structure in all compounds was estimated by a bond valence method.[8] If the value of bond valence was greater than 1.74, the compound had a stable perovskite structure. This method can be used to estimate the stability of the perovskite structure for all x values. The perovskite structure of the specimens of chosen compositions should be stable after fabrication.

The amount of perovskite phase of various x specimens for various processes was shown in Fig. 2. The free pyrochlore phase can be eliminated only at x=0.5 and the amount of pyrochlore phase increased as x increased after sintering at 1150   for 2 h in the IC process. After calcining the specimens, both MC and ASMC process could provide a full perovskite structure. But the amount of pyrochlore phase was increased as the PZN content increased for the MC process sintering samples, when x was greater than 0.7. However, it is clear that the MC method is more effective than that of IC method in reducing the pyrochlore phase. Whatever the MC method still could not remove the pyrochlore phase for all compositions after sintering.

Using EDS chemical composition analysis to investigate the atomic distribution of elements, the theoretical value of the Ba content is 1.5 at%, but it is 0.34 at% and 3.62 at% respectively in the grain and at triple junctions as shown in Fig. 3, implying that most of the Ba^{2+} ions had segregated at the grain boundaries. Furthermore, the free energy of PbO is lower than BaO,[9] so it was easier to form a perovskite structure with B-site precursor reacting by PbO. When all the A-sites were occupied by Pb^{2+} ions, the Ba^{2+} ions will segregate at the grain boundaries. When the dissolution of Ba^{2+} ions is not enough, the pyrochlore phase region forms in sintering temperature at 1150 , and can not be removed. Thus the sintered samples with compositions of x > 0.7 have a pyrochlore phase by using the MC process.

A new process by considering the mixing sequences of A-site elements, called "A-site elements sequential mixing columbite method (ASMC)" could solve this problem. All compositions of calcined powder and sintered samples could obtain the complete perovskite structure by the way of ASMC process, as shown in Fig. 2.

Only the specimens of x=0.5 for PZN-BT-PZT ceramic system can be synthesized to a complete perovskite phase by all processes. However, there are differences to the lattice structures of the perovskite phase prepared by different methods. The XRD patterns display

perovskite structures with two different sets of lattice parameters co-existing in a IC process sample at composition of x=0.5, as shown in Fig. 4. Whereas, ASMC samples clearly showed a single tetragonal perovskite structure in the XRD patterns. It had been studied that the micro-region heterogeneity would affect the phase structures and dielectric properties in PZN-PT-BT ceramic system.[10-11] In the IC approach, the full perovskite phase of BT and PZT were used to synthesize a new perovskite PZN-BT-PZT phase. The large tolerance factor and electronegativity difference of BT and PZT would form more stable perovskite phase. Therefore, it was difficult to create a homogeneous composition through a solid state diffusion. Therefore, the phase of IC samples could not be defined clearly. The results indicated that composition homogeneity did not occur in IC specimens, and it neither improved the electric properties nor created a stable perovskite structure by the addition of BT.

The minimum temperature synthesizing BT with BaO and TiO_2 is 1100 or above[12] and PZT was difficult to synthesize perovskite phase using an oxide-mixing method[15]. However the powders through both MC and ASMC processes could form a single perovskite phase after calcined at 950 for 4 h, implying that synthesis of powders may pass through various chemical routes by different processes. All ions would be sequenced appropriately during a synthesis process to occupy the sites accurately. Therefore, A-site ions with higher chemical reactivity would dissolve late to the system. This concept was used in ASMC method so it was easier to synthesize perovskite for all compositions.

The dielectric constant and dielectric loss versus temperature curves of PZN-BT-PZT for x=0.5 at 1 kHz was shown in Fig. 5. There was not clear difference between dielectric constant of MC and ASMC but the temperature for the peaks in the dielectric constant curve, T_m, was shifted by different processes. There were also differences between solid solution of Ba^{2+} ion for MC and ASMC process based upon EDS results. On the other hand, the dielectric

constant of IC samples was obviously lower than those of MC and ASMC samples. This may be attributed to the heterogeneous composition of IC samples. The dielectric loss of MC samples was larger than that of ASMC sample. The Ba^{2+} ions did not dissolve in the grains of MC samples to stabilize the structure which may induce defects in the samples. The defects would decrease dielectric constant and increase dielectric loss.

Conclusions

There were various chemical reaction routes to synthesize ceramics of the PZN-BT-PZT system. The perovskite phases of BT and PZT were too stable to decompose and diffuse into the grain to suppress the pyrochlore phase in PZN ceramics. Therefore, the route of forming solid solution between $ZnNb_5O_6$ columbite with titania or zirconia before the addition of lead oxide or barium oxide is more beneficial to the suppressing of PZN pyrochlore phase. Hence the MC method was effective in synthesizing perovskite PZN-BT-PZT ceramics. However, the important issue in synthesis was not only the mixing of B-site cations but also the mixing A-site cations. In the study, reaction of barium oxide with other oxide ingredients was difficult since barium oxide was a refractory ingredient and its dissolution only occurs under high temperatures. Finally we conclude that the ASMC method was the best process to synthesize perovskite PZN-BT-PZT ceramics.

On the other hand, the phase of structure and dielectric properties were effected directly by processing sequence. The microcompositional homogeneity was improved by the ASMC process so that the dielectric constant and dielectric loss could be advanced.

Acknowledgments

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Figure Captions

Fig. 1 experimental process (a) IC, (b) MC and (c) ASMC.

Fig. 2 the percentage of perovskite phase for variant x compound was (a) calcined powder at
950 for 4h and (b) sintering bulk at 1150 for 2 h by various methods.

Fig. 3 (a) TEM image and (b) EDS spectra at triple junction for MC specimens. The Ba^{2+} is
segregation at grain boundary.

Fig. 4 Room-temperature XRD profiles for 0.5(PZN+BT)+0.5PZT materials with various
process.

Fig. 5 The temperature dependence of dielectric constant and dielectric loss at 1 kHz for
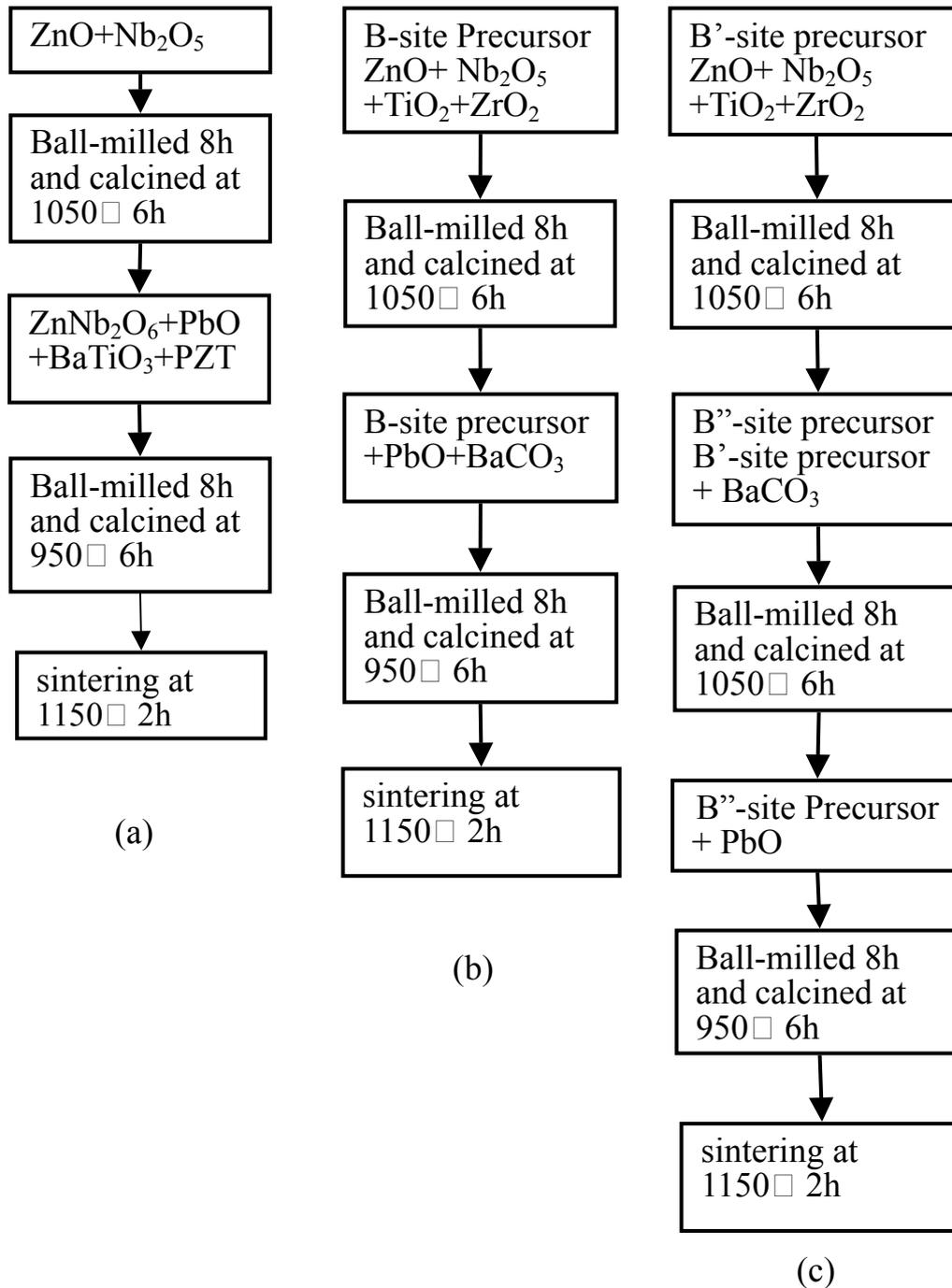0.5(PZN+BT)+0.5PZT materials with variant processes.

(a)

ZnO+Nb$_2$O$_5$
↓
Ball-milled 8h and calcined at 1050℃ 6h
↓
ZnNb$_2$O$_6$+PbO +BaTiO$_3$+PZT
↓
Ball-milled 8h and calcined at 950℃ 6h
↓
sintering at 1150℃ 2h

(a)

(b)

B-site Precursor ZnO+ Nb$_2$O$_5$ +TiO$_2$+ZrO$_2$
↓
Ball-milled 8h and calcined at 1050℃ 6h
↓
B-site precursor +PbO+BaCO$_3$
↓
Ball-milled 8h and calcined at 950℃ 6h
↓
sintering at 1150℃ 2h

(b)

(c)

B'-site precursor ZnO+ Nb$_2$O$_5$ +TiO$_2$+ZrO$_2$
↓
Ball-milled 8h and calcined at 1050℃ 6h
↓
B''-site precursor B'-site precursor + BaCO$_3$
↓
Ball-milled 8h and calcined at 1050℃ 6h
↓
B''-site Precursor + PbO
↓
Ball-milled 8h and calcined at 950℃ 6h
↓
sintering at 1150℃ 2h

(c)

Fig. 1 experimental process (a) IC, (b) MC and (c) ASMC.

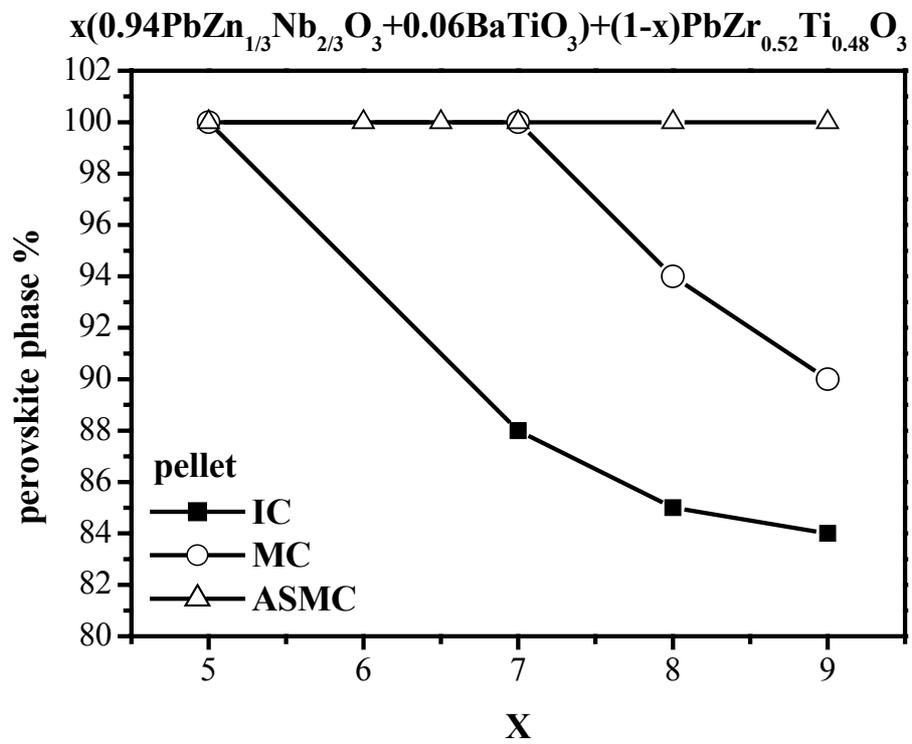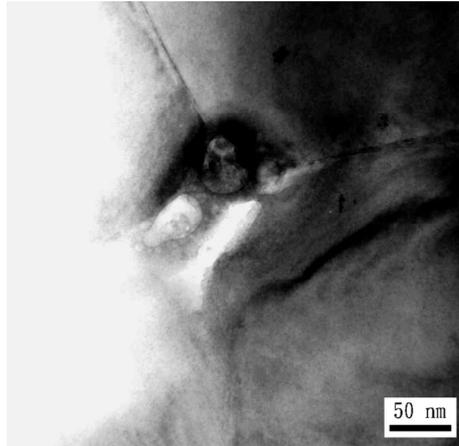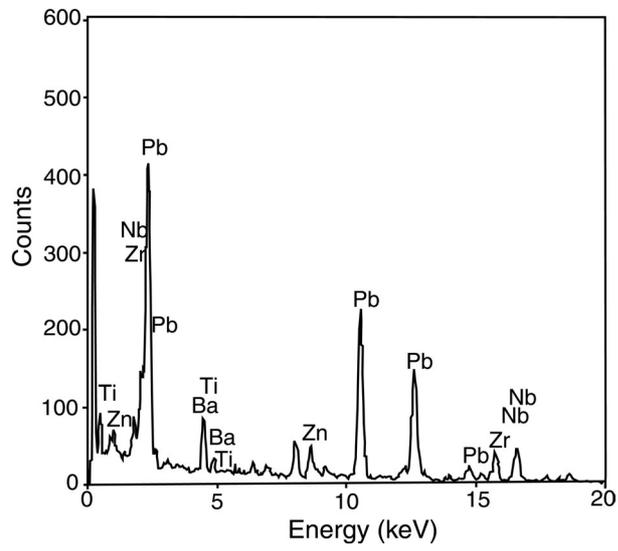**x(0.94PbZn$_{1/3}$Nb$_{2/3}$O$_3$+0.06BaTiO$_3$)+(1-x)PbZr$_{0.52}$Ti$_{0.48}$O$_3$**

Fig. 2 the percentage of perovskite phase for variant composition of PZN+BT+PZT materials, which were as-sintered at 1150 for 2 h, respectively.

(a)

(b)

Fig. 3 (a) TEM image and (b) related EDS spectrum in triple junction for x=0.5 MC specimens. The Ba^{2+} is segregation at grain boundary.
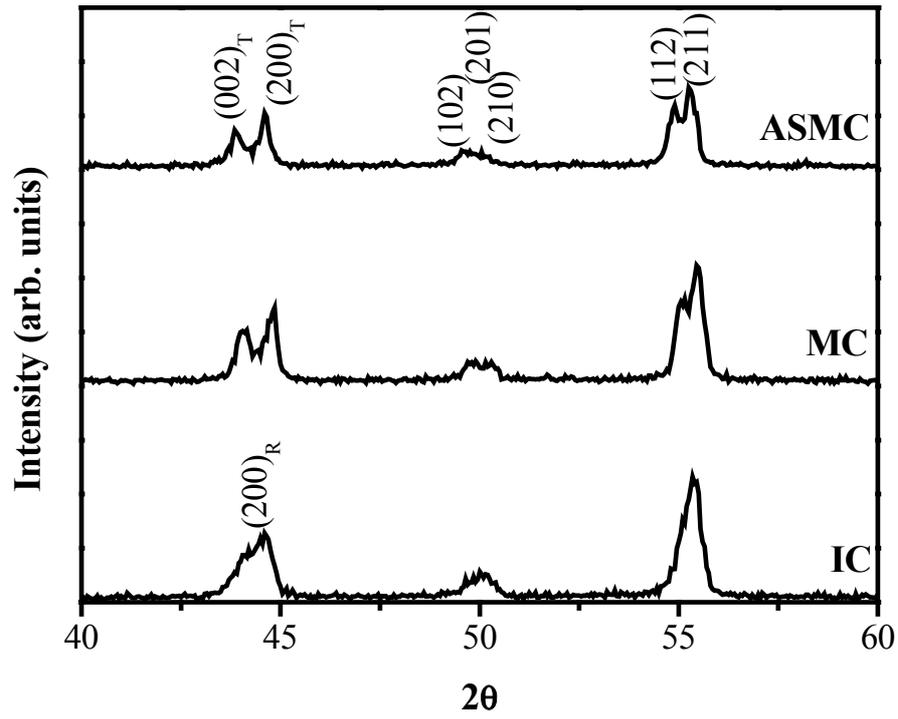
$0.5(0.94PbZn_{1/3}Nb_{2/3}O_3+0.06BaTiO_3)+0.5PbZr_{0.52}Ti_{0.48}O_3$

Fig.   4
R
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om-temperature XRD profiles for 0.5(PZN+BT)+0.5PZT materials with various process.
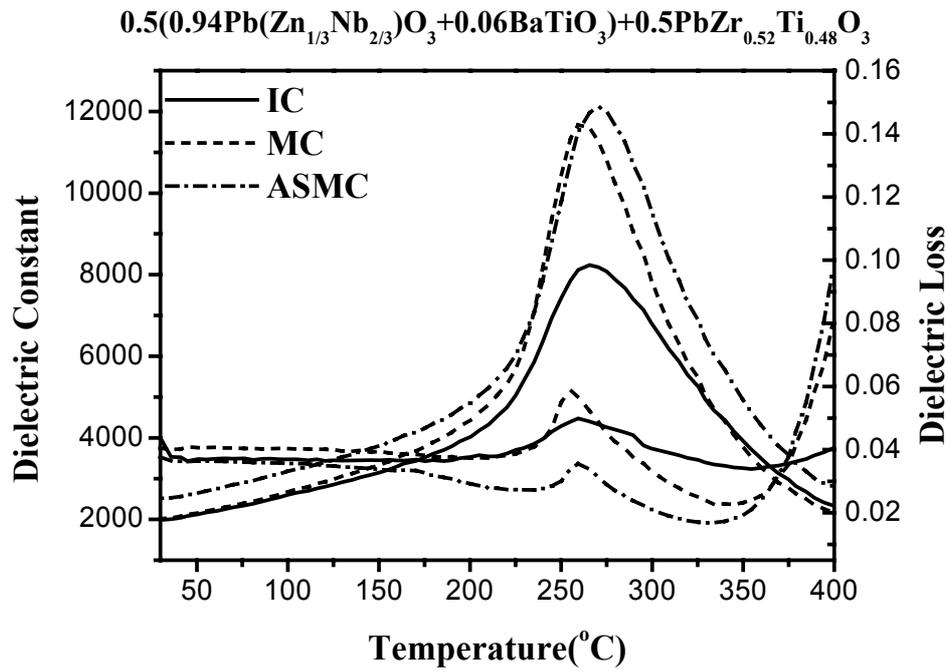
$$0.5(0.94Pb(Zn_{1/3}Nb_{2/3})O_3+0.06BaTiO_3)+0.5PbZr_{0.52}Ti_{0.48}O_3$$

Fig. 5 The temperature dependence of dielectric constant and dielectric loss at 1 kHz for 0.5(PZN+BT)+0.5PZT materials with variant processes.