PREPARATION OF LEAD MAGNESIUM NIOBATE-LEAD ZIRCONATE TITANATE FILMS AND THEIR CRYSTALLIZATION BEHAVIORS

Silvester Tursiloadi

Research Centre for Chemistry, Indonesian Institute of Sciences, Kawasan Puspiptek, Serpong, Tangerang 15314

ABSTRACT

PREPARATION OF LEAD MAGNESIUM NIOBATE-LEAD ZIRCONATE TITANATE FILMS AND THEIR CRYSTALLIZATION BEHAVIORS. The thin films with composition near morpotropic phase boundary (MPB) of the system $xPb(Mg_{1/3}, Nb_{2/3})O_3$-$yPbTiO_3$-$zPbZrO_3$ (x = 0 – 0.35, y = 0.47 and z = 0.53), were prepared by sol-gel method. The starting materials were consisted of $Pb(iso\text{-}OC_3H_7)_2$, $Zr(n\text{-}OC_4H_9)_4$, $Ti(iso\text{-}OC_3H_7)_4$, $Mg(CH_3COO)_2\ 4H_2O$ and $Nb(OC_2H_5)_5$. The 1-propanol was used as solvent. The concentration of PMN-PT-PZ in coating solution was 0.7 M, and the pH of the solution was 4.5. The thin films were prepared by dipcoating and spincoating. The crystallization behaviors of the PMN-PT-PZ thin films showed that the formation of perovskite phase at low temperature becomes difficult with increasing the content of PMN. The amounts of pyrochlore and perovskite phase in PMN-PT-PZ films depended on the heating temperatures, and PMN contents. Single-phase perovskite was found for the coated films containing 0 and 12.5 mol% after calcinating at 600 °C, 21 mol% after calcinating at 700 °C, and 30 mol% after calcinating at 750 °C. Single-phase perovskite of coated films will never be found when the content of PMN was 35 mol%.

Key words : PMN-PT-PZ films, sol-gel, crystallization, perovskite.

ABSTRAK

PEMBUATAN LAPIS TIPIS TIMBAL MAGNESIUM NIOBAT-TIMBAL ZIRKONAT TITANAT DAN KELAKUAN PENGKRISTALANNYA. Lapis tipis dengan komposisi dekat *morpotropic* phase boundary (MPB) dari sistem $xPb(Mg_{1/3}, Nb_{2/3})O_3$-0,47$PbTiO_3$-0,53$PbZrO_3$ (x = 0 – 0,35, y = 0,47 and z = 0,53) telah dibuat dengan metoda sol-gel. Bahan dasar yang dipakai adalah $Pb(iso\text{-}OC_3H_7)_2$, $Zr(n\text{-}OC_4H_9)_4$, $Ti(iso\text{-}OC_3H_7)_4$, $Mg(CH_3COO)_2\ 4H_2O$ dan $Nb(OC_2H_5)_5$. Pelarut yang digunakan adalah 1-propanol. Konsentrasi larutan (PMN-PT-PZ) yang digunakan untuk larutan celup adalah 0,7 M, dan pH larutan adalah 4,5. Lapisan tipis dibuat dengan metoda celup. Kelakuan kristalisasi dari lapis tipis PMN-PT-PZ menunjukkan bahwa pembentukan fasa *perovskite* pada suhu rendah menjadi sulit dengan naiknya kandungan PMN. Banyaknya fasa *pyrochlore* dan *perovskite* dalam lapis tipis PMN-PT-PZ dipengaruhi oleh suhu pembakaran dan kandungan PMN. Fasa tunggal *perovskite* telah didapat untuk lapisan tipis dengan kandungan PMN 0 dan 12,5 %mol setelah dibakar pada suhu 600 °C, lapisan tipis dengan kandungan PMN 21 %mol setelah dibakar pada suhu 700 °C, dan lapisan tipis dengan kandungan PMN 30 %mol setelah dibakar pada suhu 750 °C. Fase tunggal *perovskite* dari lapis tipis tidak pernah didapat untuk sampel dengan kandungan PMN 35 %mol.

Kata kunci : Lapis tipis PMN-PT-PZ, sol-gel, kristalisasi, *perovskite*.

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

Volume 3 No. 3, Juni 2002, hal : 5 - 8
ISSN : 1411-1098

possible applications in microelectronics circuit, including FRAMs (ferroelectric random access memories) and DRAMs (dynamic random access memories) elements, and capacitor [7].

Lead magnesium niobate, $Pb(Mg_{1/3}, Nb_{2/3})O_3$,(PMN) is a well-known ABO_3 type perovskite relaxor in which Mg^{2+} and 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 (-15^{o}C)[4]. Little attention has been focused on its piezo-electric properties because of its low Curie temperature. In contrast, both $PbTiO_3$ (PT) and $PbZrO_3$ (PZ) have a perovskite structure similarly to PMN and high Curie temperatures, 490^{o}C [4] and 230^{o}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 $Pb(Mg_{1/3},Nb_{2/3})O_3$ -$PbTiO_3$ - $PbZrO_3$ 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.

EXPERIMENT PROCEDURE

The film samples with composition near morpotropic phase boundary of the system $xPb(Mg_{1/3},Nb_{2/3})O_3$- $yPbTiO_3$- $zPbZrO_3$ (x = 0 - 0.35, y = 0.47 and z = 0.53), were prepared by sol-gel process. The starting solutions consisted of $Pb(CH_3COO)_2 3H_2O$, $Mg(CH_3COO)_2\ 4H_2O$, $Nb(OC_2H_5)_5$, $Ti(iso\text{-}OC_3H_7)_4$ and $Zr(n\text{-}OC_4H_9)_4$. The excess amount of 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^{o}C for 2h to remove water. The dehydrated solution was cooled to below 80^{o}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 SiO_2 and $Pi/Ti/SiO_2/Si$ 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 SiO_2 substrates have amorphous structures until heating at 450^{o}C for 30 min (Figure 1A).

However coated films on $Pi/Ti/SiO_2/Si$ 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]

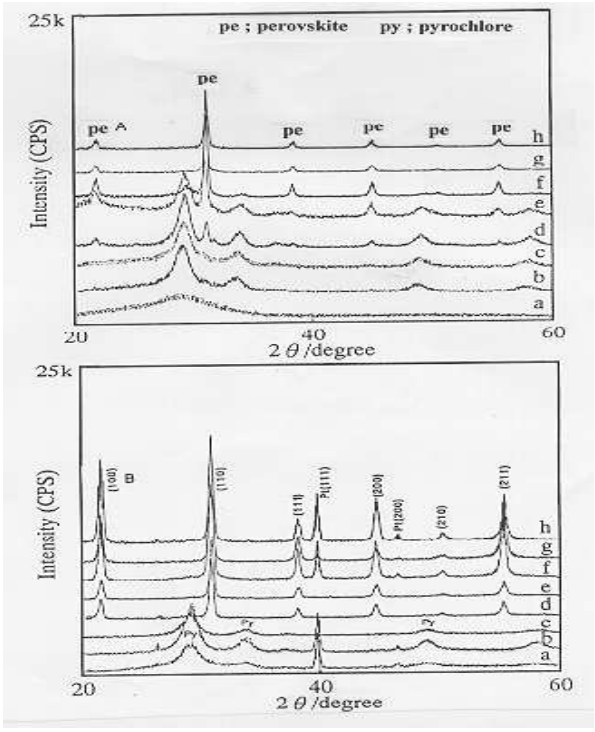

Fig. 1. The X-ray diffraction patterns for coated films with 30 mol % PMN content on (A) SiO_2 , (B) $Pt/Ti/SiO_2/Si$ after heating for 30 min. at (a) 450 ^{o}C, (b) 500 ^{o}C , (c) 550 ^{o}C, (d) 600 ^{o}C, (e) 650 ^{o}C, (f) 700 ^{o}C, (g) 750 ^{o}C, and (h) 800 ^{o}C.

$$\text{"Percent Perovskite"} = \frac{I_{perov}}{(I_{perov}+I_{pyro})} \text{ X } 100 \qquad (1)$$

Where I_{perov} and I_{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°C for 30 min the pyrochlore and perovskite phase began to appear for PMN content under 35 mol%. However the only pyrochlore phase appeared for PMN content at 35 mol% (Fig.2). This pyrochlore phase was stable until heating 650°C. Films coated on Pt/Ti/SiO_2/Si (Fig.3), the perovskite phase begin to appear after heating at 550°C and 450°C for 0 mol% and 12.5 mol % PMN content, respectively. However until at 550°C, the only pyrochlore phase appeared for PMN content higher than 12.5 mol%.

Fig.2, single-phase perovskite was found for the coated films containing 0 and 12.5 mol% after calcinating at 600 °C, 21 mol% after calcinating at 700 °C, and 30 mol% after calcinating at 750 °C. Single-phase perovskite of coated films will never be found when the content of PMN was 35 mol%. The crystallization behavior of the PMN-PZT films showed that the formation of perovskite phase at low temperature became difficult with increasing the content PMN. This maybe due to the temperature, which needed for the formation of perovskite

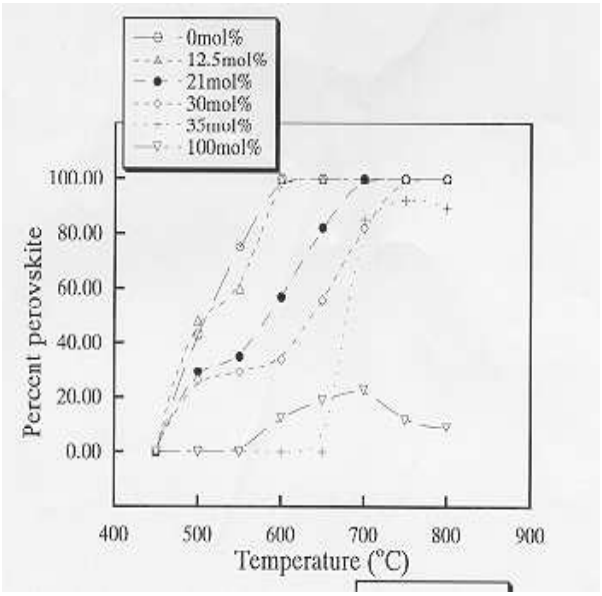

Fig. 2. Percentage of perovskite phase of coated films on SiO_2 vs temperature heating

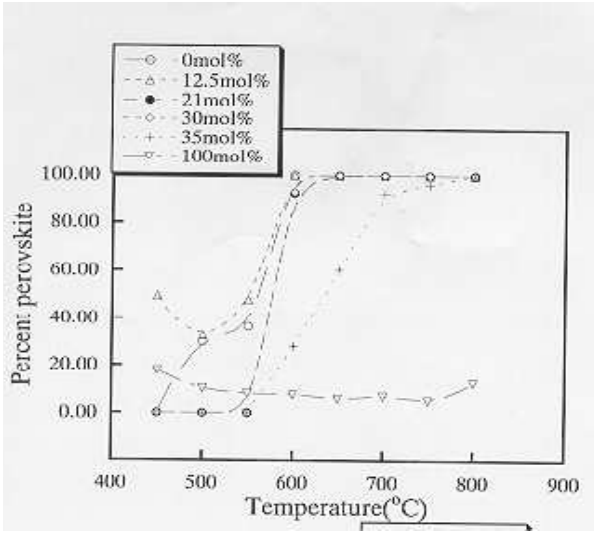

Fig. 3. Percentage of perovskite phase of coated films on Pt/Ti/SiO_2/Si vs temperature heating

phase free from pyrochlore phase of PMN was higher than that of PZT. As has been commonly known that the structure of a PMN-PT-PZ system goes towards pseudo cubic structure with increasing PMN content and at 35 mol% of PMN, the PMN-PT-PZ system belong to pseudo cubic domain. This fact implies that a single perovskite phase is difficult to be found at the 35 mol% of PMN.

In Fig.3, single phase perovskite was found after heating at 600°C for 0 mol% and 12.5 mol% PMN content, at 650°C for 21 mol% and 30 mol% PMN content, and at 800°C for 35 mol% PMN content, respectively.

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°C for PZT and above 700°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 $xPb(Mg_{1/3}, Nb_{2/3})O_3$-$yPbTiO_3$-$zPbZrO_3$ (x = 0 – 0.35, y = 0.47 and z = 0.53) system having the single perovskite phase can

Volume 3 No. 3, Juni 2002, hal : 5 - 8
ISSN : 1411-1098

be prepared on SiO_2 if the mole fraction of PMN is $x \leq 0.3$. 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^oC 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

[1]. AZAROFF, L.V., *Introduction to Solids* McGrawHill, New York, (1960)
[2]. JONA, F., and SHIRANE, G., *Ferroelectric Crystals* Macmillan, New York, (1962)
[3]. N. DE MATHAN, E. HUSSON, P. GAUCHER and A. MORELL, *Mat. Res. Bull.* **25,** (1990) 427
[4]. CHANDLER, C.D., ROGER, C., and HAMPDEN-SMITH M., *J. Chem. Rev.* **93**, (1993) 1205
[5]. K. OKUWADA, M. IMAI and K. KAKUNO, *Jpn. J. Applied Physics*, **28** (7) ,(1989) 1271
[6]. S.K. DEY, K.D. BUBB, and D.A. PAYNE, "Thin-Film Ferroelectrics of PZT by Sol-Gel Processing," pp. 80 in *IEEE Transactions on Ultrasonics, Ferroelectrics and Frequency Control*, **35** (1), January (1988).
[7]. LORRAINE FALTER FRANCIS and D.A. PAYNE, MAT. *Res. Soc. Symp. Proc.*, **200**, (Material Reseach Society), 173 (1990)
[8]. J. BERNARD, R. WILLIAM, Jr. COOK and J. HANDS, *Piezoelectric Ceramics*, **124** (1971)
[9]. S.D. BERNSTEIN, Y. KISLE, J. M. WAHL, S.E. BERNACKI, and S.R. COLLINS, "Effects of Stoichiometry on PZT Thin Film Capacitor Properties", pp. 373 in Ferroelectric Thin Films II, *Proceedings of the Materials Research Society Symposium* (Boston, MA, December, 1991). Edited by A. I. Kingon, E.R. Myers, and B. Tuttle. Materials Reasearch Society, Westerville, OH, (1992).
[10]. LORRAINE FALTER FRANCIS and D.A. PAYNE, *J.Am. Ceram. Soc*. **74** (12), (1991) 300