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An enhanced mechanical quality factor and a low dielectric loss in lithium sodium niobate lead-free ceramics

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Abstract

$(Li_{0.12}Na_{0.88})(Nb_{0.96-x}Sb_{0.04}Ta_x)O_3$ (LNNST) ceramics were fabricated by the normal sintering. These LNNST ceramics endure a phase transition from an orthorhombic phase, a coexistence of orthorhombic and tetragonal phases, to a tetragonal phase with increasing Ta content. Dense microstructure has been developed for all ceramics. The T_c decreases and the ε_r increases with increasing Ta content, together with a very low dielectric loss of less than 1.3%. A high Q_m value of ~1230 is demonstrated for the ceramic with $x = 0.06$. Enhanced piezoelectric properties are also demonstrated for the ceramic with $x = 0.03$ because of a coexistence of two phases. Therefore, this ceramic is a promising candidate for the transducer and transformer applications.

Keywords: C. Piezoelectric properties; Lead-free ceramics; Ion substitution; Mechanical quality factor

1. Introduction

Lead-based piezoelectric ceramics have been widely used in actuators, sensors, resonators, and transducers because of their excellent electrical properties and high Curie temperature [1]. However, these lead-based ceramics cause some seriously environmental problems because of a high toxicity of PbO and its high vapor pressure during sintering. Therefore, it becomes urgent to develop the lead-free piezoelectric ceramics for the replacement of these lead-based ceramics in various applications.

$(K, Na)NbO_3$ (KNN) lead-free piezoelectric ceramics have been recently considered as one of the promising candidates in the field of piezoelectric ceramics [2–13] because of a high Curie temperature, good piezoelectric properties, and environmental friendliness. In contrast, it is a tough issue to obtain dense KNN-based ceramics by using a normal sintering method because of the high volatility of alkaline elements at a high processing temperature [14]. Although piezoelectric properties of KNN-based ceramics are improved greatly by forming the solid solutions with other ferroelectric materials [15–18], a low mechanical quality factor (Q_m) is often observed for these ceramics [15–18]. In the past of several years, some sintering aids have been used to enhance the Q_m value and the density of KNN-based ceramics [19–25], but it is very difficult to concisely control the content of these sintering aids together with a complicated preparation process. A low Q_m value is also demonstrated for these KNN-based piezoelectric ceramics with Li^+ by using some sintering aids [22–25], while the pure LNN ceramic has a high Q_m value of ~530 [26], as shown in Fig. 1.

$(Li_{0.12}Na_{0.88})NbO_3$ (LNN) lead-free piezoelectric ceramics have been considered as a promising candidate for the high-frequency filter application [26–32]. Moreover, the LNN material without a K element can keep a good stoichiometric ratio [26–32]. In the present work, we introduce both Sb and Ta elements to the LNN material for further improving the Q_m value, and $(Li_{0.12}Na_{0.88})(Nb_{0.96-x}Sb_{0.04}Ta_x)O_3$ (LNNST) lead-free piezoelectric ceramics were fabricated by the conventional solid-state method. Effects of Ta content on the mechanical quality factor of LNNST ceramics were mainly investigated, and these underlying physics mechanisms were also addressed.

2. Experimental procedure

$(Li_{0.12}Na_{0.88})(Nb_{0.96-x}Sb_{0.04}Ta_x)O_3$ lead-free piezoelectric ceramics were fabricated by the conventional solid-state

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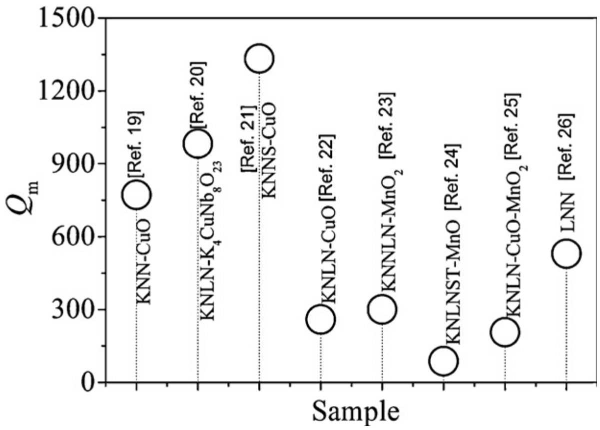

Fig. 1. Q_m value for these KNN-based ceramics with different sintering aids.

method. Raw materials were Na_2CO_3 (99.8%), Nb_2O_5 (99.5%), Li_2CO_3 (99.99%), Sb_2O_3 (98%), and Ta_2O_5 (99.99%). LNNST powders were fabricated by using the following steps, as listed below. After weighing according to the stoichiometric ratio of LNNST ceramics, these powders were mixed by a ball mill using anhydrous ethanol as the media, and then these dried powders were calcined at ~850 °C for 6 h. These powders were re-milled for 24 h for further improving the chemical homogeneity. All ceramics were sintered in the temperature range of 1150–1220°C for 2 h. Silver pastes were fired at ~700 °C for 10 min on both sides of these samples as electrodes for electrical measurements. All samples were poled at a room temperature in a silicone oil bath under a dc field of ~5.0 kV/mm for 20 min.

The crystal structure of these ceramics was examined by using an X-ray diffraction (XRD) (DX1000, PR China). Scanning electron microscopy (SEM) was employed to study the surface morphologies of these ceramics. Their dielectric behavior as a function of the measurement temperature was obtained by using an LCR meter (HP 4980, Agilent, USA). The piezoelectric constant d_{33} of these ceramics was measured using a piezo-d_{33} meter (ZJ-3A, China).

3. Results and discussion

Fig. 2(a) shows the XRD patterns of LNNST ceramics as a function of Ta content, measured at room temperature. All ceramics have a pure phase, and no secondary phases are observed in the measurement range of XRD. Fig. 2(b) plots the expanded XRD patterns of LNNST ceramics in the 2θ range of 46–48°. These LNNST ceramics with $x \leq 0.01$ have an orthorhombic phase, while a tetragonal phase is demonstrated for these ceramics with $x \geq 0.04$. Therefore, a coexistence of orthorhombic and tetragonal phases is observed for these ceramics $0.01 < x < 0.04$, as also confirmed by the temperature dependence of the dielectric constant (ε_r) of these ceramics, as shown in Fig. 4.

Fig. 3(a)–(c) shows the surface morphologies of LNNST ceramics with $x = 0$, 0.01, and 0.03, respectively. Dense microstructure has been demonstrated for these ceramics. Moreover, the introduction of Ta cannot decrease the density of LNNST ceramics, that is, small grains surround large grains for the LNNST ceramic with $x = 0.03$, as shown in Fig. 3(d). With the increase of Ta substitution, average grain size of LNNST ceramics dramatically decreases because the Ta depresses the grain growth of these ceramics.

Fig. 4(a)–(g) shows the temperature dependence of the ε_r in LNNST ceramics, measured at 1, 10, and 100 kHz. It has reported that three phase transitions are observed for pure LNN ceramic [26–32], i.e., a rhombohedral phase to an orthorhombic phase, an orthorhombic phase to a tetragonal phase (T_{o-t}), and a tetragonal phase to a cubic phase (T_c). As shown in Figs. 4(a)–(g), the T_{o-t} peak of LNNST ceramics tends to disappear with increasing Ta content, and a broadened dielectric peak is demonstrated for these ceramics with $x \geq 0.04$, confirming the involvement of a phase transition from an orthorhombic phase to a tetragonal phase. Therefore, two peaks [i.e., an orthorhombic to tetragonal phase (T_{o-t}) and a tetragonal to cubic phase (T_c)] are demonstrated for these LNNST ceramics with $x < 0.04$, while a peak of a tetragonal to cubic phase is only observed for these LNNST ceramics with $x \geq 0.04$. These results also confirm that a phase transition is involved into these

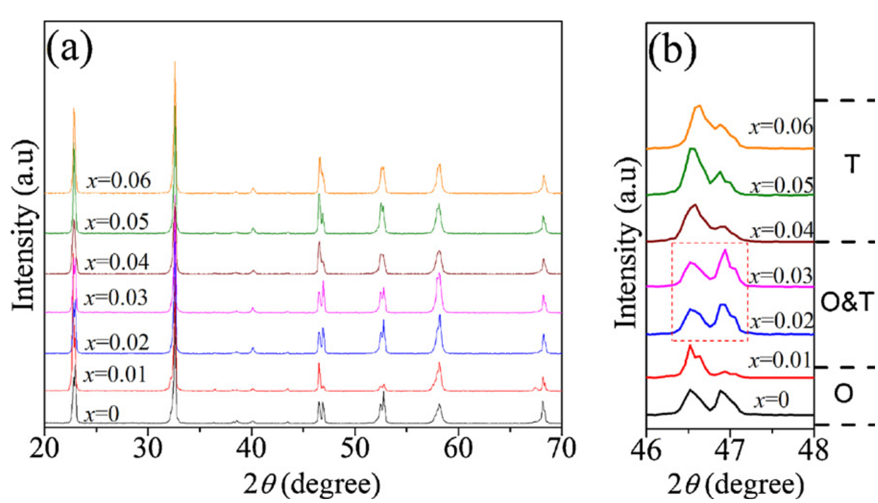

Fig. 2. XRD patterns of LNNST ceramics, measured in the 2θ range of (a) 20–70° and (b) 46–48°.

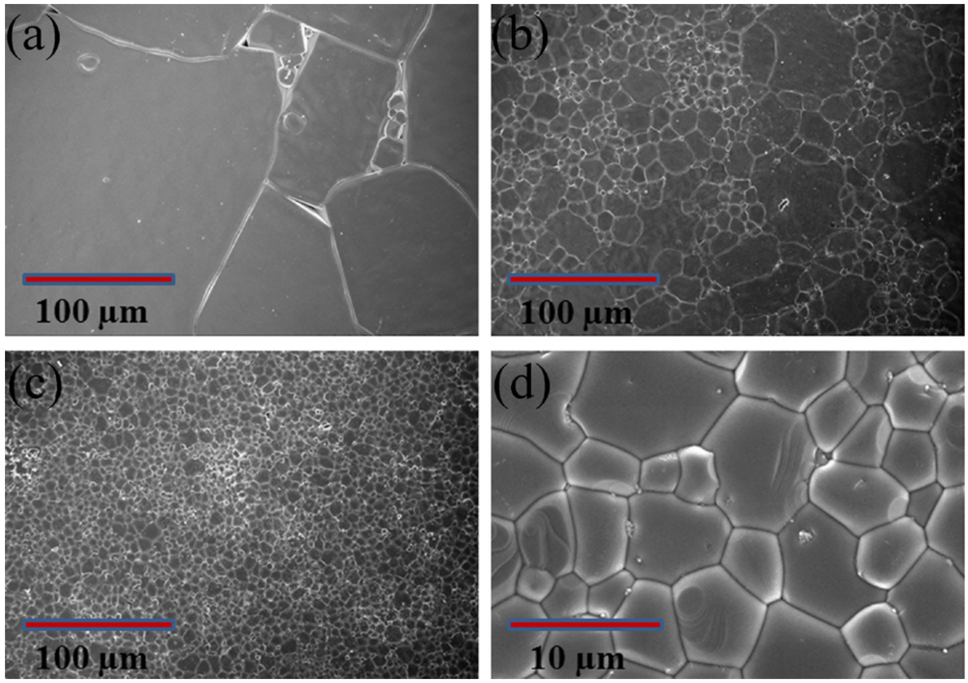

Fig. 3. SEM patterns of LNNST ceramics as a function of Ta content: (a) $x = 0$, (b) $x = 0.01$, (c) $x = 0.03$, and (d) $x = 0.03$ with a larger magnitude.

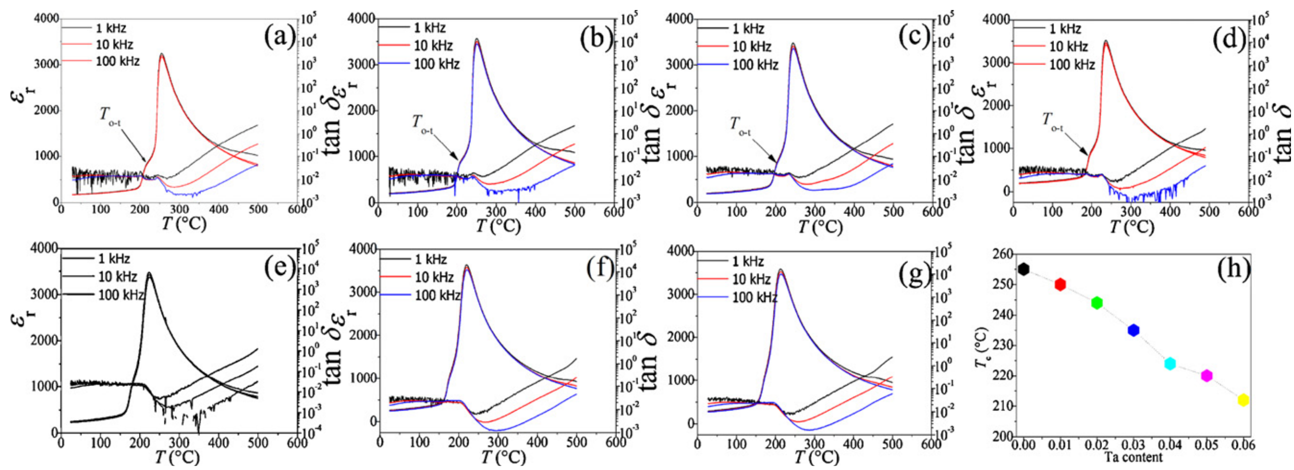

Fig. 4. Temperature dependence of the dielectric constant of LNNST ceramics as a function of Ta content: (a) $x = 0$, (b) $x = 0.01$, (c) $x = 0.02$, (d) $x = 0.03$, (e) $x = 0.04$, (f) $x = 0.05$, and (g) $x = 0.06$, measured at 1, 10, and 100 kHz. (h) T_c value of LNNST ceramics as a function of Ta content.

LNNST ceramics. The T_c value of LNNST ceramics gradually decreases with increasing Ta content [33], as shown in Fig. 4(h). As shown in Figs. 4(a)–(g), all LNNST ceramics have a low dielectric loss (tan δ) in the temperature range of room temperature $\sim$200 °C, and their tan δ values almost keep unchanged in the range of measurement temperatures, confirming the involvement of a good thermal stability in these ceramics.

Fig. 5 shows the dielectric properties of LNNST ceramics as a function of Ta content, measured at 10 kHz and room temperature. The ε_r value of LNNST ceramics gradually increases with increasing Ta content, which is well in agreement with these reported results of Ta-modified KNN-based ceramics [8,34]. However, all LNNST ceramics demonstrate a low tan δ value of less than 1.3%, which is much lower than those of KNN-based ceramics [2–13]. Therefore, the introduction of Ta and Sb enhances the dielectric properties of LNN ceramics, that is, a higher ε_r value and a low tan δ value are demonstrated for these LNNST ceramics.

Fig. 6 shows the piezoelectric properties of LNNST ceramics as a function of Ta content, measured at room temperature. The d_{33} value of LNNST ceramics increases with increasing Ta content, reaches a maximum at $x = 0.03$, and then decreases with further increasing Ta content. Similarity to the change of the d_{33} value, the k_p value also reaches a maximum for the LNNST ceramic with $x = 0.03$. It is of great interest to note that the Q_m value of LNNST ceramics increases quickly with increasing Ta content. It has been reported that Ta and Sb-modified KNN-based ceramics have a very low Q_m value [35]. The addition of some sintering aids (i.e., CuO, MnO) can

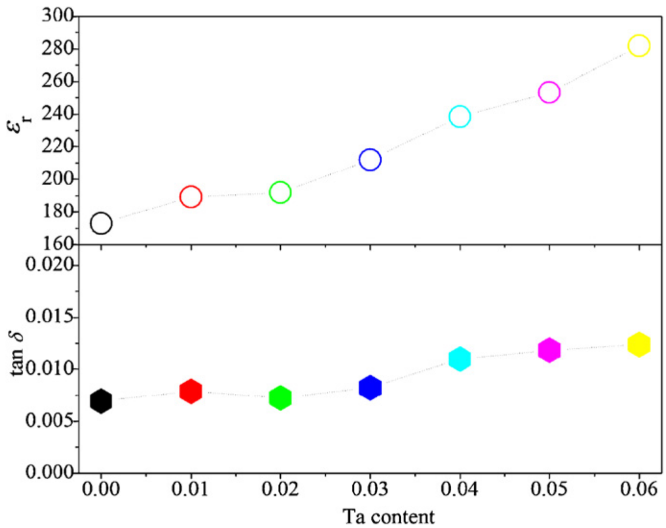

Fig. 5. Dielectric properties of LNNST ceramics as a function of Ta content, measured at 10 kHz and room temperature.

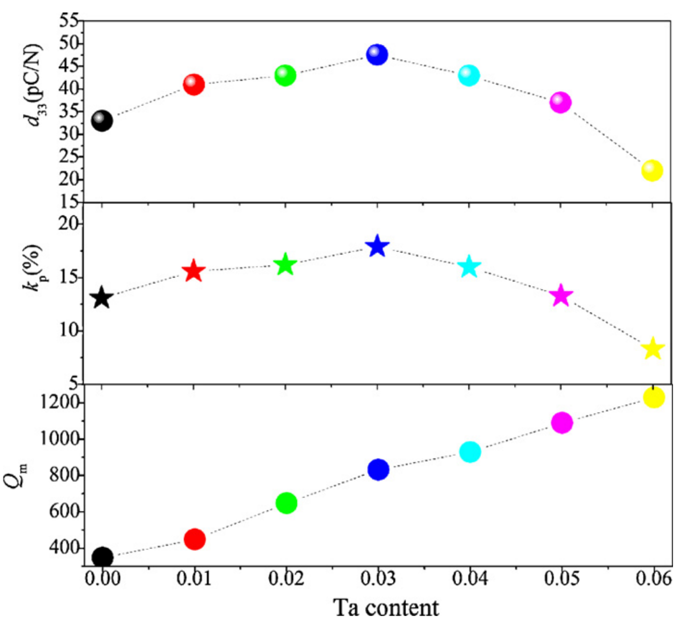

Fig. 6. d_{33}, k_p, and Q_m values of LNNST ceramics as a function of Ta content.

improve the Q_m value of KNN-based ceramics, but its preparation method is very complicated together with the formation of a relative high dielectric loss in these ceramics, as shown Fig. 1. In this work, a high Q_m value is demonstrated for these LNNST ceramics because of the introduction of Ta, and enhanced piezoelectric properties could be attributed to the coexistence of two phases in these LNNST ceramics.

4. Conclusions

$(Li_{0.12}Na_{0.88})(Nb_{0.96-x}Sb_{0.04}Ta_x)O_3$ lead-free piezoelectric ceramics have been fabricated by the conventional solid-state method. A stable solid solution with a pure perovskite structure is form for these LNNST ceramics. A coexistence of orthorhombic and tetragonal phases is demonstrated for these LNNST ceramics with $0.01 < x < 0.04$, as shown in XRD patterns and the temperature dependence of the dielectric constant. The introduction of Ta slightly decreases the Curie temperature of LNNST ceramics, the dielectric constant of LNNST ceramics gradually increases with increasing Ta content, and all ceramics exhibit a low dielectric loss of less than 1.3%. The mechanical quality factor (Q_m) of LNNST ceramics increases with increasing Ta content, and a high Q_m value of ~1230 is demonstrated for the LNNST ceramic with $x = 0.06$. As a result, the LNNST ceramic is a promising candidate for the transducer and transformer applications.

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References

[1] B. Jaff, W.R. Cook, H. Jaffe, Piezoelectric Ceramics, Academics Press, New York, 1971, pp. 115–181.
[2] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, M. Nakamura, Lead-free piezoceramics, Nature 432 (2004) 84–87.
[3] S.J. Zhang, R. Xia, T.R. Shrout, $(K_{0.5}Na_{0.5})NbO_3$ based lead free piezoelectrics with expanded temperature usage range, Appl. Phys. Lett. 91 (2007) 132913.
[4] S.J. Zhang, R. Xia, T.R. Shrout, G.Z. Zang, J.F. Wang, Characterization of lead free $(K_{0.5}Na_{0.5})NbO_3$–$LiSbO_3$ piezoceramic, Solid State Commun. 141 (2007) 675–679.
[5] J. Rödel, W. Jo, K.T.P. Seifert, E.M. Anton, T. Granzow, D. Damjanovic, Perspective on the development of lead-free piezoceramics, J. Am. Ceram. Soc. 92 (2009) 1153–1177.
[6] J.G. Wu, D.Q. Xiao, Y.Y. Wang, J.G. Zhu, L. Wu, Y.H. Jiang, Phase structure and electrical properties of $(K_xNa_{0.96-x}Li_{0.04})(Nb_{0.91-})(Nb_{0.91}Ta_{0.05}Sb_{0.04})O_3$ lead-free ceramics, Appl. Phys. Lett. 91 (2007) 252907.
[7] Y. Guo, K. Kakimoto, H. Ohsato, Phase transitional behavior and piezoelectric properties of $(Na_{0.5}K_{0.5})NbO_3$–$LiNbO_3$ ceramics, Appl. Phys. Lett. 85 (2004) 4121–4123.
[8] M. Matsubara, T. Yamaguchi, W. Sakamoto, K. Kikuta, T. Yogo, S. Hirano, Processing and piezoelectric properties of lead-free (K,Na)(Nb,-Ta)O_3 ceramics, J. Am. Ceram. Soc. 88 (2005) 1190–1196.
[9] J.F. Li, K. Wang, B.P. Zhang, L.M. Zhang, Ferroelectric, piezoelectric properties of fine-grained $Na_{0.5}K_{0.5}NbO_3$ lead-free piezoelectric ceramics prepared by spark plasma sintering, J. Am. Ceram. Soc. 89 (2006) 706–709.
[10] J.G. Wu, D.Q. Xiao, Y.Y. Wang, J.G. Zhu, Compositional dependence of phase structure and electrical properties in $(K_{0.42}Na_{0.58})NbO_3$–$LiSbO_3$ lead-free ceramics, J. Appl. Phys. 102 (2007) 114113.
[11] H.L. Du, W.C. Zhou, F. Luo, D.J. Liu, S.B. Qu, Z.B. Pei, An approach to further improve piezoelectric properties of $(K_{0.5}Na_{0.5})NbO_3$-based lead-free ceramics, Appl. Phys. Lett. 91 (2007) 212907.
[12] Y. Chang, Z. Yang, L. Wei, B. Liu, Effects of $AETiO_3$ additions on phase structure, microstructure and electrical properties of $(K_{0.5}Na_{0.5})NbO_3$ ceramics, Mater. Sci. Eng. A 437 (2006) 301–305.
[13] D. Lin, D. Xiao, J. Zhu, P. Yu, Piezoelectric and ferroelectric properties of $[Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}]TiO_3$ lead-free piezoelectric ceramics, Appl. Phys. Lett. 88 (2006) 062901.
[14] L. Egerton, D.M. Dillon, Piezoelectric, Dielectric properties of ceramics in the system potassium–sodium niobate, J. Am. Ceram. Soc. 42 (1959) 438–442.

[15] H.L. Du, D.J. Liu, F.S. Tang, D.M. Zhu, W.C. Zhou, S.B. Qu, Microstructure, piezoelectric, and ferroelectric properties of Bi_2O_3-added $(K_{0.5}Na_{0.5})NbO_3$ lead-free ceramics, J. Am. Ceram. Soc. 90 (2007) 2824–2829.
[16] R.Z. Zuo, J. Fu, D.Y. Lv, Y. Liu, Antimony tuned rhombohedral-orthorhombic phase transition and enhanced piezoelectric properties in sodium potassium niobate, J. Am. Ceram. Soc. 93 (2010) 2783–2787.
[17] R.Z. Zuo, X.S. Fang, C. Ye, Phase structures and electrical properties of new lead-free $(Na_{0.5}K_{0.5})NbO_3$–$(Bi_{0.5}Na_{0.5})TiO_3$ ceramics, Appl. Phys. Lett. 90 (2007) 092904.
[18] R.P. Wang, H. Bando, M. Itoh, Universality in phase diagram of $(K,Na)NbO_3$–$MTiO_3$ solid solutions, Appl. Phys. Lett. 95 (2009) 092905.
[19] E.M. Alkoy, M. Papila, Microstructural features and electrical properties of copper oxide added potassium sodium niobate ceramics, Ceram. Int. 36 (2010) 1921–1927.
[20] J. Hao, Z. Xu, R. Chu, Y. Zhang, G. Li, Q. Yin, Effects of $K_4CuNb_8O_{23}$ on the structure and electrical properties of lead-free $0.94(Na_{0.5}K_{0.5})NbO_3$–$0.06LiNbO_3$ ceramics, Mater. Res. Bull. 44 (2009) 1963–1967.
[21] H.Y. Park, I.T. Seo, M.K. Choi, S. Nahm, H.G. Lee, H.W. Kang, B.H. Choi, Microstructure and piezoelectric properties of the CuO-added $(Na_{0.5}K_{0.5})(Nb_{0.97}Sb_{0.03})O_3$ lead-free piezoelectric ceramics, J. Appl. Phys. 104 (2009) 034103.
[22] F. Azough, M. Wegrzyn, R. Freer, S. Sharma, D. Hall, Microstructure and piezoelectric properties of CuO added $(K, Na, Li)NbO_3$ lead-free piezoelectric ceramics, J. Eur. Ceram. Soc. 31 (2011) 569–576.
[23] J. Hao, Z. Xu, R. Chua, Y. Zhang, G. Li, Q. Yin, Effects of MnO_2 on phase structure, microstructure and electrical properties of $(K_{0.5}Na_{0.5})_{0.94}Li_{0.06}NbO_3$ lead-free ceramics, Mater. Chem. Phys. 118 (2009) 229–233.
[24] F. Rubio-Marcos, P. Marchet, X. Vendrell, J.J. Romero, F. Rémondière, L. Mestres, J.F. Fernández, Effect of MnO doping on the structure, microstructure and electrical properties of the $(K,Na,Li)(Nb,Ta,Sb)O_3$ lead-free piezoceramics, J. Alloys Compd. 509 (2011) 8804–8811.
[25] Q. Yin, S. Yuan, Q. Dong, C. Tian, Effect of CuO and MnO_2 doping on electrical properties of $0.92(K_{0.48}Na_{0.54})NbO_3$–$0.08LiNbO_3$ under low-temperature sintering, J. Alloys Compd. 491 (2010) 340–343.
[26] R.M. Henson, R.R. Zeyfang, K.V. Kiehl, Dielectric and electromechanical properties of $(Li, Na)NbO_3$ ceramics, J. Am. Ceram. Soc. 60 (1977) 15–17.
[27] R.R. Zeyfang, R.M. Henson, W.J. Maier, Temperature- and time-dependent properties of polycrystalline $(Li,Na)NbO_3$ solid solutions, J. Appl. Phys. 48 (1977) 3014–3017.
[28] Y.Y. Song, H.C. Chen, F.S. Chen, D.L. Sun, P.L. Zhang, W.L. Zhong, A new ferroelectric crystal LNN with MPB composition, J. Synth. Cryst. 18 (1989) 117–121.
[29] W.L. Zhong, P.L. Zhang, H.S. Zhao, Z.H. Yang, Y.Y. Song, H.C. Chen, Low temperature phase transition of LNN, Phys. Rev. B 46 (1992) 10583.
[30] C.M. Zhang, Y.Y. Guo, Phase relationship in Na-rich region of $Li_xNa_{1-x}NbO_3$ system, J. Inorg. Mater. 5 (1990) 257–264.
[31] R.C.R. Franco, E.R. Camargo, M.A.L. Nobre, E.R. Leite, E. Longo, J.A. Varela, Dielectric properties of $Na_{1-x}Li_xNbO_3$ ceramics from powders obtained by chemical synthesis, Ceram. Int. 25 (1999) 455–460.
[32] Y.D. Juang, S.B. Daib, Y.C. Wang, W.Y. Chou, J.S. Hwang, M.L. Hu, W.S. Tse, Phase transition of $Li_xNa_{1-x}NbO_3$ studied by Raman scattering method, Solid State Commun. 111 (1999) 723–728.
[33] D. Lin, K.W. Kwok, H.L.W. Chan, Phase structures and electrical properties of $K_{0.5}Na_{0.5}(Nb_{0.925}Ta_{0.075})O_3$–$LiSbO_3$ lead-free piezoelectric ceramics, J. Phys. D: Appl. Phys. 40 (2007) 6060–6065.
[34] M. Matsubara, K. Kikuta, S. Hirano, Piezoelectric properties of $(K_{0.5}Na_{0.5})(Nb_{1-x}Ta_x)O_3$–$K_{5.4}CuTa_{10}O_{29}$ ceramics, J. Appl. Phys. 97 (2005) 114105.
[35] F. Rubio-Marcos, P. Marchet, J.J. Romero, J.F. Fernández, Structural, microstructural and electrical properties evolution of $(K,Na,Li)(Nb,Ta,Sb)O_3$ lead-free piezoceramics through NiO doping, J. Eur. Ceram. Soc. 31 (2011) 2309–2317.