Effect of Excessive Nb$_2$O$_5$ on the Sintering and Electrical Property of Lead Metaniobate Piezoelectric Ceramics

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Abstract: PbNb$_2$O$_6$-$x$mol%Nb$_2$O$_5$ (PN--$x$=0, 5, 10, 15, 20) Piezoelectric ceramics were prepared by solid-state reaction method. The effects of excess Nb$_2$O$_5$ on the sintering and electrical properties of PbNb$_2$O$_6$ ceramics were investigated. The sintering and electrical properties were evidently improved after the addition of Nb$_2$O$_5$ into PN in the condition set for a high $T_c$ and high coupling anisotropy. The improvement may originate from NbO$_6$ octahedral distortion by excess Nb$_2$O$_5$, which prevents phase transition from rhombohedral to tetragonal during the sintering process. With excess addition of Nb$_2$O$_5$, the piezoelectric coefficient ($d_{33}$) and relative density of PN ceramics increased and reached up to 69 pC/N and 93.1%, respectively, at 5mol% addition of Nb$_2$O$_5$.

Key words: PbNb$_2$O$_6$; piezoceramics; Nb$_2$O$_5$; piezoelectric property; tungsten bronze

The tungsten bronze-type lead metaniobate PbNb$_2$O$_6$ (PN) based piezoceramics have drawn a lot of attention due to their higher $T_c$ ($T_c$: ~550 $^\circ$C) than that of Pb(Zr,Ti)O$_3$ and BiScO$_3$-PbTiO$_3$ based piezoceramics, which makes them can be applied in sensors and actuators operating in high temperatures, particularly, in the fields of aerospace and automotive industries$^{[1-3]}$. The low mechanical quality factor and acoustic impedance properties of PN are desirable in broadband ultrasonic transducers$^{[4]}$, and a high response of PN in hydrostatic pressures which can be achieved by high coupling anisotropy (comparing to longitudinal coupling, the planar coupling values are negligible) is also promising in underwater sonar field. However, it is difficult to get a single ferroelectric orthorhombic phase in pure PN ceramics. In addition, the dense PN is difficult to be achieved by solid-state fabrication techniques due to the phase transition from rhombohedral to tetragonal occurs at 1200 $^\circ$C–1240 $^\circ$C during sintering process$^{[5-6]}$, leading to porous PN ceramics with low density, obvious crack and abnormal grain growth, which makes their piezoelectric properties and fatigue resistance greatly deteriorated.

In order to obtain dense PN piezoceramics with high piezoelectric properties, the quenching method is mostly used, which can stabilize the orthorhombic phase at high temperature$^{[7]}$. However, this method is challenged in face of high quantities of processes. Another approach is appropriate doping such as Ca$^{2+}$ and Ba$^{2+}$ substitution for Pb$^{2+}$ and Ti$^{4+}$ for Nb$^{5+}$. For example, Venet et al$^{[8-10]}$ reported Ca$^{2+}$ and Ti$^{4+}$ ions can facilitate the densification of PN-based ceramics, and increase $T_c$, but also decrease the coupling anisotropy. Moreover, Dy$^{3+}$ and Ba$^{2+}$ were found to improve the sintering performance and make the densities of the ceramics higher (relative density, 92%), but meanwhile weaken the coupling anisotropy of the pure PN$^{[11]}$. The ions of Ce$^{3+}$ and Ba$^{2+}$ increased density and improve piezoelectric performance$^{[12-13]}$, while $T_c$ was reduced sharply ($T_c$, 300 $^\circ$C).

In this work, a simple method of adding excess Nb$_2$O$_5$ to PN was designed. The microstructure, sintering and electrical properties of PN ceramics with excess Nb$_2$O$_5$ were investigated.

1 Experimental

Ceramic samples with compositions of PN-$x$mol%Nb$_2$O$_5$ ($x$=0, 5, 10, 15 and 20, abbreviated as PN, PN-5, PN-10, PN-15 and PN-20, respectively) were prepared by solid state reaction method. Appropriate amounts of raw materials of Pb$_3$O$_4$ (99.00%) and Nb$_2$O$_5$ (99.90%) powders were mixed and then calcined at 800 $^\circ$C for 2 h, followed by remilling in ethanol for 24 h. All samples with the
dimension of 13 mm in diameter and 1.5 mm in thickness were sintered in air at 1260°C-1280°C for 3.5 h.

The bulk density of all the ceramics was measured by Archimedes immersion technique. The crystal structure of ceramics was characterized by X-ray diffraction (XRD, D8 ADVANCE; BRUKER, Germany) and Raman spectra (inVia, Renishaw, English), and the surface morphologies were observed using a scanning electron microscope (SEM, Hitachi, Tokyo, Japan). Both sides of the samples with the thickness of 0.5 mm were coated with a thin layer of silver paste, and were fired at 750°C for 30 min. The samples were poled in a silicone oil bath with a DC field of 6 kV/mm at 100°C for 30 min. The piezoelectric constants $d_{33}$ were measured using a $d_{33}$ meter (Model ZJ-3; Institute of Acoustics, Chinese Academy of Sciences, Shanghai, China). The temperature dependence of the dielectric constant and loss were measured by a precision impedance analyzer (E4980A, Agilent, Palo Alto, USA) from room temperature to 650°C. The electromechanical coupling factor and mechanical quality factor were calculated from data measured by the impedance analyzer (E4990A, Keysight, USA).

## 2 Results and discussion

Fig. 1 shows the typical SEM micrographs of natural surfaces of PN, PN-5, PN-10, PN-15 and PN-20 ceramic samples. For pure PN ceramics, there are abnormally grown grains with very large cracks as shown in Fig. 1(a), which is due to the phase transition from rhombohedral to tetragonal during sintering process. After the introduction of additional Nb$_2$O$_5$, it can be seen that the grain size becomes uniform and much smaller and most importantly there are less cracks from the surface images as shown in Fig. 1(b-e), which results in a significant increase of the relative density from 78% to 93%. These demonstrate that the excess of Nb$_2$O$_5$ has a positive effect on the sintering behavior of PN ceramics, which could be due to that Nb$^{5+}$ is very helpful for the mass transfer during PN ceramic sintering, as evidenced the role of Nb$^{5+}$ dopant into PZT ceramics$^{[14]}$. On the other hand, it’s known that the density of PN ceramics is mainly determined by the abnormal grain formed during transition from rhombohedral to tetragonal phase$^{[4]}$. In this study, it may be assumed that the excess of Nb$_2$O$_5$ can suppress the transition of rhombohedral to tetragonal phase in consequence of less cracks and higher density.

To further verify the assumption, thermal XRD was performed in this study. Fig. 2 shows XRD patterns of PN and PN-5 ceramic samples in the temperature range from 25°C to 1290°C. For the PN sample in Fig. 2(a), it is a rhombohedral phase at a temperature of 25°C to 1000°C, and a tetragonal phase appears at 1200°C. An orthorhombic phase occurs when the temperature rises to 1240°C, and the tetragonal phase becomes completely an orthorhombic phase when the temperature reaches 1270°C. Fig. 2(a) and (c) illustrate that the two main peaks appear at $2\theta$=45.1° and 45.2°, which suggest the presence of phase transitions of rhombohedral to tetragonal phase between 1000°C–1200°C for PN as Roth$^{[15]}$ reported. However, Fig. 2(b) and (d) show that there are no tetragonal phases at all test points within 25°C to 1290°C for PN-5 samples. It can be concluded that phase transition of rhombohedral to tetragonal which occurs in the processing of pure PN sintering is absent for PN-5 samples. So this thermal XRD result verified the previous assumption.

![Fig. 1 SEM micrographs of PN-x samples](image)

(a) $x=0$; (b) $x=5$; (c) $x=10$; (d) $x=15$; (e) $x=20$
Fig. 2 Thermal XRD peak profiles for PN–x ceramics in the temperature range from 25°C to 1290°C (a, c) x=0; (b, d) x=5

Fig. 3 shows the temperature dependence of dielectric constant (1 kHz) and dielectric loss (tanδ, 1 kHz) of samples with different content of Nb2O5 (x=0, 5, 10, 15 and 20). As it can be seen, Tc and the maximum dielectric constant of the sample increase with the increases of Nb2O5. The addition of excess Nb2O5 into the PN may produce a reaction as equation (1), resulting in vacancies and internal stresses that can enhance dielectric properties.

\[
\text{1/2Nb}_{2}\text{O}_{5} + \text{PbNb}_{2}\text{O}_{6} \rightarrow \text{Pb}_{1-\text{x}}\text{Nb}_{x}\text{O}_{3-\text{x}} + 5/2\text{V}_{\text{O}} + 5/2\text{O}_{\text{O}}
\]  

Hiroshima, et al\[16\] reported that Tc changes due to internal stresses and cation ordering. However, porosity and cracks can relieve internal stresses, resulting in the low Tc. So the internal stresses cannot explain the variation in Tc for studied samples. Another explanation of the variation in Tc is the cation ordering. The reason why Tc of the samples with excess Nb2O5 is increased should be that the excess of Nb2O5 leads to a change in the cation ordering degree in the PN.

To further study the above conjecture, the Raman spectra was performed in this section. Fig. 4 shows the Raman spectra of the Nb2O5-adding PN ceramics with different compositions. In many previous spectroscopic studies, the internal modes of oxygen octahedron BO6 are found to mainly influence the Raman spectra in tungsten bronze family\[17-25\], and moreover, show a common characteristic. There are three similar Raman active modes of tetragonal tungsten bronze with the point group of C4v and C2v, and they appear at around 250 cm\(^{-1}\) (v5, O–B–O bend vibration), 630 cm\(^{-1}\) (v2, B–O stretch vibration), and 845 cm\(^{-1}\) (v1, B–O stretch vibration). As it can be seen, there are four wavenumber regions: below 180 cm\(^{-1}\), 180 cm\(^{-1}\)–280 cm\(^{-1}\) (v5), 500 cm\(^{-1}\)–700 cm\(^{-1}\) (v2) and 700 cm\(^{-1}\)–1000 cm\(^{-1}\) (v1) for studied samples Raman lines (Fig. 4 (a)). AMira, et al\[19\] reported that the Raman spectrum of the low-frequency part corresponds to the vibrational mode of the cation in the tetragonal tungsten bronze and depends on the nature of the cations. In this study, the low-frequency region (<180 cm\(^{-1}\)) may reflect the vibrations of cations and the other region reflect the internal modes of oxygen octahedron NbO6. The modes v1, v2 and v5 of the Raman spectra of the samples added with excess Nb2O5 were broadened compared with the pure PN, which may be due to the addition of Nb2O5 into PN resulting in distortion of the NbO6 octahedron. Significant change appears in the mode v5. The mode v5 is split into 207 cm\(^{-1}\) and 256 cm\(^{-1}\) in the pure PN, while it is split into 207/238/256 cm\(^{-1}\) in the samples with excess Nb2O5. Xia, et al\[25\] reported that the mode v5 is split into 207/238/290 cm\(^{-1}\) resulting from the influence of the Li ions in the C sites on the internal vibrations of [NbO6]\(^{7-}\) for potassium lithium niobate. Therefore, the splitting of the mode v5 in the addition of Nb2O5 into PN...
sample may be due to Nb occupying the C sites on the internal vibrations of $[\text{NbO}_6]^{7-}$ (Fig. 4 (b)), which can cause cations disorder. This result is also consistent with the above conjecture.

Fig. 5 depicts the relative density, piezoelectric coefficient ($d_{33}$), mechanical quality factor ($Q_m$) and the longitudinal coupling factor ($k_{33}$), of Nb$_2$O$_5$-added PN samples. As it can be seen, the relative density first increased and then decreased with the increasing amount of Nb$_2$O$_5$ (Fig. 5(a)). The relative density of all Nb-adding samples are above 90% with a maximum density up to about 93.1% for PN-5. The variation of $d_{33}$ and the longitudinal coupling factor ($k_{33}$) is in line with the relative density (Fig. 5(b) and (c)), which may be caused by the lattice distortion due to addition of Nb$_2$O$_5$. Fig. 5(d) shows that mechanical quality factor ($Q_m$) increases with the increase of Nb$_2$O$_5$ content, which may be the result of the increased density and lattice distortion caused by the addition of excess Nb$_2$O$_5$ to PN.

3 Conclusions

An interesting way was found to solve the sintering and low relative density problems associated with pure PN, namely adding appropriate amount of Nb$_2$O$_5$ into pure PN, which could allow the modified PN with excellent properties of higher piezoelectricity, high coupling anisotropy and high $T_c$. Since the excess addition of Nb$_2$O$_5$ into the PN inhibits the phase transition from rhombohedral to tetragonal, the relative density of the samples increased and the sintering performance is improved as well. The reason why the piezoelectric performance and $T_c$ of the sample ceramics after adding excess Nb$_2$O$_5$ may be due to the ions of Nb$^{5+}$ occupying the C sites. When the PN ceramics was added with 5mol% of Nb$_2$O$_5$, $d_{33}$, relative density and longitudinal coupling factor ($k_{33}$) were 69 pC/N, 93.1% and 0.33, respectively.

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过量 Nb$_2$O$_5$对偏铌酸铅压电陶瓷烧结性能和电学性能的影响

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摘 要：采用传统的固相烧结法制备了组成为 PbNb$_2$O$_6$~x~mol\% Nb$_2$O$_5$~(x=0, 5, 10, 15, 20)的压电陶瓷样品，研究了过量 Nb$_2$O$_5$对 PbNb$_2$O$_6$压电陶瓷烧结性能和电学性能的影响。研究结果表明，过量 Nb$_2$O$_5$能够在保证 PbNb$_2$O$_6$高居里温度和明显各向异性的情况下改善其烧结性能和电学性能。这可能是因为过量 Nb$_2$O$_5$导致 PbNb$_2$O$_6$中 Nb–O 八面体的扭曲，进而抑制 PbNb$_2$O$_6$在烧结过程中的三方到四方相变。随着过量 Nb$_2$O$_5$加入到 PbNb$_2$O$_6$中，其压电系数 (d$_{33}$)和致密度均明显提高了，并且在过量 5 mol\% Nb$_2$O$_5$时达到最大值，分别为 69 pC/N 和 93.1%。

关 键 词：PN；压电陶瓷；Nb$_2$O$_5$；压电性能；钨青铜

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