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Piezoelectric Characteristics and Temperature Stability of Resonant Frequency of $PbTiO_3$ System Ceramics for High Frequency Resonator using 3rd Overtone Thickness Vibration Mode

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Abstract

In this study, $Pb_{0.88}(La_{\alpha}Nd_{1-\alpha})_{0.08}(Mn_{1/3}Sb_{2/3})_{0.02}Ti_{0.98}O_3$ system ceramics with La molar ratio α variation were manufactured for 24 MHz class resonator application. Electromechanical coupling factor, mechanical quality factor and dynamic range of 3rd overtone thickness vibration mode were measured as the variations of La and Nd molar ratio. Mechanical quality factor and dynamic range at $\alpha = 0.6$ composition ceramics showed the highest value of 2691 and 52.37 dB, respectively. The temperature coefficient of resonant frequency measured from -20℃ to 80℃ showed an excellent value of 5ppm/℃ at $\alpha = 1$ composition ceramics.

Key Words : Resonator, 3rd overtone thickness vibration mode, Temperature coefficient of resonant frequency

1. INTRODUCTION

As the crystal resonators have been recently replaced with ceramics, which can be used as clock oscillators for CD ROM, FDD and HDD, the properties of ceramic resonators have been intensively studied. For the application of resonators for frequencies higher than 20MHz, the 3rd overtone thickness vibration mode must be used because of the limitation in thinning operation associated with the fundamental thickness vibration mode for high frequencies. As far as the composition ceramics for the 3rd overtone thickness vibration mode resonators are concerned, the dynamic range expressed by the decibel ratio of resonant to anti resonant impedances must be high enough to induce stable thickness vibration. Based on such requirement, $PbLa(Ti,Mn)O_3$ ceramics, which had been reported as a composition ceramics with high mechanical quality factor and high dynamic range, have been widely used for high frequency resonators. However, the dynamic ranges of 3rd overtone thickness vibration mode between compositions with deficient and excess PbO may result in significant differences[1] in electrical characteristics primarily because of PbO evaporation during the manufacturing process. In addition, for high frequency application over 20MHz, the porosity in the ceramics must be controlled low enough since the mechanical quality factor and dynamic range are deteriorated by the absorption and dispersion of acoustic wave through the large pores. In other

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words, the first requirement for high frequency resonators is the fully dense and pore free ceramic substrate.

To eliminate pores in the ceramics, various kinds of manufacturing processes can be utilized. Those processing routes include sintering in oxygen atmosphere and hot pressing. From the standpoint of cost, however, the best choice is to utilize normal sintering in air.

In this study, $Pb_{0.88}(La_{\alpha}Nd_{1-\alpha})_{0.08}(Mn_{1/3}Sb_{2/3})_{0.02}Ti_{0.98}O_3$ system ceramics with La molar ratio α variation were produced mainly for improved densification and mechanical quality factor. Electrical, dielectric and structural characteristics were analyzed for the piezoelectric ceramics to investigate the high frequency resonator application.

2. EXPERIMENT

Compositions ceramics of $Pb_{0.88}(La_{\alpha}Nd_{1-\alpha})_{0.08}(Mn_{1/3}Sb_{2/3})_{0.02}Ti_{0.98}O_3$ with La molar ratio α variation, to which 0.1wt% PbO and 0.1wt% MnO_2 were added, were produced from the raw material oxides via conventional mixed oxide process. The oxide powders of high purity above 99% were mixed up in the ball mill for 24 h. The resulting slurry was then dried and mixture was calcined at 850℃ for 2h. The calcined powder was ball-milled again in acetone. After drying and mixing with PVA solution, the powders were uniaxially pressed at 1.33 ton/㎠ into disks of 21㎜ in diameter. After binder burn out, the disks were sintered at 1220℃ for 2h in air. The disks were lapped to the thickness of 0.32㎜ and then electroded with the 17mmφ -diameter. The microstructure was investigated by scanning electron microscopy and the grain size was measured. Poling treatments of the specimen were performed by 50 kV/㎝ for 10 min in silicon oil bath at 130℃. Electrical and piezoelectric properties of the specimens that underwent poling treatment were determined by the resonance method using frequency data obtained using a network analyzer (HP5100). The TCF_r from 20 ℃to 80℃ was calculated by measuring the resonant frequency of the thickness-mode specimen using an impedance analyzer (HP5100) in a thermostatic chamber. The equation used for calculation is as follows:

$$TCF_r = \frac{f_r(\max) - f_r(\min)}{f_r(25°C)} \times \frac{1}{100} (ppm/°c) \tag{1}$$

The dynamic range was calculated by following equation.

$$D.R. = 20\log\left|\frac{Z_{\max}}{Z_{\min}}\right| \tag{2}$$

3. RESULTS AND DISCUSSION

Figure 1 shows X-ray diffraction patterns of the specimens with La molar ratio α variation . As can be seen from Table 1 and Fig. 1, the crystal structure of the materials was identified as tetragonal. The tetragonality from 1.025 to 1.03 was smaller than that of pure $PbTiO_3$, The highest tetragonality was obtained at $\alpha = 0$ omposition. With the increased amount of α,

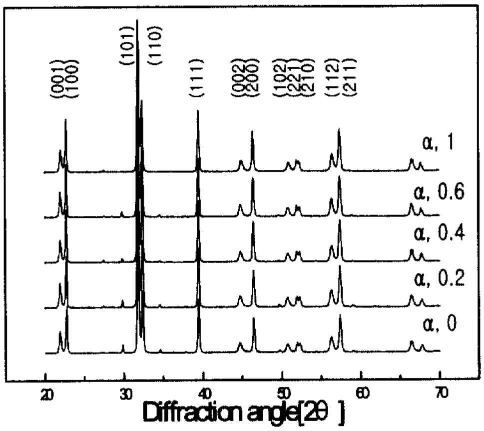
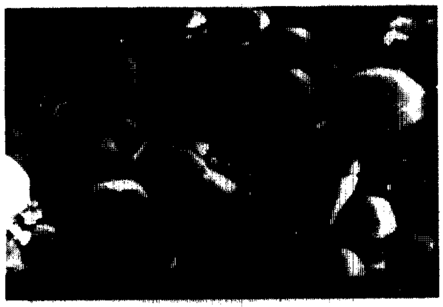


Fig. 1. XRD diffraction pattern as a function of La molar ratio variation.

tetragonality decreased. This can be illustrated by the increase of the substitution of La^{3+} (1.061 Å) ion with larger ion radius than Nd^{3+} (0.995 Å) ion. For instance, anisotropy in the coupling factor (k_t/k_p) is promoted by the substitution of rare earths of small ionic size, such as Sm or Gd for Pb. That is, anisotropy in the coupling factor (k_t/k_p) becomes higher as rare-earth ionic radius decreases. This behavior is probably related to variation in the ferroelectric domain structure caused by a change in the tetragonality of the crystal lattice.

(a) α=0



(b) α=0.6

(c) α=1

Fig. 2. Microstructure of the specimens as a function of La molar ratio variation.

Figure 2 and 3 show microstructure and grain size of the specimens sintered at 1220℃ as a function of α variation. The maximum average grain size was 1.58㎛ at α = 0.4 composition. However, as the α increased more than it, the grain growth was restrained. Such increase in grain size at the composition of La/Nd=0.4/0.6 ratio can be interpreted in terms of the improvement of solid state diffusion effect according to the substitutions of complex La and Nd ions into the A site in the ABO_3 perovskite. As shown in Fig. 3, the maximum density of 7.66g/cm^3 was obtained at the composition of α = 0 composition and thereafter decreased with increasing α. This is due to the increase of the substitution amount of lighter La (atomic weight 138.905g) than Nd (atomic weight 144.2g).

In order to increase the mechanical quality factor of $Pb_{0.88}(La_{\alpha}Nd_{1-\alpha})_{0.08}(Mn_{1/3}Sb_{2/3})_{0.02}Ti_{0.98}O_3$ ceramics, excess MnO_2 was added to the system, as shown in the composition formula. This is due to the facts that Mn^{2+} with ion radius of 0.82Å and Mn^{3+} with ion radius of 0.66Å could be substituted to Ti^{4+} ion position with ion radius of 0.68Å at smaller addition of MnO_2. In this case, holes are generated since Mn^{2+} and Mn^{3+} ions act as acceptor dopants and as a result, carrier concentration increases, leading to a decrease in resistivity and increase in mechanical quality factor, Q.[2-4].

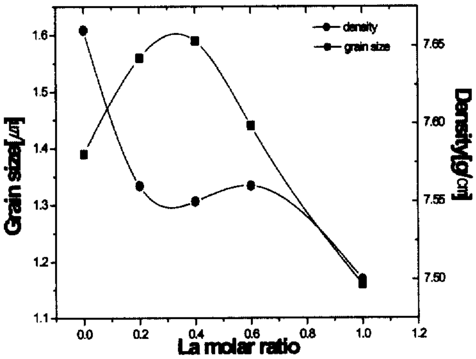


Fig. 3. Density and grain size as a function of La molar ratio variation.

Figure 4 shows the mechanical quality factor in 3^{rd} overtone thickness vibration mode, Q_{mt3} increase with increasing the partial substitution amounts of La for Pb Sites. When α was 0.6, it indicated the maximum value of 2691. This is due to the improvement of poling condition with the decrease of tetragonality. And Q_{mt3} can be influenced on the sintered density and grain size of the manufactured specimens. Generally, higher density and larger grain size can increase Q_{mt3} to some extent.[5] Accordingly, it can be concluded that the microstructural and physical properties such as the decreased tetragonality, higher density and larger grain size were increasingly acted on the Q_{mt3} at $\alpha=$ 0.6 composition.

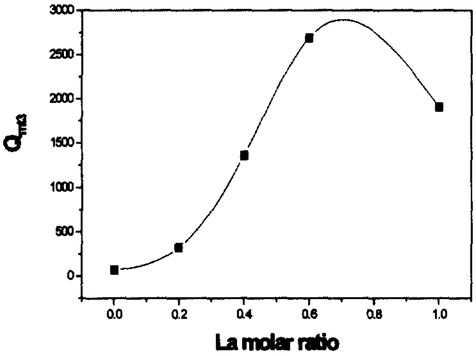


Fig. 4. Mechanical quality factor of 3^{rd} over tone mode as a function of La molar ratio variation.

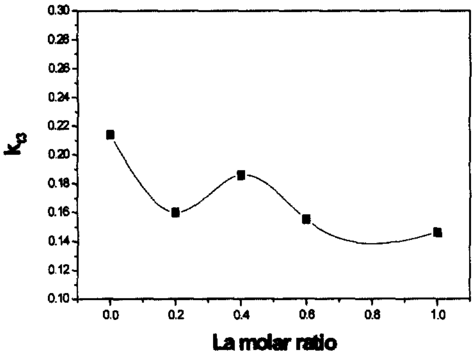


Fig. 5. Electromechanical coupling factor of 3^{rd} overtone mode as a function of La molar ratio variation.

As shown in Fig. 5, electromechanical coupling coefficient in 3^{rd} overtone thickness vibration mode, k_{t3} was decreased with increasing α. This is clearly evidenced from the weakening of ferroelectricity by the decrease of tetragonality with increasing α.

Figure 6 shows the temperature coefficient of resonant frequency [TCF_r] from -20℃ to 80℃. The TCF_r[%] may be changed with a poling electric field and a sintering temperature[6,7].

However, in this experiment, poling electric field and sintering temperature were fixed as 50 kv/cm and 1220℃, respectively. As the amount of La molar ratio α increases, the TCF_r moved

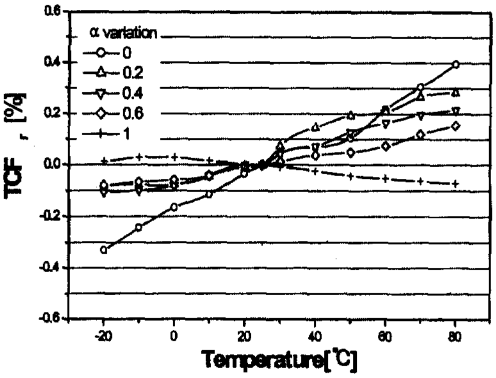


Fig. 6. Temperature coefficient of resonant frequency TCF_r[%] as a function of La molar ratio variation.

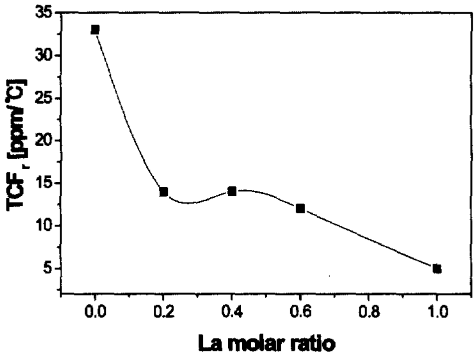


Fig. 7. Temperature coefficient of resonant frequency TCF_r[ppm/℃] as a function of La molar ratio α.

Table 1. Characteristics of third overtone vibration mode as a function of La molar ratio variation.

α variation	f_r [MHz]	f_a [MHz]	Z_r[Ω]	Z_a[Ω]	DR_3[dB]	Q_{mt3}	k_{t3}	ε_r	c/a	N_{t3}	TCF_r [ppm/℃]	Density [g/cm²]	Tc[℃]
0	23.255	23.705	1.66	7.20	12.75	69	0.21	265	1.030	7.348	33	7.66	331
0.2	24.035	24.290	0.65	40.27	35.87	324	0.16	253	1.029	7.481	14	7.56	328
0.4	24.005	24.350	0.11	20.85	45.24	1359	0.18	255	1.027	7.548	14	7.55	325
0.6	24.675	24.920	0.08	32.40	52.37	2691	0.15	263	1.027	7.600	12	7.56	326
1	23.810	24.020	0.13	46	51.32	1907	0.14	270	1.025	7.566	5	7.50	323

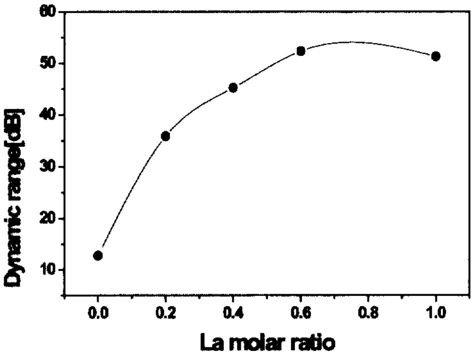


Fig. 8. Dynamic range of 3rd overtone vibration mode as a function of La molar ratio variation.

to the lower negative side. When α was 1, TCF_r showed an excellent value of 5ppm/℃ as shown in Fig. 7.

However, further studies are necessary for the variations in TCF_r according to the complex substitution of La and Nd for Pb site. Moreover, the effects of the physical factors of the materials such as compliance, stiffness and thermal expansion coefficients on the TCF_r have to be investigated additionally. Figure 8 shows the dynamic range[D.R.] in 3rd overtone thickness vibration mode with α variation. For stable vibration in the high frequency resonator, the D.R. representing the decibel ratio of resonant and anti resonant impedance has to be as high as possible[8,9]. With increasing α, the D.R. was decreasing. The maximum dynamic range of the 3rd overtone thickness vibration mode appeared to be 52.37dB at the composition of α=0.6 It is believed that the highest dynamic range can be obtained from the composition ceramics with relatively higher values of Q_{mt3}. Above experimental results are summarized as Table 1.

4. CONCLUSION

In this study, compositions ceramics of $Pb_{0.88}(La_{\alpha}Nd_{1-\alpha})_{0.08}(Mn_{1/3}Sb_{2/3})_{0.02}Ti_{0.98}O_3$ with La molar ratio α variation, to which 0.1wt% PbO and 0.1wt% MnO_2 were added, were manuctured for 24 MHz class resonator application. Electromechanical coupling factor, mechanical quality factor and dynamic range in the 3rd overtone thickness vibration mode were measured as the variations of La and Nd molar ratio. The results obtained from this experiment are as follows:

1. With the increased amount of La molar ratio α, tetragonality decreased.
2. Mechanical quality factor and dynamic range at α= 0.6 composition ceramics showed the highest value of 2691 and 52.37dB, respectively.
3. The temperature coefficient of resonant frequency measured from -20℃ to 80℃ showed an excellent value of 5ppm/℃ at α= 1 composition ceramics.

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