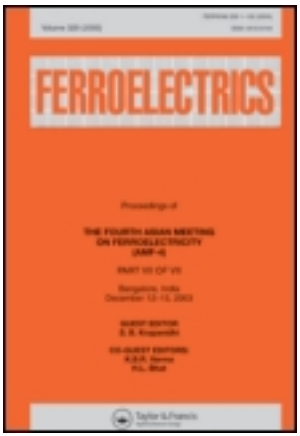

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Physical characterization and electrical properties of chelating-agents added PZT films

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PHYSICAL CHARACTERIZATION AND ELECTRICAL PROPERTIES OF CHELATING-AGENTS ADDED PZT FILMS

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In this study, the chelating agents including ethylene glycol, formamide, glycerol and acetylacetone were used to investigate their effect on perovskite formation, microstructure evolution and electrical properties of PZT films. Two different kind of heating profiles were used for comparison. With fast heating rate, PZT films added with either ethylene glycol or acetylacetone form a dense larger-grained microstructure and show a maximum Pr of ~31 $\mu C/cm^2$. On the other hand, in the heating schedule with a heating rate of 10°C/min, Pr reduction was observed except the glycerol-added PZT films because the addition of glycerol can much reduce the formation temperature of perovskite phase.

Keywords: PZT; sol-gel; chelating agents; perovskite; remanent polarization

INTRODUCTION

PZT films prepared by sol-gel method have displayed ferroelectric properties comparable to those of bulk ceramics. [1] Recently, much attention has been paid to the "hybrid" sol-gel processes with multidentate solvents such as acetic acid.[2-4] Some authors have reported that the chemistry of the alkoxide solution can be further modified for a thick PZT film by adding chelating agents to decrease the hydrolysis rate such as acetylacetone, ethylene glycol, acetic acid or glycerol.[5-7] Other authors have mentioned that ethylene glycol and

formamide are very effective as drying agents for the preparation of uniform and dense films.[8-9] Apparently, the ligand characteristics of either chelating or drying agents, which include ligand steric size and multidentate bridging ligands has played an important role in the precursor properties and crystallization behavior of the films. Therefore, the effect of the structural differences in chelating agents on phase transformation, microstructure evolution and electrical properties of PZT films added with various chelating agents will be studied in this work.

EXPERIMENTAL PROCEDURE

(1) Precursor Solutions and Fabrication of Thin Films

Following the inverted mixing order (IMO) sol-gel method proposed by Schwartz *et. al.*[2], $Pb_{1.15}(Zr_{0.52}Ti_{0.48})O_3$ (PZT) films were prepared with zirconium n-propoxide, titanium iso-propoxide and lead acetate precursors. To the final 1.0 mol% PZT solutions, a variety of chelating agents including ethylene glycol, formamide, glycerol and acetylacetone was added to modify the precursor chemistry.

(2) Characterization of Solutions and Thin Films

DTA was performed to analyze the thermal decompositions of precursor solutions. The crystal phase of the films was determined by X-ray diffraction (XRD) method. The microstructure of the films was examined using scanning electron microscopy. RT66A ferroelectric test system was used to obtain ferroelectric hysteresis loops.

RESULTS AND DISCUSSION

(1) Phase Transformation of Precursor Solutions

Figure 1 shows the DTA curves for PZT precursors added with chelating agents (CA) at a heating rate of 10°C/min. The broad exothermic peak between 450-500 °C corresponding to no additional weight loss should be probably related to the formation of pyrochlore phase according to XRD analysis. It was noted that the exothermic peak in acetylacetone (acac)-added PZT precursor is very weak and extends from 450 to 600°C, reflecting a less reactive or toward cross-linking. Following the second peak, a broad exothermic peak starting around ~ 500°C was

observed in glycerol (GL)-PZT precursor, which shows the formation of perovskite phase.

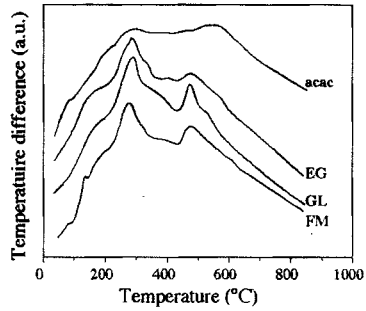

FIGURE 1. DTA curves of CA-added PZT precursors.

(2) Phase Crystallization

For pure PZT film, XRD indicated that pyrochlore phase was developed into perovskite phase at around 550-600°C.The crystallization temperature of perovskite phase is strongly influenced by precursor characteristics, which was in turn correlated with the function number and steric size. As PZT film added with the addition of glycerol (GL), Fig. 2 shows that perovskite phase can be crystallized below 500°C.

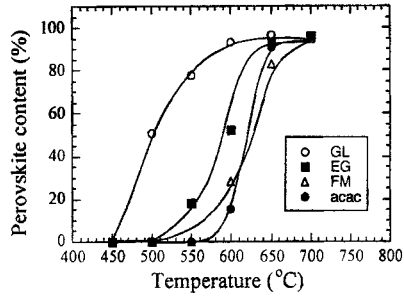

FIGURE 2. Normalized relative perovskite content for CA-added PZT films fired under 500-700°C for 0.5 h.

Similar enhanced phase transformation was also observed in EG-added PZT films. Tahan *et. al.* reported that the addition of EG can decrease

crystallization temperature of $(Ba,Sr)TiO_3$ thin films.[10] For both ethylene glycol (EG) and formamide (FM)-added PZT films, the starting formation temperature is around 520~550°C. However, in the case of acac-added PZT films, the film was required to anneal above 570°C to initiate the formation of perovskite phase due to the greatest steric characteristic of the acac ligands.

(3) Microstructure Development

(A) Heating schedule I

Under heating schedule I, the surface microstructure of FM(0.022 mol)-added PZT films, Fig. 3(a), was composed of fine grains. For GL(0.016 mol)-added PZT film, small grain-size (0.05 ~ 0.1 μm) microstructure with several micropores (Fig. 3(b)) was observed. On the other hand, as 0.016 mol EG was added into PZT precursor, a dense microstructure shown in Fig. 3(c) with larger grain size around 0.2 ~ 0.3 μm was obtained. for acac-added PZT films, the resulting microstructure for 0.02 mol acac, Fig. 3(d), displayed a heterogeneous nucleation with larger grains surrounded by a few fine-grained pyrochlore phase. The larger grain may also reflect the higher crystallization temperature and decreased surface nucleation.[5]

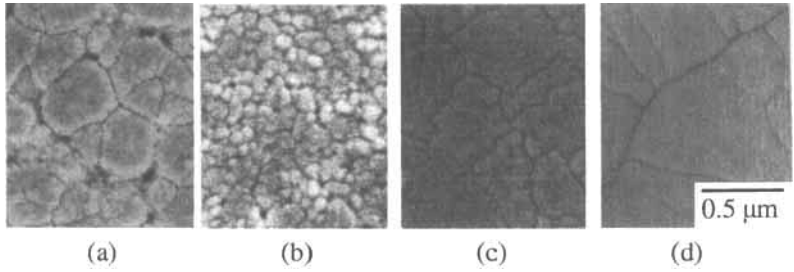

FIGURE 3. SEM micrographs of PZT films added with (a) FM, (b) GL, (c) EG, and (d) acac under schedule I.

(B) Heating schedule II

Under heating schedule II, the microstructure of FM-added PZT film presents rosettes structure and further addition promotes the formation of nanocrystalline pyrochlore. Similar microstructure evolution to FM-

added PZT film was also found in the case of EG-added PZT. As GL was used, a microstructure composed of small grains and some grain-clusters were observed. However, for acac-added PZT films, it presents spherical aggregates of polycrystalline. A further addition formed regions of light and dark contrast where no discerned grain structure could be identified.

(4) Electrical properties

Under heating schedule I, the measured Pr values shown in Fig. 4(a) slightly increase with the addition of FM from 23.7 to 25.6 $\mu C/cm^2$. A further addition of FM causes the decrease of Pr value. For the addition of EG, the Pr of PZT film rapidly raises up to 31.5 $\mu C/cm^2$ at EG ~ 0.016 mol and then decreases. On the other hand, for GL-added PZT films, a maximum Pr value was obtained at the PZT film with the addition of 0.016 mol GL, above that the measured Pr value was rapidly reduced. In addition, a fatty P-E curve was observed, which implies that there exist a certain of current leakage. In the case of acac, the Pr was apparently increased from 19.7 to 32.3 $\mu C/cm^2$. The increase in Pr is possibly attributed to the promotion of grain growth.

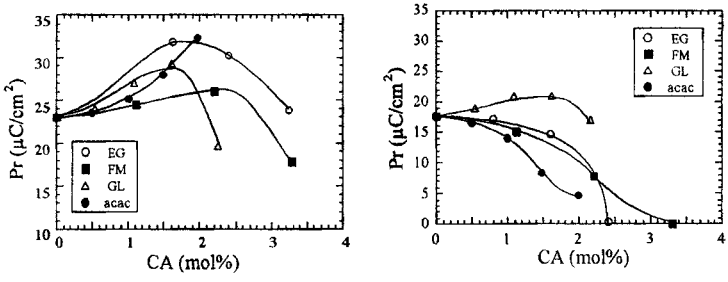

FIGURE 4. Effect of CA content on remanent polarization (Pr) of PZT films under heating schedule (a) I and (b) II.

On the other hand, under heating schedule II, shown in Fig. 4(b), the addition of FM causes Pr reduction due to the suppression of perovskite phase formation. No Pr value could be obtained at 0.033 mol. Similar variation was also found in EG-added PZT films. The Pr disappears at 0.024 mol. For acac-added PZT films, the reduction of Pr is observed

with increasing acac amount. In contrast, in the case of GL, the Pr was slightly increased from 17.4 to 20.6 $\mu C/cm^2$ due to the lower crystallization temperature and then decreased.

CONCLUSIONS

PZT films added with ethylene glycol and acac form a dense larger-grained microstructure and show a maximum P_r value around 31-32 $\mu C/cm^2$ under fast heating rate. However, a heating rate of 10°C/min gives poor electrical properties due to the suppression of perovskite formation except the addition of GL because PZT perovskite phase can be crystallized at temperature below 500°C.

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