

Piezoelectric Properties of Alkaline Niobate Perovskite Ceramics

Masahiko Kimura, Akira ANDO, Kosuke Shiratsuyu, and Yukio Sakabe

Murata Mfg. Co., Ltd. 2-26-10 Tenjin Nagaokakyo-shi Kyoto 617-8555 Japan

e-mail: mkimura@murata.co.jp

Piezoelectric properties of various alkaline niobate perovskite ceramics are reviewed and discussed. Sinterability of a typical ternary system $\text{LiNbO}_3\text{-NaNbO}_3\text{-KNbO}_3$ is firstly described. In NaNbO_3 rich composition region, well-sintered ceramics were obtained by the conventional powder processing. Dielectric permittivity of $\text{NaNbO}_3\text{-KNbO}_3$ pseudo binary system increases with increasing KNbO_3 mol fraction within 0.5. The relative dielectric permittivity is around 500 there, and it exceeded 1000 with other perovskite materials substitution such as CaTiO_3 . On the other hand in low KNbO_3 fraction composition region, relative dielectric permittivity around 100 was obtained. Materials in this composition region such as $(\text{Li}_{0.12}\text{Na}_{0.88})\text{NbO}_3$, drastically heightened their Q_m values by annealing (heat treatment). Their Q_m values jumped up to around 3000 from around 500. It is considered that their domain configuration might play important roles on this Q_m heightening phenomenon.

Key word: alkaline niobate, piezoelectric, ceramic, annealing, Q_m

1. INTRODUCTION

Piezoelectric ceramic materials are widely used in various electronic equipments. Lead based perovskite materials such as $\text{Pb}(\text{Ti,Zr})\text{O}_3$, or PbTiO_3 based materials are commonly used there. Piezoelectric properties of these lead-containing materials have been studied by large number of researchers. However study on other piezoelectric ceramic materials has still been limited.

Bismuth layer structured ferroelectrics (BLSF) have been studied by several researchers¹⁻¹⁵. However, these studies are almost for oscillator applications, because of their relatively small electromechanical coupling and high mechanical quality factor (Q_m).

Bi-perovskites such as $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ based ceramics have also been studied recently by several researchers, however their thermal stability is low because these materials have phase transition from ferroelectric phase to antiferroelectric phase at temperatures around 200°C, and their piezoelectricity disappear there¹⁶⁻²⁶. Therefore the Bi-perovskite based materials are difficult to be alternatives for the lead based perovskite piezoelectric ceramics despite their relatively large piezoelectricity.

Alkaline niobate perovskite ceramic materials have been studied by number of researchers²⁷⁻⁴¹, because of their attractive properties such as high acoustic velocities, high Curie temperatures, and relatively high electromechanical coupling properties. One of the earliest studies on the alkaline niobate ceramics was done by Egerton^{27,28} on $\text{NaNbO}_3\text{-KNbO}_3$ pseudo binary system. Nitta's pioneer work^{29,30} revealed the fundamental piezoelectric properties of pseudo binary system $\text{LiNbO}_3\text{-NaNbO}_3$. Yonezawa and Ohno indicated poor reproducibility of these pseudo binary systems³¹, and they pointed out that the drawback in reproducibility was improved by taking $\text{LiNbO}_3\text{-NaNbO}_3\text{-KNbO}_3$ ternary system.

In spite of these great pioneer's works, the alkaline niobate based materials have not been studied much.

The authors suppose that this is because alkaline niobates have successive phase transitions, and these might be some obstacles in practical applications.

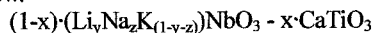
In this study, the authors reviewed dielectric and piezoelectric characteristics of the pseudo ternary system $\text{KNbO}_3\text{-NaNbO}_3\text{-LiNbO}_3$ from viewpoints of practical applications. Composition dependences of their successive phase transition were also investigated.

On the other hand, there have been limited studies³²⁻³⁴ on solid solutions between the alkaline niobate and other perovskite materials. The author had also attempted to clarify their piezoelectric properties. $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3 - \text{CaTiO}_3$ composition system was taken there as a typical example.

Furthermore, the authors revealed a characteristic change in piezoelectric properties after the heat treatment for the alkaline niobate ceramics such as $(\text{Li}_{0.12}\text{Na}_{0.88})\text{NbO}_3$ ³⁵. Their Q_m values jumped up to 3000 or higher from around 500. In this paper, this characteristic phenomenon are also reviewed and discussed.

2. EXPERIMENTAL PROCEDURES

The conventional powder processing was taken in order to make the sintered ceramic samples of $\text{LiNbO}_3\text{-NaNbO}_3\text{-KNbO}_3$ pseudo ternary system materials and their solid solutions with other perovskite materials. In this study the authors took CaTiO_3 as the other perovskite. Li_2CO_3 , Na_2CO_3 , K_2CO_3 , Nb_2O_5 , and TiO_2 were chosen as the starting materials. Their purities were 99.9% or better. These are weighed and mixed in 2-propanol to make compositions expressed below.



The mixtures were ball-milled with PSZ (Partially Stabilized Zirconia) balls ($\phi 5\text{mm}$), and the mixed powder was dried and calcined at 850°C for 2h. The poly-vinyl acetate based binder was added to the powder by amount of 5wt%, and they were well-mixed

by the ball-milling in water for 10h. The powder was dried and pulverized after a filtration.

The pulverized powder was die-pressed into disc-shaped samples. These samples were fired at temperatures between 1100°C and 1250°C. Silver electrodes were formed by paste printing and firing at 850°C. The poling treatment was carried out at 100°C in silicone oil with electric fields between 5kV/mm and 8kV/mm for 10min. Then their piezoelectric characteristics were measured with an impedance analyzer. In order to observe the characteristic change in piezoelectric properties after the heat treatment, the measured samples of some compositions around $(\text{Li}_{0.12}\text{Na}_{0.88})\text{NbO}_3$ were annealed at several temperatures, and their piezoelectric resonant characteristics were measured again.

3. RESULTS AND DISCUSSIONS

3-1 KNbO_3 - NaNbO_3 - LiNbO_3 ternary system

Sinterability:

Since these pseudo ternary system materials are difficult to sinter, good piezoelectric characteristics were obtained at limited composition areas. Firing temperature should be controlled within 10°C of fluctuation to obtain good sintered samples. Ceramic samples of the KNbO_3 rich compositions or LiNbO_3 rich compositions showed poor sinterability in this study. Well-sintered ceramics were obtained in the NaNbO_3 rich compositional region as shown in Fig. 1. The mark ■ in Figure 1 (Fig. 1) represents a composition where the well-sintered ceramic samples were obtained, and their piezoelectric properties could be measured.

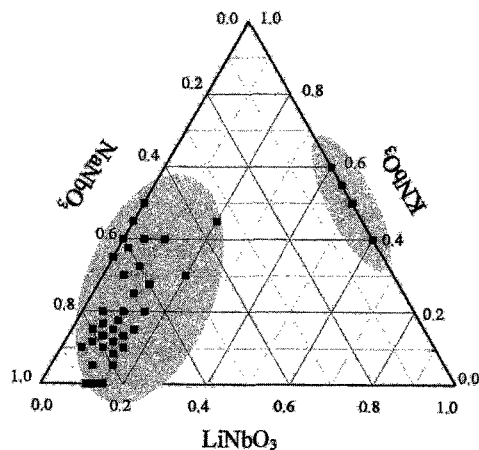


Fig.1 Compositional region where well-sintered ceramics were obtained

Dielectric and Piezoelectric properties:

Figure 2 shows dielectric permittivity of the ternary system. Relatively high values more than 500 are obtained for the composition of which KNbO_3 amount is more than 0.3 and of which LiNbO_3 amount is around 0.1. There is a tendency that dielectric permittivity increases with KNbO_3 fraction increase up to 0.3, and relatively low permittivity around 100 was observed

with low KNbO_3 fraction.

Figure 3 shows the electromechanical coupling coefficient of the planer mode (k_p) of the ternary system. There are some compositions which show the electromechanical coupling coefficient more than 40%. Curie temperatures T_c of most of the obtained ceramics samples are more than 300 °C.

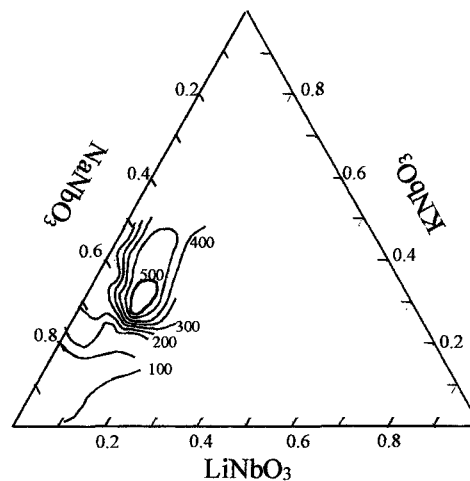


Fig.2 Dielectric permittivity in a pseudo ternary system LiNbO_3 - NaNbO_3 - KNbO_3 . The contour lines might change depending on firing conditions.

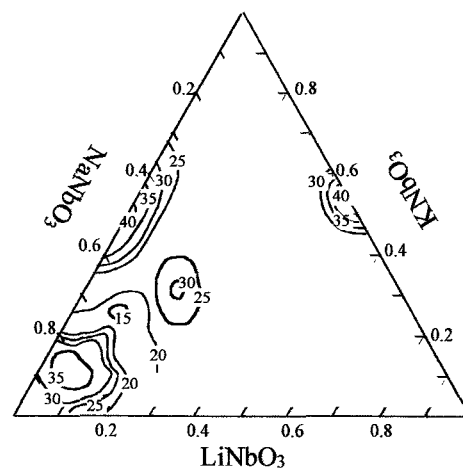


Fig.3 Electromechanical coupling coefficient in a pseudo ternary system LiNbO_3 - NaNbO_3 - KNbO_3 . The contour lines might change depending on firing conditions.

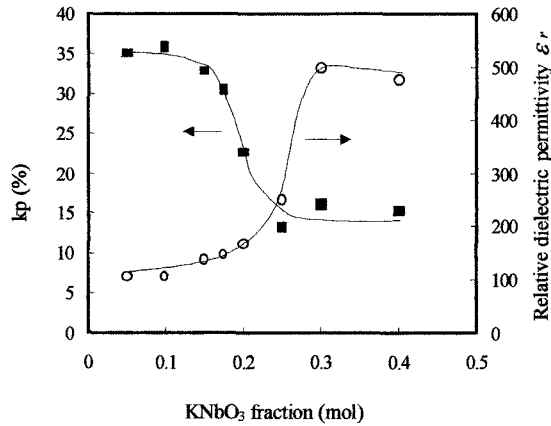


Fig.4 KNbO_3 fraction dependence of dielectric permittivity and electromechanical coupling coefficient of $\text{LiNbO}_3\text{-NaNbO}_3\text{-KNbO}_3$ with fixing LiNbO_3 fraction to 0.1

Figure 4 shows the dielectric permittivity and the electromechanical coupling coefficient against KNbO_3 fraction with fixing the LiNbO_3 fraction at 0.1. Drastic changes are observed at around 0.25 of KNbO_3 fraction.

The dielectric permittivity change against the KNbO_3 fraction shows an opposite trend to the electromechanical coupling coefficient change.

The authors expect that a spontaneous polarization is relatively unstable in the composition region with high dielectric permittivity, because an unstable spontaneous polarization means that dielectric response against an electric field becomes large. Moreover, a smaller spontaneous polarization means a lower electromechanical coupling. Therefore the dielectric permittivity and electromechanical coupling coefficient show opposite trends each other.

3-2 Solid solutions between alkaline niobates and other perovskite materials

As mentioned above, NaNbO_3 rich composition shows its relative dielectric permittivity around 150, however the dielectric permittivity increases up to around 500 with increasing KNbO_3 amount. On the other hand, the authors attempted to study the dielectric properties of their solid solutions with CaTiO_3 . The authors show the result of $x\text{-CaTiO}_3\text{-(1-x)(Na}_{0.5}\text{K}_{0.5}\text{)NbO}_3$ in Fig.5. Dielectric permittivity increases with increasing CaTiO_3 and becomes around 1500 with CaTiO_3 more than 0.08.

A few material has been reported to show high dielectric permittivity higher than 1000, beside the BaTiO_3 based material or lead based perovskite materials. Therefore, the high dielectric permittivity observed in this material system is noteworthy. The authors here show temperature dependences of dielectric permittivity and resonance frequency (planer mode) of the pseudo binary system $x\text{-CaTiO}_3\text{-(1-x)(Na}_{0.5}\text{K}_{0.5}\text{)NbO}_3$ with changing x . These are shown in Fig.6. and Fig.7.

A phase transition temperature between monoclinic (orthorhombic) and tetragonal phases T_{t-m} and a transition temperature, which is a Curie temperature T_c ,

between the tetragonal and the cubic phase were changed with the CaTiO_3 amount.

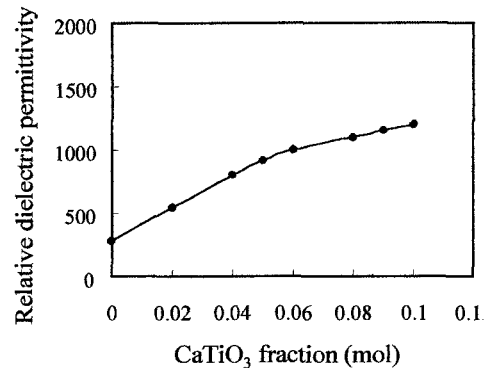


Fig.5 Dielectric permittivity change against CaTiO_3 fraction in $(1-x)\text{(Na}_{0.5}\text{K}_{0.5}\text{)NbO}_3\text{-x-CaTiO}_3$ system

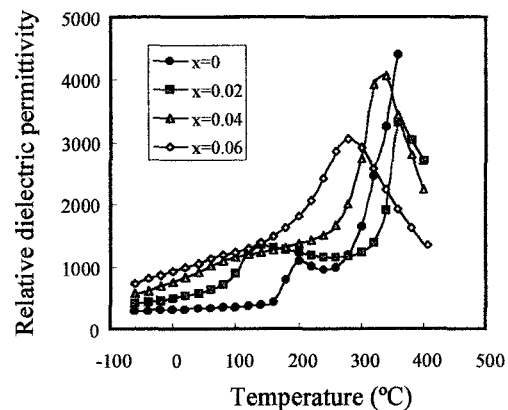


Fig.6 Temperature dependences of dielectric permittivity of $(1-x)\text{(Na}_{0.5}\text{K}_{0.5}\text{)NbO}_3\text{-x-CaTiO}_3$ system

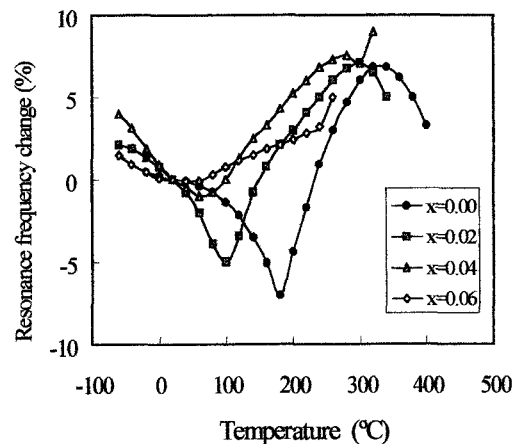


Fig.7 Temperature dependences of resonance frequency of $(1-x)\text{(Na}_{0.5}\text{K}_{0.5}\text{)NbO}_3\text{-x-CaTiO}_3$ system

The two transition temperatures lowered with increasing the CaTiO₃ fraction within 0.06. The T_{t-m} was here decided from the temperature dependence of the resonance frequency. The phase diagram is shown in Fig.8. The temperature T_{t-m} slightly increased for the CaTiO₃ amount more than 0.06. When the CaTiO₃ amount is 0.06 (mol), the transition temperature T_{t-m} lies around room temperatures. However, the dielectric permittivity does not make a clear peak against temperature as shown in Fig.6.

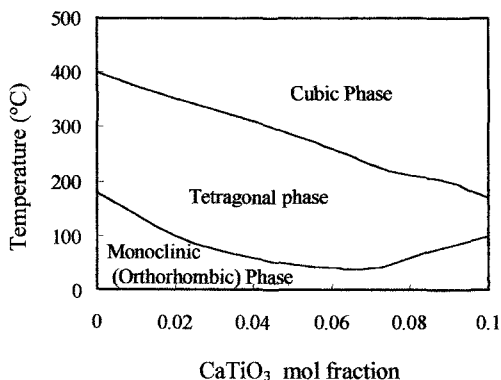


Fig.8 Phase diagram of (Na_{0.5}K_{0.5})NbO₃-CaTiO₃ system

3-3 Characteristic changes in piezoelectric properties by the heat treatment

We have seen the characteristic piezoelectric properties of the alkaline niobate based pseudo ternary system LiNbO₃-NaNbO₃-KNbO₃ especially those in the NaNbO₃-KNbO₃ pseudo binary system. Compositions which show relatively large piezoelectricity were obtained there. On the other hand, here the authors describe high Q_m characteristics of the pseudo binary system LiNbO₃-NaNbO₃.

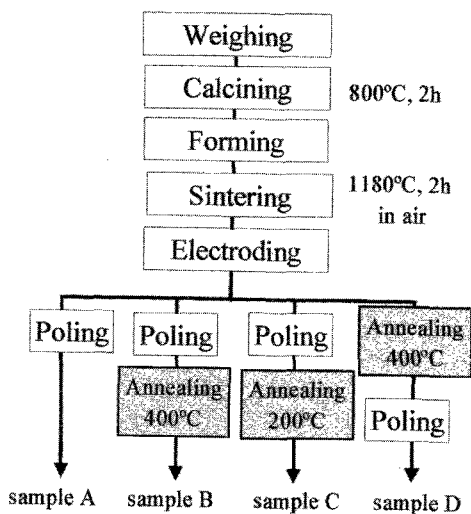


Fig. 9 Sample preparation flows

The authors discovered that ceramics with these compositions show high Q_m values by annealing (heat treatment) after their poling treatment in the previous work. Here we discuss the origin of the Q_m heightening of the pseudo binary system LiNbO₃-NaNbO₃. Sample preparation procedure which the authors took in this experiment is summarized in Fig.9. Ceramic disc samples of (Li_{0.12}Na_{0.88})NbO₃ were prepared, and the poling was done after the electrode forming. The Poling was done at 100°C (in the rhombohedral phase), and the annealing was done at 200°C (in the monoclinic phase) and 400°C (in the tetragonal phase).

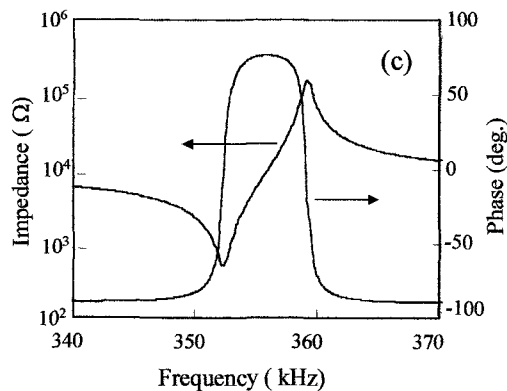
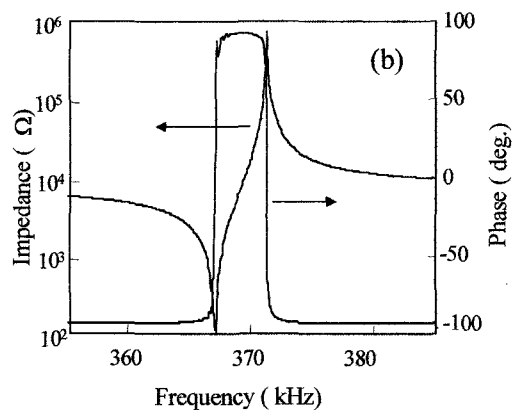
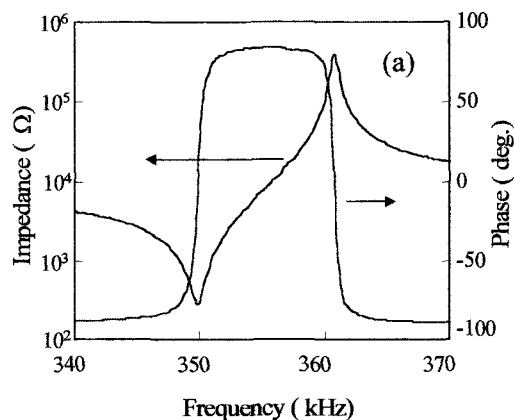


Fig.10 Impedance resonance characteristics (a) corresponds sample A and C. (b) and (c) correspond sample B and D, respectively

The sample C (annealed at 200°C) did not show a significant difference in its piezoelectric properties after the annealing. On the other hand, characteristically heightened Q_m value was observed for the sample B with the annealing of 400°C. The Q_m value changed from 500 to 3000. Since Q_m values higher than 1000 had not been reported for randomly oriented ceramics of which electromechanical coupling coefficient of a planer vibration mode is more than 20% except for lead based perovskite ceramics, the authors believe that the discovery of this Q_m heightening phenomenon would become important both in the fundamental study and applications of piezoelectric ceramic materials in the future. The impedance resonance characteristics of the samples are shown in Fig.10. The impedance resonance characteristics of sample A and sample C are as same as shown in Fig.10(a). Fig.10(b) and (c) represents sample B and D, respectively.

In order to explain the cause of the Q_m heightening, sample preparation process and piezoelectric characteristics of samples A–D were compared each other. Since sample D does not show a Q_m heightening phenomenon as shown in Fig.10(c), the origin of the Q_m heightening is not a mere quenching effect from a high temperature to room temperature.

On the other hand the difference between the sample B and C was clarified in term of crystalline structure. Sample B shows monoclinic structure, while sample C shows rhombohedral structure. Figure 11 shows the crystalline structure change with the annealing for sample B.

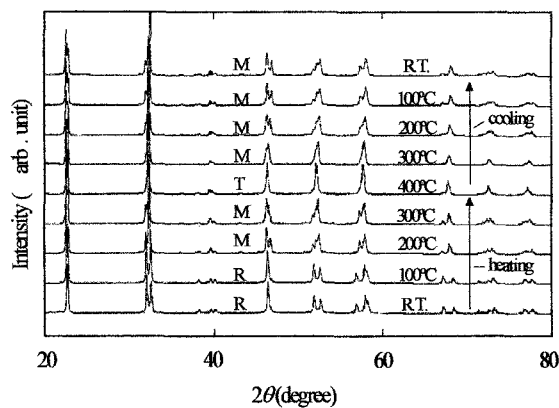


Fig.11 X-ray diffraction patterns in the annealing procedure (sample B). The Character R, M, and T represent the rhombohedral, monoclinic (orthorhombic), and tetragonal phases

From the results of experiment where the comparisons between samples A–D were done, followings were clarified.

- The Q_m heightening is not caused by the mere quenching.
- The crystalline structure after the poling procedure is rhombohedral.
- The sample which shows the high Q_m has a

monoclinic crystalline structure. The monoclinic phase is possible for a sample which has experienced the tetragonal phase at the annealing.

The authors speculate the origin of the Q_m heightening phenomenon as follows.

The origin of this Q_m heightening is considered to owe to the poling direction against the normal vector of the sample plate. Once a poling procedure was taken for the samples, (111) direction of cubic symmetry is normal to the plate after the poling. If the crystalline structure after the annealing is monoclinic so as for Sample B, then the poling direction is (110) and it has an angle of 35.3° against the (111) direction. There are three equivalent directions against the (111) directions, and they have angles of 60° against each other. Since these directions are energetically equivalent also when an electric field is applied along the (111) direction, 60° domain rotations are restricted. The Q_m value is much heightened without the non-180° domain rotation like the $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{-PbTiO}_3$ with the engineered domain structure⁴²⁻⁴³. On the other hand, the reason why the monoclinic phase appears only for the samples which experiences the tetragonal phase is still unclear. It is under investigation.

5. CONCLUSIONS

The authors reviewed the dielectric and piezoelectric characteristics of the alkaline niobate pseudo ternary system $\text{LiNbO}_3\text{-NaNbO}_3\text{-KNbO}_3$ and their solid solution of CaTiO_3 . The well-sintered ceramics were obtained for NaNbO_3 rich compositions in this study. KNbO_3 makes the dielectric permittivity higher up to around 500, and the substitution of CaTiO_3 makes it to around 1500. On the other hand, the dielectric permittivity of the low KNbO_3 fraction compositions was around 100. However, these showed characteristic Q_m heightening phenomenon after the annealing. The Q_m value reached to 3000.

Both the high dielectric permittivity and the high Q_m of the alkaline niobate system materials are noteworthy. The authors believe that they will exhibit significant importance in the future in both fundamental studies on piezoelectric materials and application oriented studies.

There have still been several unclear points on the properties of the alkaline niobate ceramic materials, especially the Q_m heightening. Further studies are necessary on them.

6. REFERENCES

- [1] S.Ikegami and I.Ueda: *Jpn. J. Appl. Phys.* **13** p.1572 (1974)
- [2] T.Takenaka, K.Shoji, H.Takai and K.Sakata: *Proc.19th Jpn. Cong. Mat.Res, Tokyo, 1975* pp.230-233 (1976)
- [3] T.Takenaka and K.Sakata: *Jpn. J. Appl. Phys.* **20** suppl.20-4 pp189-192 (1981)
- [4] A.Ando, M.Kimura, Y.Sakabe: *Proc. The 11th IEEE Intl. Symp. Appl. Ferroelectrics* pp.303-306 (1998)
- [5] A.Ando, M.Kimura, T.Sawada, K.Hayashi and Y.Sakabe: *Ferroelectrics* **268** pp.65-70 (2002)
- [6] T.Takenaka: *J. Ceram. Soc. Jpn.* **110** pp.215-224 (2002)

- [7] A.Ando, T.Sawada, H.Ogawa, M.Kimura and Y.Sakabe: Jpn. J. Appl. Phys. **41** pp.7057-7061(2002)
- [8] A.Ando, M.Kimura, Y.Sakabe: Jpn. J. Appl. Phys. **42** pp.520-525 (2003)
- [9] M.Hirose, T.Suzuki, H.Oka, K.Itakura, Y.Miyauchi and T.Tsukada: Jpn. J. Appl. **38** p.5561 (1999)
- [10] H.Oka, M.Hirose, T.Tsukada, Y.Watanabe and T.Nomura: Jpn. J. Appl. Phys. **39** p.5613 (2000)
- [11] M.Nanao, M.Hirose and T.Tsukada: Jpn. J. Appl. Phys. **40** pp.5727-5730 (2001)
- [12] K.Shibata, K.Shoji and K.Sakata: Jpn. J. Appl. Phys. **40** pp.5719-5721 (2001)
- [13] Y.Noguchi, H.Shimizu, M.Miyayama, K.Oikawa and T.Kamiyama: Jpn. J. Appl. Phys. **40**, pp.5812-5815 (2001)
- [14] M.Yokosuka: Jpn.J.Appl.Phys. **41** pp.7123-7126 (2002)
- [15] M.Demartin and D.Damjanovic: "Piezoelectric Materials in Device" Ed. by N.Setter, Lausanne (2002) pp.389-412
- [16] K.Sakata and Y.Masuda: Ferroelectrics **7** pp.347-349 (1974)
- [17] T.Takenaka and K.Sakata: Ferroelectrics **95** pp.153-156 (1989)
- [18] T.Takenaka and K.Sakata: Sensors and Materials **1** pp.123-131 (1988)
- [19] T.Takenaka, K.Sakata and K.Toda: Ferroelectrics **106** pp.375-380 (1990)
- [20] T.Takenaka, K.Maruyama and K.Sakata: Jpn.J.Appl.Phys **30** pp.2236-2239(1991)
- [21] A.Herabut, A.Safari: J. Am. Ceram. Soc. **80** pp.2954-2958 (1997)
- [22] A.Sasaki, T.Chiba, Y.Mamiya, E.Otsuki: Jpn. J. Appl. Phys. **38** pp.5564-5567 (1999)
- [23] H.Nagata, N.Koizumi and T.Takenaka: Ferroelectrics **229** pp.273-278(1999)
- [24] H.Nagata, N.Koizumi, T.Takenaka: Key Engineering Materials vols.**169-170** Trans Tech Publications, Switzerland, (1999) pp.37-40
- [25] J.Lee, K.Hong, C.Kim and S.Park: J. Appl. Phys. **91** pp.4538-4542 (2002)
- [26] T.Tani, E.Fukuchi and T.Kimura: J.Jpn.Soc.Powder and powder metallurgy **49** pp.198-202 (2002)
- [27] L.Egerton: J. Am. Ceram. Soc. **42** pp.438-442 (1959)
- [28] R.E.Jaeger and L.Egerton: J.Am.Ceram.Soc. **45**, pp.209-213 (1962)
- [29] T.Nitta and T.Miyazawa: J. Am. Ceram. Soc. **51** pp.626-629(1968)
- [30] T.Nitta and T.Miyazawa: J. Am. Ceram. Soc. **54** pp.636-637(1971)
- [31] M.Yonezawa and T.Ohno: Annual Report of Study Group on Applied Ferroelectrics in Japan **21**, pp.65-71(1975) *in Japanese*
- [32] M.Kimura, T.Ogawa and A.Ando: Japan Patent Application 1998-35713(1998) equivalent to US Patent 6093339
- [33] M.Kimura and A.Ando: Japan Patent Application 1998-35714(1998) equivalent to US patent 6083415
- [34] T.Wada, K.Toyoike, Y.Imanaka, Y.Matsuo: Jpn. J. Appl. Phys. **40**, pp.5703-5705 (2001)
- [35] M.Kimura, T.Ogawa, A.Ando, Y.Sakabe : Proc. 13th IEEE Intl. Symp. Appl. Ferroelectrics p.339 (2003)
- [36] L.Pardo, P.Duran-Martin, J.P.Mercurio, L.Nibou and B.Jimenez: J. Phys. Chem. Solid **58**, pp.1335-1339 (1997)
- [37] L.Pardo, P.Duran, C.E.Millar, W.W.Wolny and B.Jimenez:Ferroelectrics **186**, pp.281-285(1996)
- [38] C.B.DiAntonio and S.M.Pilgrim: J.Am.Ceram.Soc. **84**, pp.2547-2552(2001)
- [39] L.A.Reznitchenko, A.V.Turik, E.M.Kuznetsova and V.P.Sakhnenko: J.Phys.:Condens. Matter **13** pp.3875-3881 (2001)
- [40] T.Takenaka, T.Okuda and K.Takegawara: Ferroelectrics **196** p.175 (1997)
- [41] H.Nagata and T.Takenaka: Jpn.J.Appl.Phys. **37** pp.5311-5314 (1998)
- [42] T.Tsurumi, K.Okamoto, N.Ohashi, S.Wada, and Y.Yamashita: Trans. Mat. Res. Soc. Jpn. **25** pp.177-180 (2000)
- [43] S.Wada and T.Tsurumi: KagakuKougyo **50** pp.858-866 (1999) *in Japanese*

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