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Study on Lead-Based Relaxor Ferroelectric Ceramics for X7R Capacitors *

Zhilun Gui, Zhonglin Wu, Ying Li and Longtu Li

Department of Materials Science & Engineering
Tsinghua University, Beijing 100084, China

Lead based relaxor ferroelectric ceramics for X7R capacitors was investigated. The basic Chemical formula is Pb $(Mg_xW_yZr_zTi_u)O_3$ (PMW-PZ-PT). It was found that the ratio of Zr to Ti and sintering temperature had great influence on dielectric properties. The experimental results revealed that increasing the ratio of Zr to Ti could shift the Curie point to lower temperature and doping small amount of ZnO could make the ε-T curve appear double peaks therefore decreasing the temperature coefficient of capacitance (T.C.C). The typical parameters of the ceramics are as follows: S.T. = 930℃ -1000℃, ε = 3000-3600, tan $\delta < 1.0 \times 10^{-2}$, $\rho \geqslant 5 \times 10^{12} \Omega \cdot$ cm, $E_{B.D.} \geqslant 5$KV / mm, $\triangle C / C(-55℃ \rightarrow +125℃) \leqslant 15\%$. The results satisfied X7R characteristics of EIA standard. The microstructure of the material was analyzed by means of XRD and SEM.

1. INTRODUCTION

The lead-based relaxor ferroelectric ceramics with complex perovskite structure has been studied extensively due to its excellent dielectric characteristics and relatively low sintering temperature. A number of relaxor ferroelectric compositions meeting Z5U and Y5V characteristics of the EIA standard have been reported in recent years. Generally, the ceramic compositions used for X7R capacitors are based on barium titanate ($BaTiO_3$) materials. Although low temperature sintering $BaTiO_3$ based ceramics has been made a great progress, its further development is limited by the system itself. Therefore, low temperature sintering relaxor ferroelectric ceramics for X7R capacitors is taken into consideration.

Lead magnesium tungstate Pb $(Mg_{1/2} W_{1/2}) O_3$ (PMW) was studied by smonleski and co-workers [1], and it was found to be an antiferroelectric material at temperature below 39℃. At room temperature, PMW has an orthorhombically distorted complex perovskite structure. Binary system Pb $(Mg_{1/2} W_{1/2}) O_3$- $PbTiO_3$ was studied by kraninik et al.[2] A continuous series of solid solutions forms with the perovskite structure in the range of compositions from 5-70mol% $PbTiO_3$. These relaxor type ferroelectric materials showed a remarkable frequency dispersion in the dielectric constant of 5500. Recently, Yukio Sakable et al.[3] reported the dielectric properties of PMW-PZ-PT ceramics and found certain compositions meet Y5P characteristics of EIA standard.

This paper investigated the ceramics composed of PMW-PZ-PT for X7R ceramic

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capacitors.

2. EXPERIMENTAL PROCEDURE

The compositions studied are given as follow: $Pb(Mg_xW_yZr_zTi_u)O_3$, where $X=0.20-0.30$, $y=0.20-0.30$, $z=0.25-0.46$, $u=0.02-0.30$, $x+y+z+u=1$.

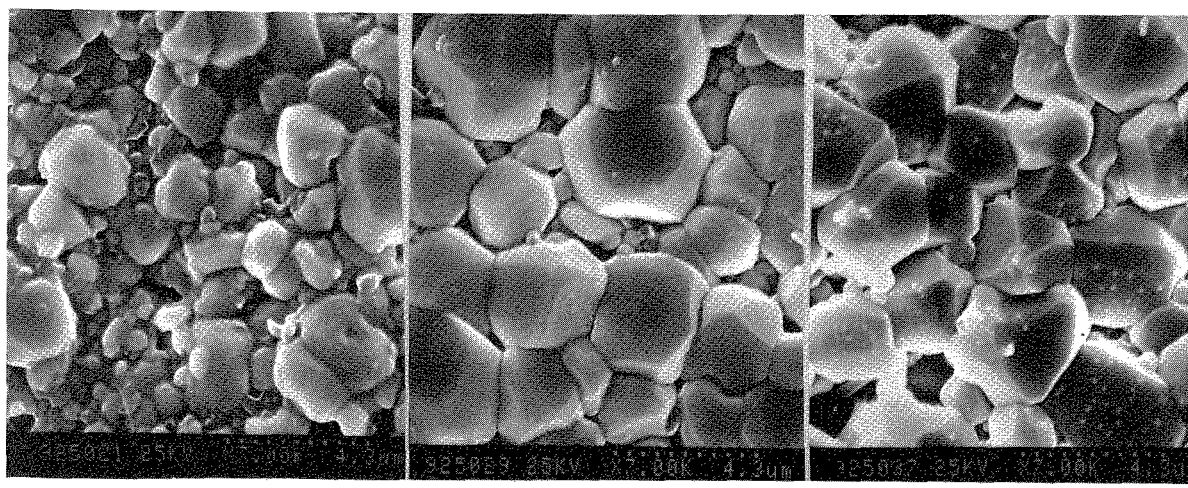
The chemical grade and analytical grade raw materials of Pb_3O_4, ZrO_2, $Mg(OH)_2 \cdot 4MgCO_3 \cdot 6H_2O$, TiO_2, etc. were used. PMW-PZ-PT powders were synthesized by direct formation method. Disc samples for testing were pressed at about 100MPa and sintered at 900-1020℃ for 2-4hrs. The phase composition of the synthesized powders and the sintered samples were analyzed by XRD. The dielectric constant and dielectric loss were measured by automatic bridge. The break-down strength were measured by high voltage supply DC and the resistivity were measured by super-high resistance meter. The microstrcture of the material was analyzed by means of XRD and SEM.

3. RESULTS AND DISCUSSIONS

3.1 Effect of the Sintering temperature

Figure shows the SEM micrographs of PMW-PZ-PT samples sintered at 970℃, 1000℃ and 1020℃ respectively. It can be seen that the higher the sintering temperature, the larger the average grain size. As the sintering temperature rises, the average grain size is enlarged from 1-μm at 970℃ to 3-4μm at 1020℃ respectively. X-ray diffraction patterns are shown in Figure 2. The typical perovskite structure is obtained.

The plots of dielectric constant VS. temperature at 1KHz for the PMW-PZ-PT ceramics fired at 970℃, 1000℃ and 1020℃ were shown in Figure 3. It can be found that an increase of sintering temperature resulted in a seperation of the original single peak into dual peaks and a corresponding increase in the dielectric constant of room temperature. Also, the rise of sintering temperature shifts the Curie point leftward.



970℃ 2hrs　　1000℃ 2hrs　　1020℃ 2hr

Figure 1. SEM micrographs of PMW-PZ-PT ceramics

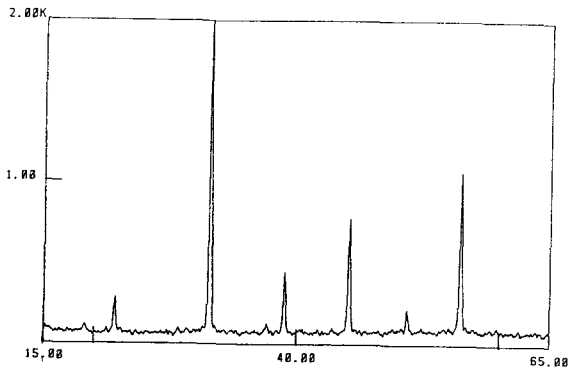


Figure 2. XRD of PMW–PZ–PT ceramics

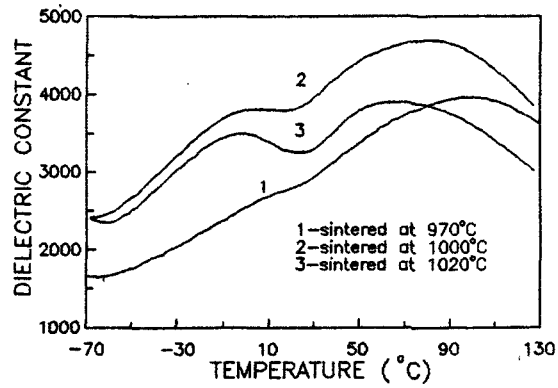


Figure 3. The dependent of dielectric constant VS. temperature at 1KHz of sample 4

3.2 Effect of ratio of Zr to Ti

The ceramics with various ratio of Zr to Ti were studied. The ratio of Zr to Ti increased from 0.08 / 0.42 to 0.18 / 0.32. Suitable content of ZnO was added into the compositions. The result indicated that there was only one peak in ε–T curve at both the low ratio and the high ratio Zr to Ti. Only at proper ratio did dual peaks appear. While the ratio increased, both of them shift toward lower temperature and the temperature range between the two peaks shortened.

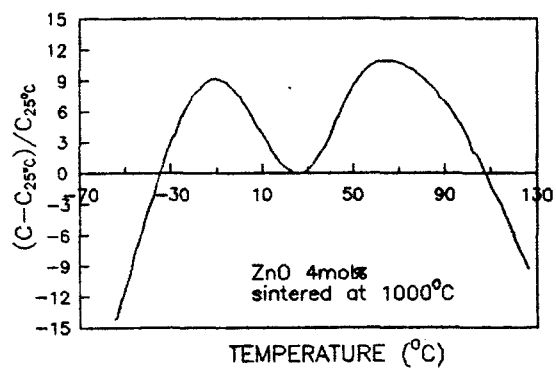


Figure 4. The plot of $\triangle C / C$ VS. temperature of sample 5

The dielectric constant at room temperature changed with different Zr / Ti ratio. At suitable ratio of Zr to Ti (0.10 / 0.40–0.16 / 0.34), the ε_{RT} reaches its minimum and the capacitance change curve for the sample 5 with 4 mol% ZnO became flat and satisfied the X7R standard. It is showed in Figure 4 sample 5 is excellent in other properties, too. Its $\varepsilon = 3000$–3600, $\tan \delta < 1.0 \times 10^{-2}$, $\rho \geq 5 \times 10^{12} \Omega \cdot$ cm, $E_{B.D} \geq 5$KV / mm.

3.3 Effect of ZnO

0–10mol% ZnO was added in the PMW–PZ–PT ceramics. Figure 5 represented the curve of dielectric constant VS temperature at 1KHz of PMW–PZ–PT with different ZnO content. and the samples were sintered at 1000℃ 2hrs. The Figure revealed that doping of ZnO did make the ε–T curve appear double peaks therefore decreasing the temperature coefficient of capactiance.

The mechanism of occurring dual–peak is quite interesting and complicate. It is clear that doping ZnO is an important factor for appearing double peaks, of course, the sintering

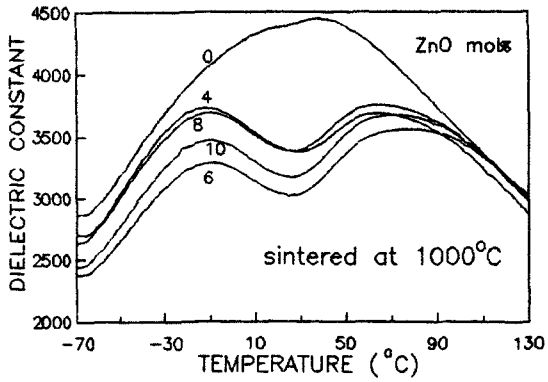


Figure 5. Dielectric constant VS. temperature at 1KHz of PMW–PZ–PT with different ZnO content

temperature and ratio of Zr to Ti are also influence factors too. From the experimental result showed that dual–peak mechanism was closed related to the ageing pheonomenon caused by adding ZnO, and the TEM result reveals that there is some glassy phase Zn^{2+} and Mg^{2+} occur in the grains and boundaries although some of the Zn^{2+} did enter the lattice. According to ionic radius Zn^{2+} may enter Mg^{2+} site. In our former research result showed that impurities, pores, glassy phases, defects etc may have higher ageing effect than that of the pure perovskite structure [6]. In this study proper glassy phase may be helpful for lowering the T.C.C therefore satisfying the X7R standard. So how to control the microstructure in order to achieve the X7R properties is still a lot of work and analysis must be done in the future.

4. CONCLUSIONS

4.1. The relaxor ferroelectric ceramics composed of PMW–PZ–PT with suitable content ZnO have good electrical properties and satisfy X7R standard.

4.2. Increasing the ratio of Zr to Ti shifts the curie point to lower temperature.

4.3. Doping small amount of ZnO makes ε–T curve appear dual peaks which is related to the sintering temperature and the ratio of Zr to Ti.

4.4. Ageing phenomenon is an influence factor for occurring dual–peak of ε–T curve.

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