INTRODUCTION

Sol-gel processing has generated considerable interest in recent years as a chemical method for ceramic preparation. It is a pure, homogeneous, stoichiometric processing and applicable to a wide range of ceramics. The typical sol-gel method [1,2] shapes gels such as monoliths, film coating, which can be formed in the course of the sol-gel transformation. The coating film by sol-gel process is easier in composition control and film homogeneity, easier in fabrication of large area of thin film, low cost and short fabrication cycle.

Perovskite phase (ABO$_3$) materials are exhibiting a variety of interesting properties such as ferroelectric, pyroelectric and piezoelectric behavior [1,2,3]. In order to take advantage of the electrical properties of these materials for certain applications, it is desirable to develop low temperature synthetic routes to dense crystalline thin films [4]. The development of thin films and coatings are the most interesting application of sol-gel technology [5]. The sol-gel processing is a relatively inexpensive method and it is compatible with a variety of substrate materials [6]. Recent years are marked by growing interest in sol-gel processes films for...
possible applications in microelectronics circuit, including FRAMs (ferroelectric random access memories) and DRAMs (dynamic random access memories) elements, and capacitor [7].

Lead magnesium niobate, \( \text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_{3} \) (PMN) is a well-known \( \text{ABO}_{3} \) type perovskite relaxor in which \( \text{Mg}^{2+} \) and \( \text{Nb}^{5+} \) are randomly distributed in the B site sublattice [2]. The ceramics of PMN has a high dielectric constant and a high electrostrictive strain coefficient. However, it is very difficult to prepare perovskite (PMN) thin films free from pyrochlore [2,3] and it has a low Curie temperature (-150°C)[4]. Little attention has been focused on its piezoelectric properties because of its low Curie temperature. In contrast, both \( \text{PbTiO}_{3} \) (PT) and \( \text{PbZrO}_{3} \) (PZ) have a perovskite structure similarly to PMN and high Curie temperatures, 490°C [4] and 230°C [8], respectively. The combination of the PMN and PT-PZ(PZT) should confirm the following assumptions: (1) accelerate the formation of perovskite phase PMN, because perovskite phase PZT is formed at lower temperature than perovskite phase PMN. (2) Elevate Curie temperature and increase in spontaneous polarization for PMN, because PZT has a large spontaneous polarization and a high Curie temperature. (3) Elevate dielectric constant for PZT, because perovskite phase PMN has a large dielectric constant.

For these reasons, films with a ternary system \( \text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_{3} \)-\( \text{PbTiO}_{3} \)-\( \text{PbZrO}_{3} \) composition near morphotropic phase boundary (MPB) have been prepared in this study at low temperature by sol-gel method. The crystallization behaviors of the films were then investigated by X-ray diffraction.

**EXPERIMENTAL PROCEDURE**

The film samples with composition near morphotropic phase boundary of the system \( x\text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_{3} \)-y\( \text{PbTiO}_{3} \)-z\( \text{PbZrO}_{3} \) \( (x = 0 \sim 0.35, \ y = 0.47 \ and \ z = 0.53) \) were prepared by sol-gel process. The starting solutions consisted of \( \text{Pb(CH}_{3}\text{COO})_{2} \text{H}_{2}\text{O}, \text{Mg(CH}_{3}\text{COO})_{2} \text{H}_{2}\text{O, Nb(OC}_{2}\text{H}_{5})_{5}, \text{Ti(iso-OC}_{3}\text{H}_{7})_{4} \text{and Zr(n-OC}_{3}\text{H}_{7})_{4} \) The excess amount of \( \text{Pb} \), 10 mole % than the stoichiometric composition was used to prepare the solution, (in order to reduce the crystallization temperatures of dense perovskite microstructure [9]). The lead acetate trihydrate was dissolved in acetic acid and then heated at 105°C for 2h to remove water. The dehydrated solution was cooled to below 80°C before the required quantity of zirconium tetra-n-butoxide was added. After adding zirconium tetra-n-butoxide, the solution was stirred at room temperature for 1h, and titanium (IV) tetra-i-propoxide in n-propanol was then added. After stirring at room temperature for 1h, niobium pentaethoxide in n-propanol was also added and stirring is continued at room temperature for 1h. Water, magnesium acetate, n-propanol and ethylene glycol were added to the solution and stirred at room temperature for 2h. Ethylene glycol was used as an additive in order to prevent cracking of the films during drying and to improve the surface smoothness of the films. The concentration of solution was kept 0.7 M, pH around 4.5, and 4 times of the theoretically required amount of water was added for hydrolysis. By dip coating with a withdrawal speed of 10 cm/min and spin coating with speed 3000 rpm for 30 second, PMN-PT-PZ films were prepared on \( \text{SiO}_{2} \) and \( \text{Pt/Ti/SiO}_{2}/\text{Si} \) substrates. In order to prepare thick films, dip coating, spinning and heating processes were repeated. The films were characterized by X-ray diffraction (RAD-C system, Rigaku Co.).

**RESULTS AND DISCUSSION**

The crystallization behaviors were studied at room temperature by X-ray diffraction analysis. All PMN-PT-PZ films on \( \text{SiO}_{2} \) substrates have amorphous structures until heating at 450°C for 30 min (Figure 1A).

However coated films on \( \text{Pt/Ti/SiO}_{2}/\text{Si} \) substrate have pyrochlore structure for films containing PMN (Figure 1B). The amorphous structure will be transformed into perovskite phase through pyrochlore phase. The transformation of the pyrochlore to the perovskite can be monitored by X-ray diffraction. The relative amount (mol %) of perovskite phase could be calculated from [4]
where \( I_{\text{perov}} \) and \( I_{\text{pyro}} \) are the intensities of the major X-ray peaks (110) at \( d = 3.056 \) Å and (222) at \( d = 2.877 \) Å of the perovskite and pyrochlore phases, respectively.

The percentage of perovskite in the PMN-PT-PZ films varied content of PMN at various heating temperatures was shown in Fig. 2 and 3, on the each heating temperature, the percentage of perovskite decreased with increasing the content of PMN. Coated films on SiO\(_2\) substrates, after heating at 500\(^\circ\)C for 30 min the pyrochlore and perovskite phase began to appear for PMN content under 35 mol\%.

Fig. 2, single-phase perovskite was found for the coated films containing 0 and 12.5 mol\% after calcinating at 600\(^\circ\)C. Films coated on Pt/Ti/SiO\(_2\)/Si (Fig.3), the perovskite phase begin to appear after heating at 550\(^\circ\)C and 450\(^\circ\)C for 0 mol\% and 12.5 mol % PMN content, respectively. However until at 550\(^\circ\)C, the only pyrochlore phase appeared for PMN content higher than 12.5 mol\%.

In Fig. 2 and 3 show the temperature formation of pyrochlore and perovskite phase films coated on Pt/Ti/SiO\(_2\)/Si lower than that films coated on SiO\(_2\). The crystallization behaviors of PMN-PT-PZ showed, if the content of PMN increases, that the formation of perovskite phase at low temperature became difficult. It is due to the temperature needed for formation of single perovskite phase of PMN, which is higher than that of PZT. The temperature formation perovskite phase is 600\(^\circ\)C for PZT and above 700\(^\circ\)C for PMN [10]. Single perovskite phase coated films on Pt/Ti/SiO\(_2\)/Si which content of PMN upper 12.5 mol\%, occurred on temperature lower than that of films coated on SiO\(_2\). This is due to the results from the crystallographic and d-spacing matching of PMN-PT-PZ (111) at \( d = 2.348 \) Å to Pt(111) at \( d = 2.259 \) Å, so the (111) plane of platinum may thus accelerate the crystallization of perovskite phase PMN-PT-PZ.

CONCLUSION

Ferroelectrics ceramic films in the \( x\)Pb(Mg\(_{1/3}\),Nb\(_{2/3}\))O\(_3\)-\( y\)PbTiO\(_3\)–\( z\)PbZrO\(_3\) \( (x = 0–0.35, y = 0.47 \) and \( z = 0.53\) ) system having the single perovskite phase can
be prepared on SiO$_2$ if the mole fraction of PMN is $x < 0.3$. Single-phase perovskite was found for the coated films on both SiO$_2$ and Pt/Ti/SiO$_2$/Si substrates, containing up to 12.5 mol% PMN and heated at 600°C or higher temperatures. Single-phase perovskite of coated films on SiO$_2$ will never be found when the content of PMN was 35 mol%. The amounts of pyrochlore and perovskite phase depended on the heating temperature, PMN content and kind of substrates. The temperature formation of perovskite phase coated films higher than 12.5 mol% PMN on Pt/Ti/SiO$_2$/Si is lower than that on SiO$_2$ substrate.

REFERENCES