Microstructural, Dielectric and Electrical Properties of (Pb,La,Ce)TiO_3 Ceramics for High Frequency Ceramic Resonator as a function of MnO_2 Addition

Ju Hyun Yoo, Dong On Oh, and Chang Yub Park
Department of Electrical Engineering, Semyung University, Jechon, Chungbuk 390-711, Korea

Ji Hong Kim
Department of Electronic Engineering, Semyung University, Jechon, Chungbuk 390-711, Korea

Sung Ill Lee
Department of safety Engineering, Chungju University, Chungju, Chungbuk 380-762, Korea

Sung Lim Ryu
Department of materials Science and Engineering, Chungju University, Chungju, Chungbuk 380-762, Korea

E-mail : juhyun57@semyung.ac.kr

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In this study, microstructural, dielectric and electrical properties of $(Pb_{0.83})(La_{0.2}Ce_{0.8})_{0.08}TiO_3$(PCT) ceramics as a function of MnO_2 addition and electrode size variation were investigated for 30 MHz high frequency ceramic resonator application. Grain size was gradually increased according to the increase of MnO_2 addition amount. Moreover, the density showed a constant value with increasing MnO_2 addition amount. Dielectric constant was decreased with increasing MnO_2 addition amount. Curie temperature of all the composition ceramics was nearly constant around 330℃. The maximum D.R.of 50.5 dB and maximum Q_{mt3} of 1842 in the 3^{rd} overtone vibration mode were appeared at the composition of 0.3wt% MnO_2, respectively.

Keywords : 30 MHz high frequency ceramic resonator, Grain size, dynamic range (D.R.)

1. INTRODUCTION

In comparison with quartz resonators, recently, ceramic ones with the merits of low cost and high rising time for oscillation have been widely utilized. And also, in order to increase the speed of hard disk drive (HDD) and floppy disk drive (FDD), the operating frequency of oscillator or resonator generating clock is necessary to be higher. However. In order to increase operating frequency of resonator, 3^{rd} overtone thickness vibration mode must be utilized in the high frequency resonators because the devices using fundamental mode thickness vibration for high frequency have the difficult problems such as lapping and polishing in diminishing its thickness [1,2]. As far as the composition ceramics used for resonator using 3^{rd} overtone mode thickness vibration are concerned, the dynamic range (D.R.) represented as the decibel ratio of resonant impedance to anti resonant impedance must be higher to induce a stable thickness vibration. Based on the facts, PbLa(Ti,Mn)O_3 ceramics[3], which had been reported as the composition ceramics with high mechanical quality factor and higher dynamic range, have been widely used for high frequency resonators. However, the dynamic ranges of 3^{rd} overtone thickness vibration mode between deficient PbO composition and excess PbO one may accompany the remarkable differences because of PbO evaporation through the manufacturing process. Moreover, in the high frequency resonators more than 20 MHz, the resonator with large porosity show a decreased mechanical quality factor and D.R.because of an absorption and dispersion of acoustic wave through the large pore.

To make high frequency ceramic resonators, $PbTiO_3$

ceramic materials are better than PZT material because the mechanical Q_{mt} is larger and the dielectric constant is smaller[4]. Also, $PbTiO_3$ materials are more suitable for making 3rd overtone mode resonators rather than fundamental mode ones because it is theoretically impossible to make fundamental frequencies using a trapped mode. In this study, the $(Pb,La)TiO_3$ system ceramic substituted to (Ce) was manufactured with the variations of MnO_2 addition amount in order to increase mechanical quality factor. Electrical, dielectric and structural characteristics were analyzed for the manufactured piezoelectric ceramics to investigate 30 MHz high frequency resonator application.

1. EXPERIMENTAL

Compositions of 0.25 wt% CuO added $(Pb_{0.83})(La_{0.2}Ce_{0.8})_{0.08}TiO_3$(PCT) with different amount of MnO_2 were produced from the raw material oxides via conventional mixed oxide process. High purity oxide powders more than 99% were mixed up in the ball mill for 24 h.

The resulting slurry was then dried and mixture was calcined at 900℃ for 4h. The calcined powder was again ball-milled in acetone. After drying and mixing with PVA solution, the powders were uniaxially pressed at 3 ton/㎠ into disks 30 ㎜ in diameter. After burning out the binder, the disks were sintered at 1200℃ for 2h in air. The sintered disks were lapped to thickness of 0.255 ㎜ and then electroded.

The SMD type ceramic resonators with the size of 3.7× 3.1× 0.255 ㎣ were fabricated from the disc as shown Fig.1. The microstructure was investigated by scanning electron microscopy and the grain size was measured from the SEM micrographs using linear intercept method. Poling treatments of the specimen were performed by 70 kV/㎝ for 10 min in a 120℃ silicon oil bath. Electrical and piezoelectric properties of the specimens that underwent poling treatment were determined by resonance method using frequency data obtained using a network analyzer (HP4294A).

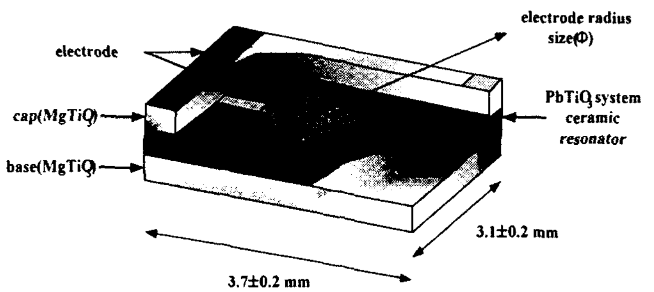


Fig. 1. Dimension and structure of SMD type ceramic resonator.

2. RESULTS AND DISCUSSION

Figure 2 shows X-ray Diffraction Patterns of the specimens with different MnO_2 compositions. As can be seen from Table1 and Fig.2, the crystal structure of the materials was identified as tetragonal. The tetragonality showed smaller values from 1.033 to 1.036, than that of pure $PbTiO_3$. As MnO_2 addition was more than 0.7wt%, tetragonality was increased. For the increase of tetragonality, additional investigations are necessary. And also, as MnO_2 addition amount is more than 0.5wt%, Unknown phase was apparently appeared. It is perhaps considered that excess MnO_2 addition make second phase with 0.25wt% added CuO.

Figure 3 shows microstructure of the specimens sintered at 1200 ℃ as a function of MnO_2 addition. The

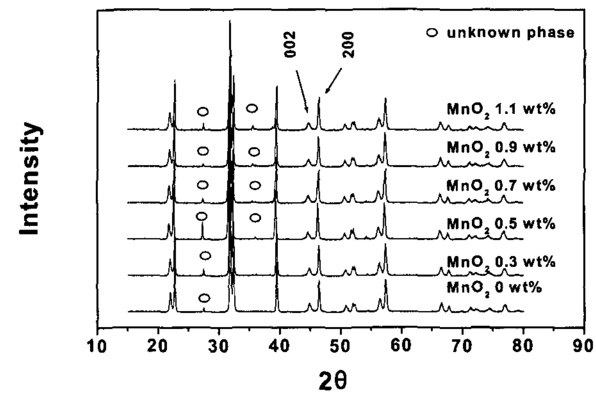
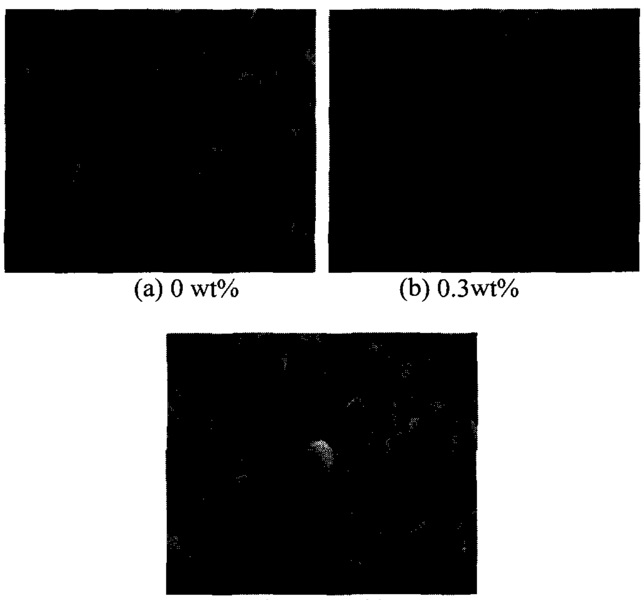


Fig. 2. X-ray diffraction patterns with MnO_2 addition.



(a) 0 wt% (b) 0.3wt%

(c) 0.9 wt%

Fig. 3. Microstructures with MnO_2 addition.

average grain size of specimen with no impurity was 1.406 ㎛. However, as the MnO_2 addition amount is increased, the grain growth occurred. As shown in Table 1, the density showed a constant value with increasing MnO_2 addition amount.

Table 2 (a) and Fig 4 shows D.R. and mechanical quality factor(Q_{mt3}) in the 3rd overtone vibration mode as a function of MnO_2 addition and electrode size variation. The maximum D.R.of the 3rd overtone vibration mode was appeared as 50.5 dB at the composition of 0.3wt% MnO_2 addition amount.

Table 1. Physical properties of sample with MnO_2 addition.

MnO_2 [wt%]	Dielectric constant	Density [g/cm³]	Tc[℃]	Grain size [㎛]	Tetragonality (c/a)
0	350	7.58	331	1.406	1.0337
0.3	245	7.56	332	1.424	1.0337
0.5	231	7.54	335	1.444	1.0338
0.7	230	7.53	331	1.538	1.0338
0.9	231	7.56	325	1.759	1.0347
1.1	235	7.54	331	1.957	1.0364

The maximum Q_{mt3} of 1842 was also obtained at the composition of 0.3 wt % addition amount. Thereafter, it was decreased with increasing MnO_2 addition amount. This is due to the facts that Mn^{2+} and Mn^{3+} could be substituted to Ti^{4+} ion position with ion radius of 0.68Å at the composition of 0.3wt% MnO_2 addition. Then, holes are generated since Mn^{2+} and Mn^{3+} ions act as acceptor dopants and as a result, carrier concentration increases, leading to a increase in mechanical quality factor, Q_{mt}[5,6]. At the composition ceramics more than 0.3wt% MnO_2 addition amount, D.R. and mechanical quality factor(Q_{mt3}) in the 3rd overtone vibration mode were decreased because of increasing second phase.

At the composition of 0.3wt% MnO_2, D.R. and Q_{mt3} with the change in electrode radius size are shown in Fig.5 and Table 2 (b). Sample with electrode radius size of 0.77mm showed the highest D.R. and Q_{mt3} values by decreased resonant resistance. When the electrode radius size is 0.77mm, the vibration energy is focused on the electrode part while it is extremely damping in the outer non-electrode part. That is, an energy- trapping effect in

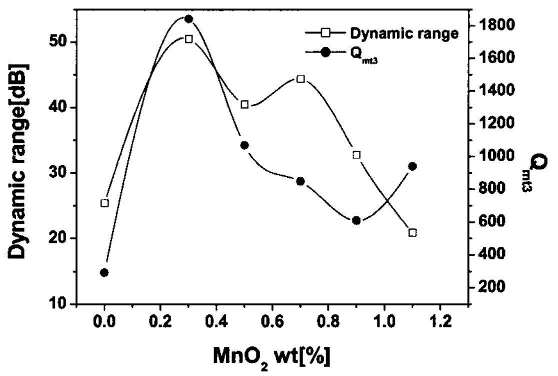


Fig. 4. Dynamic range(D.R.) and mechanical quality factor(Q_{mt3}) as a function of MnO_2 addition at electrode radius size 0.77mm.

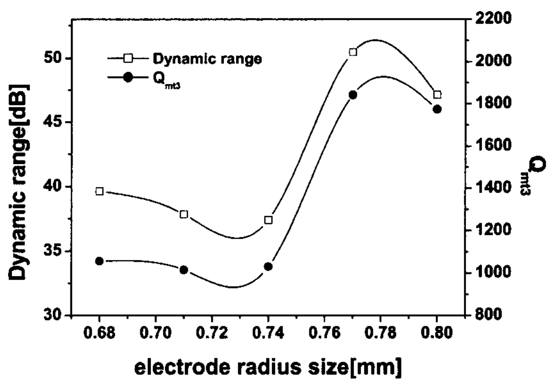


Fig. 5. Dynamic range($D.R_3$) and mechanical quality factor(Q_{mt3}) as a function of electrode radius size at the 0.3wt% MnO_2 addition

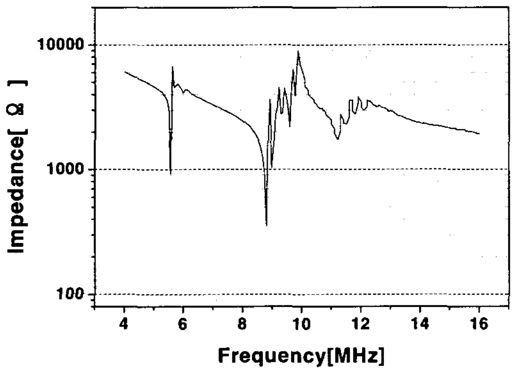
Table 2. Resonant and piezoelectric characteristics as a function of MnO_2 addition and electrode radius size variation.

(a) MnO_2 addition

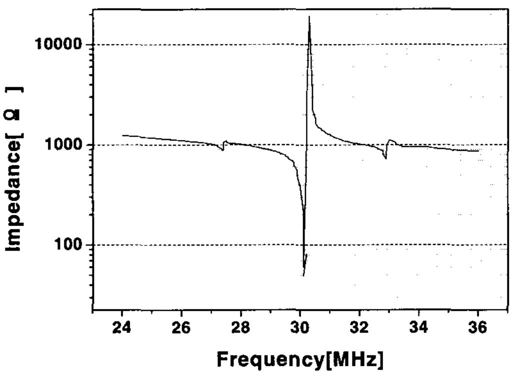
MnO_2 [wt%]	f_r [MHz]	f_a [MHz]	Z_r [Ω]	Z_a [Ω]	D.R [dB]	Q_{mt3}	k_{t3}
0	29.79	29.91	343	6300	25.36	291	0.099
0.3	30.06	30.24	52	17443	50.48	1842	0.120
0.5	29.91	30.06	120	13600	40.48	1068	0.110
0.7	30.06	30.22	140	24430	44.35	848	0.113
0.9	29.92	30.08	210	8926	32.76	609	0.113
1.1	29.44	29.5	313	3466	20.85	938	0.070

(b) electrode radius size variation

electrode radius size[mm]	f_r [MHz]	f_a [MHz]	Z_r [Ω]	Z_a [Ω]	D.R [dB]	Q_{mt3}	k_{t3}
0.68	30.09	30.27	137	13117	39.66	1057	0.120
0.71	30.06	30.24	124	9922	37.86	1015	0.120
0.74	30.06	30.24	108	9683	37.41	1030	0.120
0.77	30.06	30.24	52	17443	50.48	1842	0.120
0.8	30.08	30.26	59	12630	47.12	1774	0.120



(a) Fundamental vibration mode



(b) 3rd overtone vibration mode

Fig. 6. Impedance curves of fundamental and 3rd overtone thickness vibration mode at 0.77mm electrode radius size with 0.3wt% MnO_2.

the 3rd overtone vibration mode was strongly generated at that electrode radius size.

Figure 6 shows impedance curves of fundamental and 3rd overtone thickness vibration mode at 0.77mm electrode radius size at 0.3wt% MnO_2 addition composition. Energy trapping effect in the fundamental vibration mode was not appeared because of smaller Poisson's ratio less than 0.3.

4. CONCLUSION

The structural, piezoelectric and dynamic range characteristics of modified $PbTiO_3$ ceramics were investigated as a function of MnO_2 addition. Grain size was gradually increased according to the increase of MnO_2 addition amount. Moreover, the density showed a constant value with increasing MnO_2 addition amount. Dielectric constant was decreased with increasing MnO_2 addition amount. Curie temperature of all the composition ceramics was nearly constant around 330℃. The maximum D.R. of 50.5 dB and maximum Q_{mt3} of 1842 in the 3rd overtone vibration mode were appeared at the composition of 0.3wt% MnO_2, respectively.

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