Effect of Y doping on Mn valence in BaTiO$_3$ dielectric system

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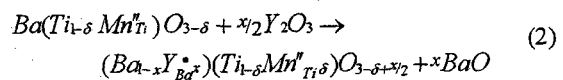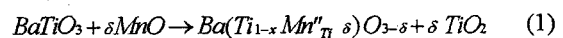
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The donor/acceptor doping technique has been commonly used for improving the reliability of BME-MLCCs, especially on the HALT. It is well known that the acceptor doping, i.e. Mn-doping provides, the reduction resistance and the donor doping, i.e. Y-doping, creates the cation vacancies in BaTiO$_3$ lattice, which compensate the oxygen vacancies. Generally, in the explanation above, the valence of Mn ion is always "+2". However, the valence of Mn is thought to be strongly depended by surrounding atmosphere and other defects, such as V_{Ba}, V_{Ti}, V_O and Y_{ba}. It is necessary to identify the valence of Mn ion in order to understand the mechanism of MLCCs reliability improvement by donor/acceptor doping. In this study, the valence of Mn ion was detected using ESR and XANES and the role of Mn doping or reliability improvement in MLCCs were discussed.

Key word: MLCCs , HALT ,Valence of Mn ,ESR, XANES

1. INTRODUCTION

The high volumetric efficiency of multilayer ceramic capacitors (MLCCs) has made them valuable components in electronics, where the constant downsizing has become the norm. Central to the continued cost-effectiveness of MLCCs has been the use of Ni electrodes, which however has necessitated compositional modifications to combat the degradation of insulation resistance resulting from sintering in reducing atmospheres. The authors have previously found that the resistance degradation measured in the highly accelerated life tests (HALT) was caused by oxygen ion vacancy migration[1-3]. The oxygen ion vacancies were created by MnO substitution to prevent the reduction of insulation resistance. Furthermore, the authors have reported that donor doping such as Y^{3+} for BaTiO$_3$-based ceramics is an excellent method for improving the resistance degradation in HALT for Ni electrode MLCCs.[1-3] It is thought that the reduction in resistance degradation in HALT was due to the compensation of oxygen vacancies $V_O^{\cdot\cdot}$ by barium vacancies V_{Ba}'', which in turn were created by Y^{3+} addition, the proposed process can be summarized as follows:

$$BaTiO_3 + \delta MnO \rightarrow Ba(Ti_{1-x}Mn''_{Ti\ \delta})O_{3-\delta} + \delta\ TiO_2 \quad (1)$$

$$Ba(Ti_{1-\delta}Mn''_{Ti})O_{3-\delta} + {}^x/_2Y_2O_3 \rightarrow$$
$$(Ba_{1-x}Y^{\cdot}_{Ba^x})(Ti_{1-\delta}Mn''_{Ti\delta})O_{3-\delta+x/2} + {}^xBaO \quad (2)$$

In the explanation above, the valence of Mn ion was always "+2." However, the valence of Mn is thought to be strongly depended by surrounding atmosphere and other defects, such as V_{Ba}'', V_{Ti}'''', $V_O^{\cdot\cdot}$ and $Y_{Ba}^{\cdot}$. Furthermore, according to eq.2, it is expected that the ratio of Mn to rare earths is 1:2 as the ratio with a least oxygen vacancy concentration. However, according to the detailed experiments, it became clear that the ratio of Y to Mn which improved the reliability in HALT was at equimolar or excess of Y [3]. It is observed that the reliability deteriorates adversely when the quantity of Y$_2$O$_3$ and MnO addition increased. It is necessary to identify the valence of Mn ion and consider the compensation effect of Y and Mn in order to understand the above contraction. In this study, the valence of Mn ion was determined by ESR and XANES so that we consider the role of Mn-Y co-doping on the reliability improvement of MLCCs.

2. EXPERIMENTAL PROCEDURE

The dielectric compositions for reliability measurements were $(Ba_{1-x}Ca_xO)_m(Ti_{1-y}Zr_yO_2)$ + a MnO + $bSiO_2$ (BCTZ system) with x=0-0.07, y=0.18, m=1.004, a=0.25 mol%, b=0.1 wt%, while Y_2O_3 was added in the same atomic ratio as MnO. The starting materials, $BaTiO_3$, $BaZrO_3$ and $CaTiO_3$, were highly pure hydrothermally synthesized powders. The other powders were at the reagent grade. The raw mixtures were prepared by wet ball-milling for 16 hours using 10 mm and 3 mm ϕ ZrO_2 balls. MLCCs were prepared by the so-called sheet methods. Green sheets with a controlled thickness of 15 microns were formed by doctor blade casting method. After casting, Ni electrodes were printed with a screen printing method. Next, 4 layers of the sheets were stacked, laminated, and cut into green chips. The chips were fired for binder burn-out then sintered at 1300 degree Celsius. During sintering, the oxygen partial pressure was controlled between 10^{-8} and 10^{-13} MPa by adjusting the amounts of H_2 and H_2O in the N_2-H_2-H_2O gas mixture. The chips were then annealed at 1100 degree Celsius in 10^{-7} MPa Po_2 in order to reoxidize the dielectrics. After sintering, In-Ga electrodes were painted to evaluate their electrical properties. The disk specimens for valence analysis were prepared by pressing and firing with the same firing condition as that of MLCCs. Four samples as shown in table 1 were prepared in order to study the annealing and Y-doping effect.

Table.1 The specimens and preparing conditions for valence analysis and the HALT.

		compositon	Mn (at%)	Y (at%)	Sintering Temp. (°C)	Po² (MPa)	Annealing Temp. (°C)	Po² (MPa)
NO.1	Mn-NA	$(Ba_{0.93}Ca_{0.05})(Ti_{0.82}Zr_{0.2})O_3$, A/B=1.004 +MnO +$Y_2O_3$ +SiO_2 (0.1wt%)	0.25	0	1300	2*10⁻¹²	non-annealed	
NO.2	Mn-A						1100	4*10⁻⁷
NO.3	MnY-NA			0.25			non-annealed	
NO.4	MnY-A						1100	4*10⁻⁷

The quantities of Mn^{2+} and Mn^{4+} ions in dielectrid were measured by ESR. ESR spectra were taken with the BRUKER ESP350E operated at the microwave frequency of 9.44GHz, with the sweep magnetic field of 0 to 1T, and measurement temperature at 20K. The strength of ESR signal was corrected using the copper sulfate 5 hydration as a standard sample in order to calculate the Mn^{2+} concentration.

XAFS (X-ray absorption fine structure) is classified into Pre-Edge, XANES (X-ray Absorption Near Edge Structure) and EXAFS (Extended X-ray Absorption Fine Structure) by the origin of X-ray radiation.

In this study, valence of Mn ion was determined by measuring the chemical shift of K-edge XANES spectra using the synchrotron radiation. Mn-K edge XANES spectra were measured in fluorescence mode at BL12C, KEK-PF. As the references to estimate the valence of Mn ion, several Manganese oxides such as MnO(II), Mn_3O_4(II,III), Mn_2O_3(III) and MnO_2(IV) were also measured.

3. RESULT AND DISCUSSION

Figure.1 shows the ESR spectra for Mn-doped and Mn-Y doped samples with annealed and non-annealed condition. Six peaks peculiar to Mn^{2+} which has g=2.006 were observed in all the sample. The tetra-valence of Mn ion signal, which has different g value, was not observed. Therefore, it is expected that the state of Mn ion in those dielectrics is the mixture of Mn^{2+} and Mn^{3+}. The Quantity of Mn^{2+} was estimated by the peak strength of ESR signal, and Mn^{3+} was calculated from the total amount of Mn and Mn^{2+}. Table 2 shows the quantity of Mn^{2+}, Mn^{3+} and net-charge of Mn ion. The net-charge of Mn ion were calculated from ESR indicated the valence was between "2+" and "3+".

Figure 2 shows the XANES spectra. These results also suggested that apparent valence of Mn ion was from "2+" to "3+", because all Mn-K edge peak were observed between MnO and Mn_2O_3 peaks. The valence of Mn ion was determined from the calibration data for the reference's chemical sifts. Table 3 showed results of the net-charge of Mn ion for No.1-.4 samples. These results mentioned that there are numerical differences of Mn valence between ESR and XANES results, however the change in Mn ion valence caused by the sample preparation showed the same tendency in both ESR and XAFS results. According to the result, XANES is the superior method to determine the net-

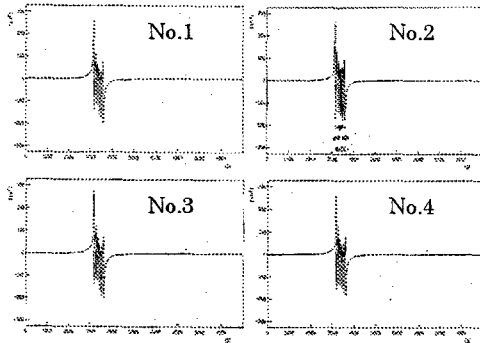charge of Mn ion in $BaTiO_3$.

Figure 1 ESR spectra for Mn-doped and Mn-Y co-doped sample with annealed and non-annealed conditions.

Table.2 The results of Mn ion valences and oxygen vacancy concentration estimated from ESR.

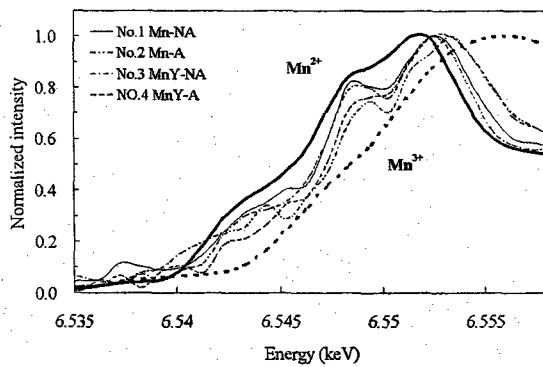|		Mn^{2+} [/g]	Mn^{2+} [/cm³]	Mn^{2+}/Mn [%]	Net charge Mn	[Vo] [1/cm³]
NO.1	Mn-NA	$1.2*10^{19}$	$7.2*10^{19}$	94.2	2.06	$7.4*10^{19}$
NO.2	Mn-A	$0.87*10^{19}$	$5.2*10^{19}$	69.0	2.31	$6.0*10^{19}$
NO.3	MnY-NA	$1.3*10^{19}$	$7.8*10^{19}$	84.2	2.16	$3.1*10^{19}$
NO.4	MnY-A	$1.0*10^{19}$	$6.0*10^{19}$	71.0	2.29	$1.6*10^{19}$

Figure 2 XANES spectra of Mn-doped and Mn-Y co-doped samples with annealed and non-annealed conditions.

Table.3 The results of Mn net-charege and oxygen vacancy concentration estimated from XANES spectra.

		Net charge Mn	[Vo] [1/cm³]
NO.1	Mn-NA	2.70	$1.0*10^{20}$
NO.2	Mn-A	2.90	$8.5*10^{19}$
NO.3	MnY-NA	2.65	$8.5*10^{19}$
NO.4	MnY-A	2.75	$7.7*10^{19}$

The valence change of Mn ion from Mn^{2+} to Mn^{3+} by annealing is thought that oxidation of Mn occurred in annealing process as shown below.

$$2Mn_{Ti}^{"}+2Vo^{"}+1/2O_2 \rightarrow 2Mn_{Ti}^{'}+Vo^{"}+Oo \quad (3)$$
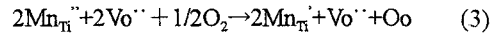
The results of Talbe 2 and 3 indicated that the valence of Mn ion sifted to "2+" by Y doping, and that change of Mn valence became smaller by annealing. It is thought that these effects originate from the stabilizing the lower valence Mn ion by the $Y_{Ba}^{'}$ generation. The reason for stabilizing Mn^{2+} ion was considered as shown below. When Y doped into $BaTiO_3$, Y substituted for the Ba site, and created the $3/2Oo$ and $1/2V_{Ba}^{"}$ as shown in eq.4

$$1/2Y_2O_3 \rightarrow Y_{Ba}^{'}+3/2Oo+1/2V_{Ba}^{"} \quad (4)$$
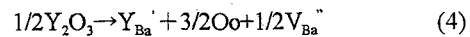
The excess Oo generated by Y doping accelerates the reaction from right to left described in eq.3. Thus the concentration of MnTi decreases and net charge of Mn become smaller.

Table 4 shows the result of HALT for the MLCC with Ni electrode, which prepared by the same condition as that of No.1-4. The lifetime in HALT was improved by annealing, and the Y-doping more improved it. $BaTiO_3$ -based dielectrics for MLCCs often contain MnO in order to prevent the reduction during low P_{O2} sintering. The Mn^{2+} ion is considered to induce the oxygen vacancies during sintering, and inhibit the reducing reaction as shown in eq. 8 and 9. On the other hand, the addition of a donor such as Y^{3+} to $BaTiO_3$-based materials is thought to create the $V_{Ba}^{"}$ and compensate for the oxygen vacancies generated by acceptor doping as shown in eq 10 and 11. Thus the decrease in free oxygen vacancy concentration resulting from donor doping is considered to be a reason for the improved life time in HALT.
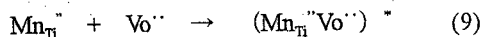
$$Oo \rightarrow 1/2O_2+Vo^{"}+2e^{'} \quad (5)$$

$$MnO \rightarrow Mn_{Ti}^{"} + Vo^{"} \quad (6)$$

$$1/2Y_2O_3 \rightarrow YB^{'} +3/2Oo +1/2V_{Ba}^{"} \quad (7)$$

$$V_{Ba}^{"} + Vo^{"} \rightarrow (V_{Ba}^{"} Vo^{"})^{*} \quad (8)$$

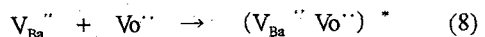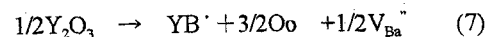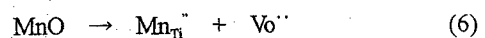$$Mn_{Ti}^{"} + Vo^{"} \rightarrow (Mn_{Ti}^{"}Vo^{"})^{*} \quad (9)$$
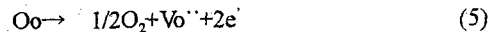
Table.4 The results of the lifetime in HALT under 10V/um at 200C.

		HALT (hr)
NO.1	Mn-NA	0.00
NO.2	Mn-A	1.00
NO.3	MnY-NA	3.40
NO.4	MnY-A	15.50

It is expected that Vo·· also forms the defect pairs with Mn_{Ti}'' as shown in eq.12. However, it is assumed that binding energy of $(Mn_{Ti}'' \, Vo··)^{\times}$ depends on the valence of Mn ion. Probably the binding energy of Vo·· and Mn_{Ti}'' is larger than that of Vo·· and Mn_{Ti}' due to Coulomb force. Thus, Mn_{Ti}'' compensate the free oxygen vacancy effectively.

According to the eq 5-9, it is expected that the ratio of Mn to Y for the improving the lifetime in HALT is at 1:2. However, in the previous work, we observed the optimum Mn and Y ratio was close to 1:1 in the detailed composition of experiments as shown the Fig.3. It is supposed that the results would be explained by the assumption of the Mn ion valence between "2+" and "3+". In this study , we applied the Net-charge of Mn for above defect equation in order to solve these contradiction, and studied the relationship between Vo concentration and Net-charge in Y-Mn composition map using the ESR and XANES, because the quantity of oxygen vacancy gives influence strongly to the reliability in HALT.

The generated Vo density is led with equation

$$[Vo] =[Yba]-[MnTi]=[\, Y \,]- (4\text{-chargeMn}) *[Mn]. \quad (10)$$

Figure.5 show the valence of Mn ion net-charge and the concentration of Vo in Y-Mn map. The valence of Mn ion sifted to +3 with Mn increases. On the other hand, the valence of Mn ion sifted to +2 by the doping of Y. It it suggested that lest Vo concentration region corresponds to the Mn:Y =1:1. Furthermore, Net-charge increased by the addition of MnO and Y_2O_3 increases, then the Vo concentration increase. It is considered that the most suitable Mn/ Y ratio depend on the quantity of defect such as V_{Ba}, Mn_{Ti}, Y_{Ba}, Vo as a result of donor acceptor co-doping

3.CONCLUSIONS

The valence of Mn ion in Y-Mn co-doped $BaTiO_3$- dielectric for MLCCs was determined by ESR and XNES. And the effect of Y-doping on the resistance degradation of MLCCs with Ni electrodes under HALT was studied and the following conclusions were obtained.

The valence of Mn ion was between "2+" and "3+" in

the $BaTiO_3$ based dielectric sintered under reducing atmosphere. In the analysis of ESR measurement, Mn^{4+} was not observed in $BaTiO_3$. The valence of Mn ion estimated from XAFS corresponded to that of the data calculated from ESR

The doping of Y stabilizes the lower valence of Mn and induces the excess Oo which inhibits the oxidation of Mn_{Ti}''. The lower valence of Mn ion, e.g. Mn^{2+}, create the strong defect pair such as $(Mn_{Ti}'' \, Vo··)^{\times}$. The doping of Y also generate the V^{Ba}, then create $(V_{Ba}'' \, Vo··)^{\times}$. These defects improve the life time in HALT.
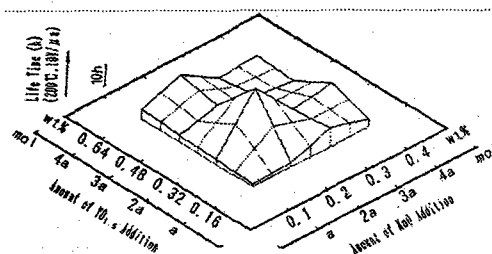
Figure 3   Effect of Mn-and Y-oxide addition on the life time under HALT

	Mn				
	0.00	0.10	0.25	0.50	1.00
0.00		2.37	2.40		2.77
0.10					
Y 0.25		2.15	2.48	2.62	2.72
0.50			2.48	2.52	
1.00		2.14	2.40		2.67

	Mn				
	0.00	0.10	0.25	0.50	1.00
0.00		5.5E+19	1.4E+20		4.2E+20
0.10					
Y 0.25	-	4.4E+19	1.5E+20	3.5E+20	
0.50			-	8.2E+19	
1.00		-	-		1.1E+20

Figure4   Net-charge and Oxygen vacancy concentration calculated from ESR and XANES

4.References

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