Effects of Manganese Addition on Piezoelectric Properties of the (K, Na, Li) (Nb, Ta, Sb)O₃ Lead-Free Ceramics

Enzhu LI, Hirofumi KAKEMOTO, Satoshi WADA and Takaaki TSURUMI

Department of Inorganic Materials, Faculty of Engineering, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152-8552

Recently, it was reported that the alkaline niobate-based (K, Na, Li) (Nb, Ta, Sb)O₃ (LF4) perovskite ceramics showed excellent piezoelectric properties and has been regarded as a new candidate of lead-free piezoelectric materials. However, the effects of additives on the piezoelectric property of LF4 have not been studied intensively so far. In this study, the effect of MnCO₃ addition to the LF4 was investigated. The sample showed a tetragonal phase at room temperature. The MnCO₃-doping changed the LF4 to “hard” piezoelectric ceramics with an improvement of Q_m from 26 to 73. [Received November 7, 2006; Accepted February 15, 2007]

Key-words : Lead-free, Piezoelectric, Ceramic, LF4, Manganese, Mechanical quality factor Q_m

1. Introduction

Since the discovery of the excellent electrical properties of lead-based PZT at a morphotropic phase boundary (MPB) composition, considerable work has been focused on the development of related lead-based piezoelectric, ferroelectric ceramics and their adaptation to several types of devices. However, it is recently desired to use lead-free materials for environmental protection. Nowadays, the search for alternative piezoelectric materials is focused on alkali niobates, modified bismuth titanates and other systems with MPB.^{1)–3)} The piezoelectric properties of (K, Na) NbO₃ (KNN) were first reported by Egerton and Dillon.⁴⁾ This material has superior properties, such as a high Curie temperature of more than 400 and a relatively large electromechanical coupling factor, and it is also a promising candidate for the development of lead-free piezoelectrics. However, it is extremely difficult for KNN to achieve high density under conventional processing because of the volatility of the alkaline element. Hence, the application of hot pressing or spark plasma sintering (SPS) techniques is usually required in order to obtain densified samples.^{5)–7)} Numerous researchers have attempted to sinter KNN under atmospheric pressure by adding copper-based sintering aids like K₄CuNb₈O₂₃(KCN) or K₄CuNb₈O₂₃(KCT) without degradation of their piezoelectric properties.^{8),9)} Saito et al. in Toyota Central R&D laboratories reported alkaline niobate-based (K, Na, Li) (Nb, Ta, Sb)O₃ (LF4) perovskite ceramics as lead-free piezoelectric materials which showed high piezoelectric constant d_{33} .¹⁰⁾

The niobate-based LF4 ceramics seem to be a suitable substitution for PZT ceramics. However, a high mechanical quality factor (Q_m) should be required for practical piezoelectric applications particularly for ultrasonic applications. Li et al.¹¹⁾ reported that CuO addition changed the LF4 to “hard” ceramics. Kamiya et al.¹²⁾ reported the effects of MnO₂ addition on piezoelectric properties of PZT. They found that Q_m was improved by MnO₂ addition. However, the similar study on LF4 has been limited and the mechanism of the property control by the Mn addition was ambiguous so far. In this study, MnCO₃ was selected as a dopant of LF4 and variations of the microstructure and piezoelectric properties due to MnCO₃ addition was investigated.

2. Experimental procedure

The samples (Li_{0.04}Na_{0.44}K_{0.52}) (Nb_{0.86}Ta_{0.1}Sb_{0.04}) O₃ + x MnCO₃ (mol%), for $x=0.114, 0.227, 0.455$ and 0.682 , and short for Mn1, Mn2, Mn3 and Mn4, respectively, were

prepared using conventional solid reaction processing from K₂CO₃ (99.5%), Na₂CO₃ (99.5%), Li₂CO₃ (99.99%), Nb₂O₅ (99.9%), Ta₂O₅ (99.99%), Sb₂O₅ (99.99%) and MnCO₃ (99.9%) starting powders. The powders were mixed with the aid of ZrO₂ balls in dehydrated acetone for 24 h. The mixture was calcined at 780°C for 4 h and then ball milling again with dehydrated acetone for 24 h. Finally, the powders were pressed into 20 mm diameter pellets by means of cold isostatic pressing (CIP) at 337 kg/cm². The green compacts were sintered at temperatures ranging from 1155°C to 1170°C.

The sintered ceramics were characterized by X-ray diffraction (XRD) analysis. To measure the electrical properties, the sintered compacts were cut into pieces with dimensions of 12 × 4 × 1 mm³ with a diamond cutter and Au electrodes were sputtered on both sides of the ceramics. A poling treatment was conducted using a DC power supply at 5 kV/mm in silicon oil at 80°C for 30 min. for Mn-doped samples and 90 min for pure LF4. The piezoelectric properties were determined using the resonance-antiresonance method. The resonance frequency was measured with an impedance analyzer (Agilent, 4294A). The piezoelectric constant d_{31} , the electromechanical coupling factor (k_{31}) was obtained from the resonance frequency (f_R) and anti-resonance frequency (f_A). The mechanical quality factor (Q_m) was estimated from $Q_m = \omega_0 / \Delta\omega$, where $\Delta\omega$ is the full width at half maximum of admittance. P - E hysteresis loops were evaluated by a Virtual Ground mode at 500 Hz and room temperature.

3. Results and discussion

Figure 1 shows the relative densities and the optimum sintering temperatures of LF4 as a function of MnCO₃ (x) content, where an optimum sintering temperature means the temperature at which the highest sintering density is obtained. With increasing amounts of 1135°C, the optimum sintering temperature increased from 1135°C to 1165°C and the relative density improved from 95% to 99% by the addition of 0.227 mol% MnCO₃. Above 0.227 mol% MnCO₃, the relative density gradually decreased, however, still above 95%. **Figure 2** shows XRD profiles of the LF4 with various MnCO₃ contents sintered at their optimum sintering temperatures. After sintering, a tetragonal single phase was obtained. **Figure 3** illustrates the lattice parameters and c/a ratio as a function of the amount of MnCO₃ (x). It can be seen that with small amount of MnCO₃ added (Mn1 and Mn2), the lattice parameters and c/a ratio changed greatly which means that the Mn ions reacted with LF4 lattice. Higher amount of MnCO₃ (Mn3 and

Fig. 1. Relative densities and the optimum sintering temperatures of MnCO₃-doped LF4 ceramics.

Fig. 2. XRD profiles of MnCO₃-doped LF4 ceramics.

Mn4) led to a steady value is because of the solubility limit of Mn ions into lattice.

Figure 4 shows the microstructures of LF4 ceramics doped with different amounts of MnCO₃. With increasing amount of MnCO₃-addition, the average grain size increased slightly but almost remained the same.

In order to characterize the ferroelectricity, *P-E* hysteresis loops were evaluated at 500 Hz as shown in Fig. 5. The coercive field E_c in pure LF4 is high may because the A-site defects, caused by the volatility of alkali metals during sintering, pin the domain wall motion leading to a high E_c . The addition of Mn ions reacted with the lattice and reduced the defects leading to a lower E_c . And the additions of a large amount of Mn ions act as acceptor ions and increase oxygen vacancies from the viewpoint of the charge neutrality. The oxygen vacancies will pin domain wall motion leading to a higher E_c as shown in Fig. 5(b). The remnant polarization P_r decreased as increasing amount of MnCO₃ which indicates the

Fig. 3. Lattice parameters and *c/a* ratio of MnCO₃-doped LF4 ceramics.

Fig. 4. SEM photographs of MnCO₃-doped LF4 ceramics.

Fig. 5. (a) *P-E* hysteresis loops of MnCO₃-doped LF4 ceramics, and (b) coercive field and remanent polarization as a function of the amount of MnCO₃ added.

Fig. 6. Frequency response of impedance and phase of pure LF4 and Mn2 ($x=0.227$ mol%) specimen.

tetragonality decreased.

Figure 6 shows the frequency response of impedance and phase of pure LF4 and Mn2 ($x=0.227$ mol%) specimen. Three important parameters, temperature (R.T. $\sim 200^\circ\text{C}$), DC bias field (2–5 kV/mm) and soaking time (10–90 min),

Fig. 7. Change of d_{31} and k_{31} and with the amount of MnCO₃ added.

Fig. 8. Change of Q_m and $\tan\delta$ with the amount of MnCO₃ added.

were well considered to determine an optimum condition in the poling treatment. However, the phase angle was limited to a maximum of around 5° for LF4 and 25° for Mn-doped samples in the present poling conditions as follows: temperature of 80°C , DC bias field of 5 kV/mm and soaking time of 90 min for LF4 while 30 min for Mn-doped samples. We can not conclude whether difficulty in the poling is due to the sample problem or inherent problems in such a composition with high T_c . Research is in progress to improve poling procedures for the full poling state.

The changes of d_{31} and k_{31} with the amount of MnCO₃ addition is shown in **Fig. 7**. The d_{31} and k_{31} decreased from the pure LF4 by the addition of MnCO₃ and remained almost the same which corresponded to the data of P_r . **Figure 8** illustrated the changes of Q_m and $\tan\delta$ with the amount of MnCO₃. It was found that the addition of MnCO₃ was effective to increase the Q_m . The maximum value of $Q_m=73$ was obtained at Mn2. The mechanisms for the electromechanical loss fall into four general categories, defined in terms of fundamental characteristics of the material, namely in relation to: (1) domain wall motion, (2) the lattice type, (3) the microstructure, and (4) the conductivity of the material (highly ohmic samples).¹³⁾ For ceramic piezoelectric, it is the first category that most strongly characterizes the loss. Here we can see that the oxygen vacancies will pin domain wall motion leading to a high Q_m . However, the Q_m value is not as high as reported Cu-

doped KNN^(8),9),14) and Cu-doped LF4.⁽¹¹⁾ The change of $\tan \delta$ can be interpreted by the change of oxygen vacancy concentration but the more accurate data should be necessary for detailed analysis. From the results, we found that the MnCO_3 -doping changed the LF4 to “hard” piezoelectric ceramics with improvement of Q_m . However, the effect is not as notable as in PZT. The further search of chemical composition should be necessary to make LF4 useful for practical applications as real “hard” piezoelectric ceramics.

4. Conclusion

In this study, the effects of MnCO_3 -doping on the micro-structure and piezoelectric properties of LF4 were investigated. The Mn ions acted as acceptor changed the property of LF4 to “hard”. The Q_m was improved from 26 of pure LF4 to 73 by the addition of 0.227 mol% of MnCO_3 .

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