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Citation: AIP Advances 5, 097120 (2015); doi: 10.1063/1.4930820
View online: http://dx.doi.org/10.1063/1.4930820
View Table of Contents: http://aip.scitation.org/toc/adv/5/9
Published by the American Institute of Physics
Improved electrical properties for Mn-doped lead-free piezoelectric potassium sodium niobate ceramics

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(Received 24 June 2015; accepted 27 August 2015; published online 8 September 2015)

The un-doped and doped lead-free piezoelectric potassium sodium niobate (K0.5Na0.5NbO3, KNN) ceramics with different amounts of Mn were prepared. The decreased dielectric losses and the improved electrical properties were observed in the Mn-doped KNN ceramics. However, the variation of electrical properties with the Mn contents was not continuously. The 0.5 mol.% Mn-doped KNN ceramic shows the highest dielectric loss and the worst electrical properties. The KNN ceramics doped with less than and more than 0.5 mol.% Mn all show improved electrical properties. The change of lattice position of Mn ions in KNN ceramics was the main reason. When the Mn content is less than 0.5 mol.%, the Mn ions occupied the cation vacancies in A-site. When the Mn content is higher than 0.5 mol.%, the Mn ions entered B-site of KNN perovskite structure and formed the defect complexes (Mn′′−V′′O) and (Mn′−V′−Mn′′O). They both led to a lower defect concentration. However, When the Mn content is up to 1.5 mol.%, the electrical properties of KNN ceramic became degraded because of the accumulation of Mn oxides at grain boundaries.

I. INTRODUCTION

Lead titanate (PbTiO3, PT) and lead zirconate titanate (Pb(Zr, Ti)O3, PZT) ceramics are piezoelectric materials that have been widely used for various applications such as filters, oscillators and actuators. However, since lead-based ceramics contain more than 60 wt.% Pb, which induces serious environmental problems, a large amount of researches have been conducted with the aim of replacing these materials. Among several lead-free materials, the potassium sodium niobate (K0.5Na0.5NbO3, KNN) has been recognized as a leading candidate for lead-free piezoelectric host materials. Since Saito et al. have demonstrated that the KNN ceramics modified with Li, Ta, or Sb exhibit sufficient piezoelectric properties comparable to commercially available PZT-based ceramics, considerable interests have been devoted to improve the piezoelectric properties of KNN ceramics. Doping is a mandatory solution to tailor the properties of KNN for specific applications. For Mn-doped KNN and KNN based ceramics, the improved electrical properties were observed. However, the compositions in these reports are not pure KNN but complicated ones doped with other metal-ions. The actions of Mn doping were considered to promote the sintering process and suppress the grain-growth abnormally. In this article, the KNN ceramics were doped only with one kind of metal ion (Mn), possessing a more simple composition. Meanwhile, the emphasis of this article is put on the decrease of the leakage current density of KNN ceramics after Mn doping. The decreased leakage current density of Mn-doped specimens was attributed to the absorption of holes originated from the increased valence-state of Mn. The final valence-state of Mn ions was determined. Combined the crystal phase and electrical properties, the lattice-site of

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Mn ions in KNN perovskite structure was evaluated, which plays an important role in tailoring the electrical properties.

II. EXPERIMENTAL PROCEDURE

The KNN ceramics un-doped and doped with 0.1 mol.%, 0.2 mol.%, 0.5 mol.%, 0.8 mol.%, 1.0 mol.% and 1.5 mol.% Mn were fabricated by conventional solid-state reaction method. K$_2$CO$_3$, Na$_2$CO$_3$, Nb$_2$O$_5$ and MnO were mixed by ball milling in alcohol, dried, sieved, and calcined at 850 °C for 2 h in an alumina crucible. After final ball milling, drying, and sieving, pellets with the diameter of 10 mm and the thickness of 1 mm were formed by uniaxial and cold isostatic pressing at 500 MPa. A sealed sintering at 1090 °C for 4 h in air resulted in the ceramics with the density of ~96 %. The final ceramics were polished and coated with silver paste on the double surfaces for the electrical measurements.

X-ray diffractometer (XRD, D/Max-2400, Rigaku, Japan) with a Cu Kα radiation has been used to identify the phase structure of the sintered cylindrical pellets. The capacitances and dissipation factors of the samples were measured at room temperature in a wide frequency range from 1 kHz-10 MHz using a precision impedance analyzer (HP 4294A, Agilent, USA), with a ac voltage of 500 mV. The temperature dependent dielectric properties of them were characterized by an LCR analyzer (HP 4980, Agilent, USA) at certain frequencies. A standard ferroelectric test system (TF Analyzer 2000 Systems, aixACCT, Germany) was used to measure the ferroelectric properties of all ceramics at the frequency of 10 kHz. The $d_{33}$ of the poled samples was obtained with a commercial Berlincourt-type $d_{33}$ meter (ZJ-3A, China). The poling was completed at 150 °C in a silicone oil bath by applying a dc field of 3.5 kV/mm for 20 minutes. The effects of Mn doping on the chemical states of elements in KNN ceramics were checked by the x-ray photoelectron spectroscopy (XPS, S4PIONEER4KW, Brucker, Germany), with the binding energies referenced to the C 1 s at 285.0 eV. The Roman spectroscopy (RS, HR 800, Horiba Jobin YVON, Japan) was used to further evaluate the phase transition of KNN ceramics and lattice site of Mn ions in KNN structure. The final valence-state of Mn ions was also identified by an electron spin resonance spectrometer (ESR, JES-FA 200, JEOL, Japan).

III. RESULTS AND DISCUSSION

A. Lattice site of Mn ions in KNN structure

1. Variation of lattice parameters

The XRD patterns of un-doped and doped KNN ceramics with different contents of Mn are shown in Fig. 1(a). A pure perovskite phase was observed in all KNN ceramics, indicating that the Mn doping less than 1.5 mol.% results in the formation of stable solutions of KNN. It is found that all ceramics have similar diffraction patterns, which the peaks at about 45 ° were split and the
Variation of lattice parameters (a, b and c) and interplanar spacing (d) of KNN ceramics with the Mn contents.

Intensities of left peaks for all samples are higher than those of right ones. The characterization of XRD peaks should be corresponded to a orthorhombic crystal symmetry instead of tetragonal one.\textsuperscript{8,9,18} Fig. 1(b) shows the \{100\} diffraction lines for all KNN ceramics in the 20 range between 21.5° and 24.5°. It can be clearly noticed that the diffraction peaks shifted to the lower angels with increasing the Mn contents, apart from the 0.5 mol.% and 1.5 mol.% Mn doped KNN ones, manifesting an enlarged lattice parameters after Mn doping. As later discussed, the Mn ions in KNN ceramics are Mn\textsuperscript{3+} and Mn\textsuperscript{4+}. By comparing the ionic radii of Mn\textsuperscript{3+} (0.65 Å)/Mn\textsuperscript{4+} ions (0.53 Å) with K\textsuperscript{+} (1.64 Å)/Na\textsuperscript{+} (1.39 Å)/Nb\textsuperscript{5+} (0.64 Å), it is believed that unless the Mn ions occupy the cation vacancies, the dramatic shift to lower angels for XRD peaks can not be occurred. In KNN ceramics, the cation vacancies in A-site were easily formed as the volatilization of alkaline ions. Consequently, the Mn ions should preferentially occupy the alkaline-ions’ vacancies in the A-site of KNN perovskite structure.

Figure 2 shows the lattice parameters (a, b and c) and interplanar spacing (d) of all the specimens as a function of the Mn contents, which were calculated by a software Jade 5.0. When the Mn content is lower than 0.8 mol.%, the order of lattice parameter is c > a > b for the KNN ceramics. With increasing the Mn content to 0.8 mol.% and above, the order turned into c > b > a. For 0.5 mol.% Mn doped KNN ceramic, the lattice parameter b closes to a, indicating an onset of crystalline-structure change. The continuously increase of Mn content hardly affected the lattice parameters of KNN ceramics, suggesting that the 0.8 mol.% Mn content in KNN ceramics reaches to the saturation. There are Mn ions accumulated at grain boundaries as the Mn oxides when the Mn content is to 0.8 mol.% and above.

It is well known that a large amount of cation vacancies existed in the KNN ceramics as the volatilization of alkaline ions during heat-treatment. As above mentioned, the Mn ions first entered the cation vacancies in A-site in KNN ceramics. Consequently, when the Mn content is low, such as 0.1 mol.% and 0.2 mol.%, the Mn ions entered the cation vacancies, leading to an increased interplanar spacing as the strong repulsion force between Mn and alkaline ions, so the d value increased and the XRD peaks shifted to lower angles with increasing the Mn content. However, one can notice that the 0.5 mol.% Mn doped KNN ceramic shows a smaller d, indicating the Mn ions entered the B-site and substituted for the Nb\textsuperscript{5+} ions. Because of the lower electronegativity of Mn (1.55) than Nb (1.60), the interaction between Mn and O is weaker than that between Nb and O. As a result, the interplanar spacing, d increased with increasing the Mn content, when the Mn ions entered the B-site. The decreased d value and high-angle’s shift of XRD peaks for 1.5 mol.% Mn doped KNN ceramic is attributed to the formation of trace secondary phase (accumulation of Mn oxides at grain boundaries).

2. Temperature dependent dielectric properties

Figure 3 shows the temperature dependent dielectric properties of all KNN ceramics. There are mostly two dielectric peaks for all ceramics, corresponding respectively to two phase transition
FIG. 3. Temperature dependent dielectric properties for the KNN ceramics un-doped and doped with different contents of Mn. The inset shows the variations of $T_{O-T}$ and $T_C$ with the Mn contents.

temperatures upon heating. One is from the orthorhombic to the tetragonal phase ($T_{O-T}$, around 200°C), the other is from the tetragonal to the cubic phase transition ($T_C$, around 400°C). The variations of $T_{O-T}$ and $T_C$ with the contents of Mn are shown in the inset of Fig. 3. The $T_C$ of Mn-doped KNN ceramics is lower than the un-doped one. With increasing the content of Mn, the $T_C$ changed slightly in the range of 399-396°C. The $T_{O-T}$ of 0.1 mol.% and 0.2 mol.% Mn-doped KNN ceramics is almost the same as that of un-doped one. However, it rapidly decreased with increasing the content of Mn to 0.5 mol.% When the Mn content is up to 0.8 mol.% and above, the $T_{O-T}$ is almost constant. The change of $T_{O-T}$ for KNN ceramics with the content of Mn corresponds to the change of incorporating sites of Mn in KNN structure. That is, when 0.5 mol.% Mn ions were introduced into the KNN ceramics, they began to enter B-site of KNN perovskite structure and the $T_{O-T}$ of KNN ceramics almost kept constant.

3. XPS analysis

Based on the above analyses, the 0.1 mol.% and 1.0 mol.% Mn-doped samples are almost the same as the 0.2 mol.% and 0.8 mol.% Mn-doped samples, respectively. So in later discussions, the un-doped, 0.2 mol.% and 0.8 mol.% Mn-doped KNN ceramics were chosen as the subjects. Their XPS spectra have been obtained to check the effect of Mn doping on the chemical states of each element in KNN ceramics. The XPS spectra for K 2p, Na 1s, Nb 3d and O 1s for all measured KNN ceramics are shown in Fig. 4(a)–4(d). The K 2p, Na 1s and Nb 3d lines of 0.2 mol.% Mn doped KNN ceramic are the same as the un-doped one, as shown in Fig. 4(a)–4(c), suggesting that the introduction of 0.2 mol.% Mn hardly affected the chemical states of the elements in KNN ceramics. This also supports the conclusion that the Mn ions entered the cation vacancies in A-site of KNN perovskite structure. With increasing the Mn content to 0.5 mol.% and above, the
FIG. 4. XPS spectra of each element in KNN ceramics un-doped and doped with different contents of Mn, (a) K 2p, (b) Na 1s, (c) Nb 3d and (d) O 1s.

K 2p, Na 1s and Nb 3d peaks all shifted to higher binding energy. The substitution of Mn for Nb ions in B-site of KNN perovskite structure is the main reason. The substitution of Mn ions for Nb ions in B-site led to the formation of oxygen vacancies for charge neutrality. As a result, the density of electron cloud of metal ions in KNN lattice position increased, leading to the higher binding energy of K/Na/Nb.

However, the XPS spectra of all metal elements in 1.5 mol.% Mn doped KNN ceramic shifted to lower binding energy again, attributed to the formation of more Mn oxides at grain boundaries as a trace secondary phase.

Fig. 4(d) presents the O 1s peaks of all measured KNN ceramics. The peak centered on 529.5 eV is assigned to the oxygen in perovskite lattice. Another peak in high binding energy of 531.5 eV arises from the chemisorbed oxygen species. The substantial chemisorption of oxygen species implies the possible creation of oxygen vacancies. As shown in Fig. 4(d), the 0.5 mol.% and 0.8 mol.% Mn-doped KNN ceramics show strong oxygen peaks in high binding energy, indicating the existence of a large number of oxygen vacancies. This result also supports the conclusion that the Mn ions entered the B-site in KNN perovskite structure when the content of Mn is up to 0.5 mol.% and above. As for the 1.5 mol% Mn-doped KNN ceramic, the XPS spectrum of oxygen shows the same result as that of un-doped and 0.2 mol.% Mn-doped ones, attributed to the accumulation of Mn oxide at grain boundaries. The XPS spectrum of metal oxides also shows stronger O 1s peak, accompanied with a high binding energy shoulder, due to the physical and chemical absorption.

4. Raman spectra analysis

Raman spectrum is considered to be useful in analyzing the structure and phase transition of ferroelectric ceramics. Typical Raman spectra of KNN ceramics un-doped and doped with different contents of Mn is shown in Fig. 5(a). The vibrations are separated into translational modes of the isolated cations and internal modes of coordination polyhedral. The peaks in the region lower
FIG. 5. (a) Raman spectra of KNN ceramics un-doped and doped with different amounts of Mn, (b) variation of spectral band position and FWHM of the $\nu_1$ stretching mode for Mn-doped KNN ceramics as a function of Mn contents.

than 200 cm$^{-1}$ are mainly assigned to the translational modes of Na$^+$/K$^+$ cations. The vibration modes of NbO$_6$ octahedra consist of $\nu_1$, $\nu_2$, $\nu_3$, $\nu_5$ and $\nu_6$. Among these vibration, $\nu_1$, $\nu_2$ and $\nu_3$ are stretching modes, while $\nu_4$, $\nu_5$ and $\nu_6$ are bending modes. The modes of $\nu_1$-$\nu_5$ are specified in the Fig. 5(a). The $\nu_6$ is generally not distinguishable and may appear in the lower wave-number region. Since the ceramics are polycrystalline materials, the measured Raman spectra, especially the band intensities, may differ from each other at different measuring locations owing to the variation of grain orientations and the presence of grain interactions. As a result, we ignored the change of band intensities and focused on the shift of bands. The asymmetric $\nu_1$ band (611 cm$^{-1}$) of measured KNN ceramics was chosen. Plots of the spectral band position and of the full width at half maximum (FWHM) of the $\nu_1$ bands for KNN ceramics as a function of Mn amount are shown in Fig. 5(b). From the plots, one can recognize that the band representing the $\nu_1$ stretching mode first shifts to lower wave numbers up to 0.8 mol.% and then shifts to higher wave numbers with increasing the Mn content. Similarly, the band first becomes narrow with increasing the Mn content up to
0.8 mol.% and then broadened. The red shift of the peak position for $\nu_1$ mode and a reduction of its FWHM in KNN ceramics doped with less than 0.8 mol.% Mn suggest an alleviation of the large distortion of O-Nb-O angles together with a decrease in the binding strength after Mn doping.\(^{27}\) The distortion of O-Nb-O angels was originated from the existence of a large number of cation vacancies in un-doped KNN ceramics. When introducing the Mn ions, they preferentially enter cation vacancies. The interaction between Mn ions and oxygen ions makes the binding strength of Nb and O reduced, meanwhile, the distortion of O-Nb-O angles became alleviated. With increasing the Mn content, the Mn ions substitute for Nb ions and cause a small distortion of O-Nb-O angles again. Because of the lower electronegativity of Mn (1.55) than Nb (1.60), the interaction between Mn and O is weaker than that between Nb and O, leading to an slightly increased binding strength of octahedron. As a result, with a further increase in Mn amount to 0.8 mol.% and above, the peak position will not shift towards lower wave-numbers but towards higher ones.

B. Electrical properties of all KNN ceramics

Fig. 6(a) shows the frequency dependent dielectric constants and losses of the un-doped and doped KNN ceramics with different amounts of Mn. The dielectric property of un-doped KNN ceramic shows obvious frequency-dependence in low frequency, indicating a poor leakage current. After 0.1 mol.% and 0.2 mol.% Mn were introduced, the losses of KNN ceramics obviously decreased. This was attributed to the lowered leakage current density as the absorption of holes acted as the carriers of leakage current by Mn ions.\(^{28}\) Continuously increased the Mn content to 0.5 mol.%, the loss became higher as the formation of new oxygen vacancies originated from the substitution of Mn ions for Nb ions. As later discussed, the Mn ions existed in the form of $\text{Mn}^{3+}$ and $\text{Mn}^{4+}$ ions in final crystallized KNN ceramics, so the two kinds of mutually compensating charge defect complexes are formed, such as $(\text{Mn}_{\text{Nb}}^{3+} - V_{\text{O}}^0)$ and $(\text{Mn}_{\text{Nb}}^{4+} - V_{\text{O}}^- - \text{Mn}_{\text{Nb}}^{3+})$. When the 0.5 mol.% Mn doped, the Mn ions just began to enter B-site, that is, the Mn ions in B-site is less. Consequently, it might be difficult for $(\text{Mn}_{\text{Nb}}^{3+} - V_{\text{O}}^- - \text{Mn}_{\text{Nb}}^{3+})$ defect complex to stably form, leading to the formation of mobile $V_{\text{O}}^-$ for charge neutrality. Therefore, the dielectric loss for the 0.5 mol.% Mn-doped
KNN ceramic was increased. Further increasing the Mn contents, the \((\text{Mn}_\text{Nb}^\prime - \text{V}_{\text{O}} - \text{Mn}_\text{Nb}^\prime)\) could be formed and the mobility of the \(\text{V}_{\text{O}}\) became difficult.\textsuperscript{29} As a result, the dielectric loss originated from the leakage current decreased. The slightly increased dielectric loss for the 1.5 mol.% doped KNN ceramic is attributed to the formation of trace secondary phase as Mn oxides, as above mentioned. The variation of the dielectric losses for all specimens with the Mn contents was shown in Fig. 6(b).
The continuous decrease in dielectric constants at 1 kHz for all specimens with increasing the Mn content, apart from the 0.5 mol.% Mn doped one in Fig. 6(b) was originated from the decreased losses. The exception for the 0.5 mol.% Mn doped KNN ceramic is owing to the high loss from the leakage current. Altogether, the best dielectric properties were obtained in the KNN ceramics doped with lower amount of Mn, showing higher dielectric constants (460-500) with lower dielectric loss (4-7%) at 1 kHz.

Figure 6(c) presents the polarization-electric field (P-E) hysteresis loops of all KNN ceramics. The un-doped KNN ceramic shows a round P-E loop and lower breakdown electric field, suggesting a poor leakage current. The 0.1 mol.% and 0.2 mol.% Mn doped KNN ceramics show the best ferroelectric properties, showing typical and square P-E hysteresis loops with the remnant polarization ($P_r$) of 24 $\mu$C/cm$^2$. When the Mn content is 0.5 mol.%, the KNN ceramic shows degraded P-E loops as the higher dielectric loss. Thereafter, the ferroelectric properties improved with increasing the Mn contents as the decreased dielectric loss. The worse performance for 1.5 mol.% Mn doped KNN ceramic than 1.0 mol.% doped one was attributed to the higher defect content. To clearly observe the variation of $P_r$ values with the Mn contents, the $P_r$ values of KNN ceramics at the same electric field of ~27 kV/cm were chosen and their variation with the Mn contents was plotted, as shown in Fig. 6(d). The $P_r$ continuously decreased with increasing the Mn contents. Combined the hysteresis loops and the change trend of $P_r$ values at the same electric filed, the best ferroelectric properties were also obtained in the KNN ceramics doped with lower amount of Mn. The variation of piezoelectric coefficient, $d_{33}$ with the Mn contents in Fig. 6(d) also shows the almost same trend as the dielectric and ferroelectric properties. The lowered $d_{33}$ for 0.8 mol.% Mn doped KNN ceramic than 0.5 mol.% Mn doped one might be an abnormality. The continuously decreased dielectric constants, $P_r$ and $d_{33}$ with the Mn contents for the KNN ceramics doped with more than 0.5 mol.% Mn may attribute to the formation of defect complexes. These complexes can impede domain wall motion and may contribute to ferroelectric “hardening”.

C. Valence state of Mn ions in KNN ceramics

The improved electrical properties of KNN ceramics after Mn doping were considered to be mainly originated from the absorption of holes acted as the carriers of leakage current, same as the KNN single crystals and films. This process was accompanied by the increased valence state of Mn ions, as reported in Refs. 28 and 31. Therefore, the electron spin resonance (ESR) was used to clarify the valence-state of Mn ions in final crystallized KNN ceramics. Fig. 7 shows the ESR spectra at room temperature for crushed KNN powders un-doped and doped with 0.2 mol.%, 0.5 mol.%, 0.8 mol.%, and 1.5 mol.% Mn. The ESR spectrum of un-doped KNN ceramic shows a straight line, without the paramagnetic characteristic. The ESR spectra of all Mn-doped KNN ceramics exhibit six prominent lines. The line-width for six lines is in the range of 2.7-6.1 mT with a $g$-value of ~2.00, indicating the typical Mn$^{4+}$. The signal of Mn$^{3+}$ ions can not be detected since it is silent in ESR measurement, but the mixed valence states of Mn$^{3+}$ and Mn$^{4+}$ in KNN perovskite structure should be considered. In addition, the hyperfine structure with six prominent lines of typical isolated Mn$^{2+}$ was not observed, suggesting that the initial Mn$^{2+}$ ions were completely oxidized into Mn$^{3+}$ and Mn$^{4+}$ in final crystallized KNN ceramics. The different shapes for the ESR spectra of KNN ceramics are attributed to the different Mn contents.

IV. CONCLUSIONS

The un-doped and doped KNN ceramics with different amounts of Mn were prepared by a conventional solid-state reaction method. All the ceramics show pure KNN perovskite structure. The Mn doped KNN ceramics show decreased dielectric loss and improved electrical properties compared to the un-doped one. The dielectric losses of KNN ceramics decreased with increasing the Mn content, apart from the 0.5 mol.% Mn doped one. Accordingly, the worst electrical properties were observed in the 0.5 mol.% Mn doped KNN ceramic. The improved electrical properties for the KNN ceramics doped with less than 0.5 mol.% Mn was attributed to the reduction of
cation vacancies as the A-site occupation of Mn ions and the absorption of holes acted as the carriers of leakage current. For the KNN ceramics doped with more than 0.5 mol.% Mn, the main reason for improved electrical properties is the formation of defect complexes (Mn$^{''''}$\nb$-V^{'}\n$) and (Mn$^{''}$\nb$-V^{'}\n$-Mn$^{'''}\nb$), as the B-site occupation of Mn ions in KNN structure. When the Mn content is up to 1.5 mol.%, as the accumulation of Mn oxides at grain boundaries as secondary phase, the electrical properties became degraded.

ACKNOWLEDGEMENTS

The authors would like to thank for the financial supports from the National Natural Science Foundation of China, under Grant Nos. 51202184, 51332003 and 91323303, from the Fundamental Research Funds for the Central Universities, under Grant No. 0105-08143078.

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