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Preparation and characterization of lead iron tantalate thick films

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Abstract

Thick film compositions based on solid solutions of relaxor ferroelectric $Pb(Fe_{1/2}Ta_{1/2})O_3$ and normal ferroelectric $PbTiO_3$ were prepared and applied for class II capacitors. The dielectric layers were fired at 870 °C. In order to shift the temperature of ferroelectric–paraelectric transition upwards the addition of 10, 15 and 20 mol% of $PbTiO_3$ was used. Introduction of 0.1–0.5 mol% of MnO_2 or Co_3O_4 to the pastes resulted in an increase in their resistivity. The electric permittivity and dissipation factor of the layers were determined in the temperature range from −55 to 180 °C and in the frequency range 10 Hz–1 MHz. Resistivities of the thick films were measured in the temperature range 20–500 °C. Microstructure of the layers was characterized by a scanning electron microscope. The advantageous features of the developed thick films were: lack of any nonferroelectric fluxes, dense microstructure, relatively high dielectric permittivity (300–1900), high resistivity (about 10^{12} Ωcm), low temperature coefficient of capacitance and low electrical field dependence of capacitance.

Keywords: Thick-films; Dielectric properties; Lead iron tantalate; Capacitors

1. Introduction

Thick film technology has successfully been applied in microelectronics for several years in the production of conductors, resistors, capacitors, inductors, sensors etc. Using this simple and relatively cheap technique, one can screen print on an insulating substrate conductive, resistive and dielectric layers with the thickness of a few to a few tens micrometers. Flexibility of manufacturing procedures, good miniaturization and reliability of elements are other advantages of this deposition method.

Lead based relaxor ferroelectrics with general formula $Pb(B'B'')O_3$ are very attractive materials for multilayer ceramic chip capacitors owing to their high dielectric permittivity, broad dielectric maxima and relatively low firing temperatures. $Pb(Fe_{1/2}Ta_{1/2})O_3$ is a member of this family rather scarcely studied [1,2]. Little attention has also been paid to utilization of thick film technology in manufacturing relaxor ferroelectric layers [3–5].

In this work the solid solutions of relaxor ferroelectric $Pb(Fe_{1/2}Ta_{1/2})O_3$ (PFT) and the normal ferroelectric $PbTiO_3$ (PT) were used to prepare thick film pastes. The relatively low sintering temperature of lead iron tantalate enables one to fire thick films based on this compound at temperatures typical of the applied technology (about 850 °C). The addition of any glass or other nonferroelectric fluxes, which would cause a significant decrease in dielectric permittivity of layers as compared with bulk ceramics, was not necessary.

2. Experimental

Relaxor ferroelectric PFT was synthesized by the two-step "wolframite" method described by Swartz and Shrout [6]. This synthesis method facilitates the formation of the desired phase with perovskite structure without significant amounts of parasitic pyrochlore-type phases. The substrates were mixed in appropriate proportions, ball-milled in alcohol, dried and pelletized before calcination. The addition of 10–20 mol% of $PbTiO_3$ was used to shift Curie temperature of PFT-based compositions. Small amounts of MnO_2 or Co_3O_4 (0.1–0.5 mol%) were introduced to the batches in order to increase resistivity and decrease dissipation factor [7,8]. The first synthesis step consisted in the reaction of the oxides of B-site cations (Fe_2O_3 and Ta_2O_5) at 1000 °C for 4 h. During the second calcination step the product – $FeTaO_4$ – reacted with

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PbO at 850 °C for 4 h. The pelletized powders were placed in closed alumina crucibles and covered with $PbZrO_3$ enriched with PbO in order to restrict lead evaporation. Phase compositions of the powders after the syntheses were determined by X-ray diffraction analysis using a Philips X'Pert diffractometer.

Thick film pastes were prepared by mixing synthesized PFT powders, previously ball milled, with an organic vehicle – ethyl cellulose solution in terpineol.

Thick film capacitors were screen printed on 96% Al_2O_3 substrates. The bottom and top electrodes made of ESL 9916 Ag paste or ITME 402 Pt paste were fired in a VI-zone BTU belt furnace at peak temperature of 850 or 880 °C, respectively, according to a standard thick-film profile. The dielectric layers were deposited using a 260-mesh screen, dried and then fired during 45 min cycle at a peak temperature of 870 °C held for 10 min. Double or triple dielectric layers were applied with the thickness of 20 and 30 μm, respectively. The thickness of layers was examined by the use of a Taylor–Hobson profilograph.

Resistivity measurements of the samples were carried out in the temperature range 20–500 °C by means of a 6517 A Keithley electrometer and a Philips resistance meter. Capacitance and dissipation factor of thick film capacitors were determined in the temperature range from −55 to 180 °C at frequencies 10 Hz–1 MHz using a LCR QuadTech meter model 7600 B. Changes in capacitance after aging under the dc field of 1 kV/mm at 20 °C for 1–500 h were also measured.

A Joel scanning electron microscope 5400 and a Link Isis X-ray microprobe 300 were used to study the microstructure and the chemical composition of thick film dielectrics as well as the interaction between the ceramic layers and the electrodes made of Ag and Pt pastes.

3. Results and discussion

The X-ray diffraction analysis has confirmed that PFT phase did form as a result of the synthesis. Small amounts of another phase with the composition $Pb_{1.34}Ta_2O_{6.34}$, close to the regular pyrochlore $Pb_3Ta_4O_{13}$, were also found; however, its content was apparently decreasing during the sintering process.

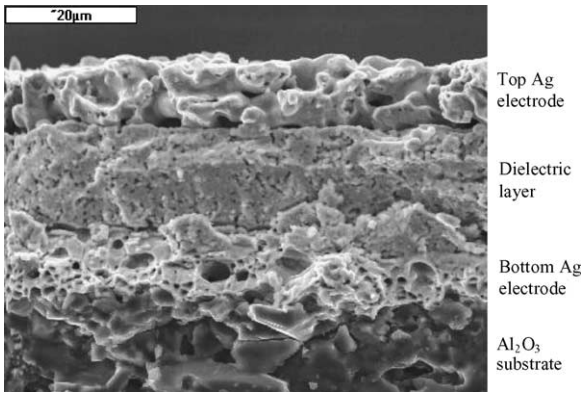

Fig. 1. SEM micrograph of a fracture of the thick film capacitor with 0.8PFT–0.2PT dielectric layer.

It was stated that the developed layers could be densified without any glass addition during the conventional thick film firing process at peak temperature of 870 °C.

Fig. 1 illustrates a scanning electron micrograph of a fracture of the thick film capacitor with 0.8PFT–0.2PT dielectric. The relaxor layer is dense, with small porosity, looking like a fine-grained ceramic.

The dielectric properties of PFT based layers fired at 870 °C are presented in Table 1. In Figs. 2 and 3 the comparison of temperature dependencies of relative electrical permittivity (ε_r) and temperature coefficient of capacitance ($TCC = 100\%(C_T - C_{20^\circ})/C_{20^\circ}$) measured at 1 kHz are given for some of the investigated layers.

The properties of thick films based on pure PFT were worse than those with PT addition. They are characterized by a lower permittivity (430–540), a higher dissipation factor and a lower resistivity (10^{11} Ωcm) as compared with PFT–PT compositions. All the examined layers exhibit relatively low values of TCC, meeting Y5R (−25 to +85 °C, −15% < TCC < +15%) EIA specifications. The layers 30 μm thick withstood 300–500 V load.

Table 1
Dielectric properties of thick films based on PFT fired at 870 °C at frequencies 10 Hz–1 MHz

Composition, mol fraction	PFT (0.5% Co_3O_4)	0.9PFT–0.1PT (0.5% MnO_2)	0.85PFT–0.15PT (0.5% MnO_2)	0.8PFT–0.2PT (0.5% MnO_2)	0.8PFT–0.2PT (0.5% Co_3O_4)
Curie temperature (°C)	−25	0–10	0	10	10
Second peak temperature (°C)	120–140	110–130	90–120	120–130	130–170
ε_r at Curie temperature	430–540	300–1000	700–1800	700–1400	900–1900
tgδ at 20 °C	0.008–0.12	0.005–0.05	0.006–0.08	0.005–0.08	0.001–0.02
Dc resistivity at 20 °C (Ωcm)	10^{11}	3.10^{12}	4.10^{12}	10^{12}	6.10^{11}
TCC (1 kHz) (%)					
+10 to +85 °C	−10 to +4	−5 to +4	−2 to +2	0 to +11	−2 to +13
−25 to +85 °C	−10 to +14	−10 to +10	−6 to +3	−5 to +11	−2 to +13
−55 to +125 °C	−10 to +17	−13 to +32	−13 to +3	−12 to +18	−12 to +33
$\Delta C/C$ after dc aging (1 kV/mm, 20 °C, 500 h) (%)	0.05 to 1	0.05 to 0.3	0.1 to 0.45	0.2 to 0.6	0.1 to 0.5

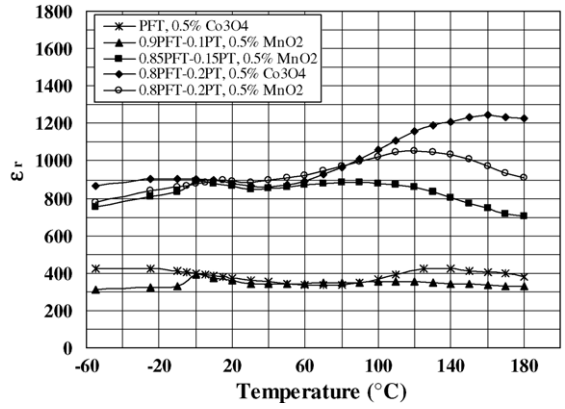

Fig. 2. Temperature dependencies of dielectric permittivity for PFT based thick films at 1 kHz.

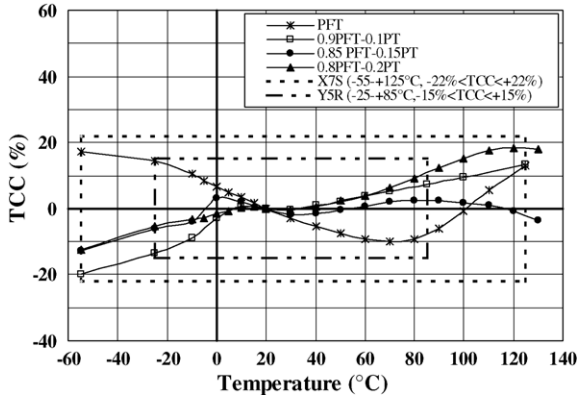

Fig. 3. Temperature coefficient of capacitance for PFT based thick film capacitors in the temperature range from −55 to 125 °C at 1 kHz.

The highest values of dielectric constant were achieved for 0.8PFT–0.2PT and 0.85PFT–0.15PT layers. Fig. 4 illustrates the temperature dependence of dielectric permittivity for the 0.85PFT–0.15PT thick film (+0.5 mol% MnO_2), measured in the frequency range 10 Hz–1 MHz. The maximum dielectric constant for this layer was 700–1800 and was observed at 0 °C. The advantageous features of this composition are: a very low temperature coefficient of capacitance (from −13 to 3% in the temperature range −55 to 125 °C), meeting X7R specifications (−55 to +125 °C, −15% < TCC < +15%) and a high resistivity, exceeding 10^{12} Ωcm.

The layers with composition 0.8PFT–0.2PT (+0.5 mol% Co_3O_4) showed the maximum dielectric constant value of 900–1900 at 10 °C, a rather low dissipation factor of 0.001–0.02 at room temperature and a high resistivity at 20 °C (about 10^{12} Ωcm). The TCC values were low, fulfilling Y5R specifications (−25 to +85 °C, −15% < TCC < +15%).

The influence of frequency on the location and the magnitude of the maximum in $\varepsilon_r = f(T)$ curves for the thick films developed in this work was not so significant as in the case of bulk relaxor ceramics. The Curie temperatures corresponding to ferroelectric–paraelectric transition seem to be almost independent of frequency. At higher temperatures in the range 140–180 °C a second set of broad peaks was observed, related to dielectric relaxation. The height of these peaks increases with decreasing frequency.

The values of relative permittivity presented in this work for thick films were, of course, lower than those of the bulk ceramics with the same compositions (about three to four times). For example, for 0.8PFT–0.2PT composition, the ε_r values for the thick films were 900–1900 and for the bulk ceramics 4500–5200.

Temperature dependence of dc electrical conductivity σ for the examined thick films followed well the Arrhenius law:

$$\sigma = \sigma_0 \exp \frac{E}{k_B T}$$

where E is activation energy of electrical conductivity, k_B Boltzmann constant, and T temperature.

Two segments of the Arrhenius plots with different slopes can be distinguished in the temperature range 20–500 °C. This behavior is illustrated in Fig. 5 for the 0.8PFT–0.2PT

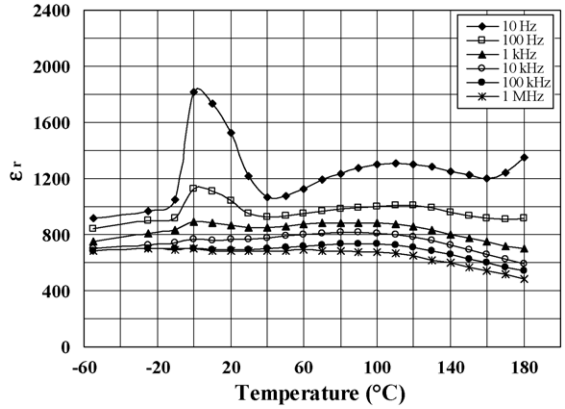

Fig. 4. Temperature dependence of dielectric permittivity for 0.85 PFT–0.15PT thick film.

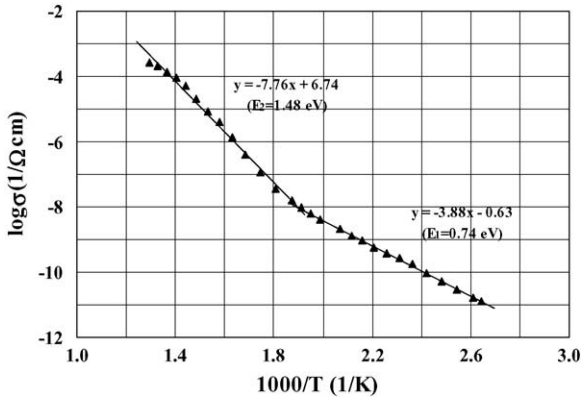

Fig. 5. Temperature dependence of electrical conductivity for 0.8PFT–0.2PT thick film.

thick film. The change in the slope of the plots is observed at about 280 °C, indicating a change in the conduction mechanism. The activation energies corresponding to the lower temperature range for the investigated PFT–PT thick films were 0.6–0.75 eV and those for the higher temperature range much higher – at the level of 1.35–1.50 eV.

Aging of the PFT–PT layers under the direct field of 1 kV/mm during 1–500 h led to a small capacitance change in the range 0.05–0.6%. It was found that after approximately 100 h under the applied voltage the stabilization of the capacitance took place.

4. Conclusions

The pastes based on $Pb(Fe_{1/2}Ta_{1/2})O_3$–$PbTiO_3$ were developed, destined for thick film capacitors. The dielectric layers made of these pastes are characterized by: dense microstructure in spite of lack of any glass addition, a low firing temperature (870 °C), relatively high dielectric permittivity (300–1900), high resistivity (about 10^{12} Ωcm), low temperature coefficient of capacitance and small changes of capacitance after dc bias aging.

References

1. Zhu, W. Z., Kholkin, A., Mantas, P. Q. and Baptista, J. L., Preparation and characterization of $Pb(Fe_{1/2}Ta_{1/2})O_3$ relaxor ferroelectric. *J. Eur. Ceram. Soc.*, 2000, **20**, 2029.
2. Yamashita, Y. and Ichinose, N., Can relaxor piezoelectric materials outperform PZT (Review). In *Proceedings of the 14 IEEE International Symposium on Applied Ferroelectrics, vol. 1*, 1996, p. 71.
3. Fu, S. L. and Chen, G. F., Low firing thick film dielectrics in the system $Pb(Fe_{2/3}W_{1/3})_x$ $(Fe_{1/2}Nb_{1/2})_{0.86-x}Ti_{0.14}O_3$–$Bi_2O_3/Li_2O$. *Am. Ceram. Soc. Bull.*, 1987, **66**(9), 1397.
4. Yasumoto, Y., Iwase, N. and Harata, M., High dielectric constant thick film capacitors fireable in air and nitrogen atmosphere. *Intern. J. Hybr. Microelectron.*, 1989, **12**(3), 156.
5. Kim, Y. and Huan, M. J., Low-firing lead magnesium niobate–lead titanate–lead germanium silicate ferroelectric compositions for thick film capacitor applications. *Int. J. Microcircuits Electron. Packaging*, 1999, **22**(2), 137.
6. Swartz, S. L., Shrout, T. R., Schulze, W. A. and Cross, L. E., Dielectric properties of lead–magnesium niobate ceramics. *J. Am. Ceram. Soc.*, 1984, **67**(5), 311.
7. Zhou, L., Vilarinho, P. M. and Baptista, J. L., Role of defects on the aging behavior of manganese-doped lead iron tungstate relaxor ceramics. *J. Am. Ceram. Soc.*, 2000, **83**(2), 413.
8. Miranda, C., Vilarinho, P. M. and Zhou, L., Dielectric properties of cobalt and chromium doped lead iron tungstate relaxor ceramics. *Ferroelectrics*, 1999, **223**, 269.