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Synthesis and Study of Structure, Microstructure and Physical properties of the ceramic system of PZT 82.5/17.5 doped with Ta^{5+}

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***Abstract*—In this paper, synthesis and study of structure, microstructure, dielectric, ferroelectric, and pyroelectric properties of the (1-x) PZT 82.5/17.5 – xTa_2O_5, where x = 0; 0.5; 1; 1.5; 2% mol is presented. From experimental results, it was showed that the fabricated ferroelectric systems are of pure perovskite phase, rhombohedral structure, good microstructure, good dielectric, ferroelectric properties and strong pyroelectric effect. All samples are good ferroelectric ceramics such as the ceramic density ρ = 7.30 - 7.51(g/cm^3), the dielectric constant ε = 226 - 314, the dielectric dissipation factor tgδ = 0.008 - 0.023, hysteresis loops of rectangular forms with the permanent polarizations Pr = 23.2 - 32.4 (μC/cm^2), electric coercive fields E_c = 6.8-8.9 (kV/cm), strong pyroelectric effect with maxima of pyroelectric coefficients γ = 6.1 - 12.4 (10^{-2}.μC.cm^{-2}.K^{-1}), and pyroelectric coefficients at room temperature: 2.19 - 5.80 (10^{-3}.μC.cm^{-2}.K^{-1})**

Keywords—PZT, Zr - rich PZT ferroelectric ceramics, pyroelectric, doped with Ta

I. Introduction

The ferroelectric ceramic system based on the Pb(Zr, Ti)O_3 with various dopants is of advanced properties. In this paper, the author will present new experimental results of PZT82.5/17.5 – x % mol Ta_2O_5, where x = 0, 0.5, 1, 1.5, 2 % mol. The effects of Ta^{5+} concentrations on structure, microstructure, dielectric, ferroelectric, pyroelectric properties and improvement of technology are presented and discussed.

II. Experimental

A. *Synthesis and estimating quality of ceramics*

A.1.Synthesis: The ferroelectric ceramic systems of PZT 82.5/17.5 – x% mol. Ta_2O_5 with x = 0, 0.5, 1, 1.5, 2% mol. called M0, M1, M2, M3, M4 are respectively fabricated and studied. Raw materials are oxides PbO, ZrO_2, TiO_2, and Ta_2O_5 with purity 99% (Merck Germany).

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The ceramic powder of PZT 82.5/17.5 is fabricated by traditional ceramic technology with parameters: primary milling during 8h, pressed at 800kG/cm^2 into disks of Φ = 25mm, calcinated at 850^{0}C during 2h. The ceramic powder of PZT 82.5/17.5 and Ta_2O_5 are primary milled and weighed in desired ratios, mixed together with five types of samples. Then they are dissolved in ethanol solution and processed by high power ultrasonic wave from ultrasonic device of 70W during 70 minutes. After being dried, ceramic powders are pressed at the pressure of 1.2T/cm^2 into disks of Φ = 12mm. After processing and covering Ag electrodes, samples are polarized under DC high voltage of 30kV/cm during 15 minutes in silicone oil at the temperature of 125^{0}C.

A.2.Estimating quality of samples:

a. Phase and structure: In Figure 1 are presented XRD patterns of M0, M1, M2, M3, M4 samples. All samples are of pure perovskite phase with rhombohedral structure. With increasing Ta^{5+}, all peaks in XRD patterns did not displace, only intensities changed slightly. The perovskite phase did not change, and only lattice parameters slightly changed. Lattice parameters are showed in Table 1.

TABLE I. LATTICE PARAMETERS a AND c

Sample	a	c
M0	5.8282	14.3628
M1	5.8361	14.3684
M2	5.8258	14.3590
M3	5.8133	14.3262
M4	5.8224	14.3290

b. Microstructure: From SEM images in Figure 2, we see M0, M1, M2 samples are of homogenously large grain size with small pores closely placed. In M3, M4 samples show smaller grain size of the lower homogeneity and with larger pores. It is in agreement with ceramic densities in Table 2.

c. Ceramic density: In Table 2 the ceramic densities of the M0, M1, M2, M3, and M4 samples of the PZT82.5/17.5 –Ta^{5+} system are presented. All of the ceramic compositions are of high density ρ = 7.30-7.51 (g/cm^3), well-sintered and the chosen parameters are good. Here we used the power ultrasonic for processing ceramic powder instead of the second milling and mixing of the traditional technology as mentioned above.

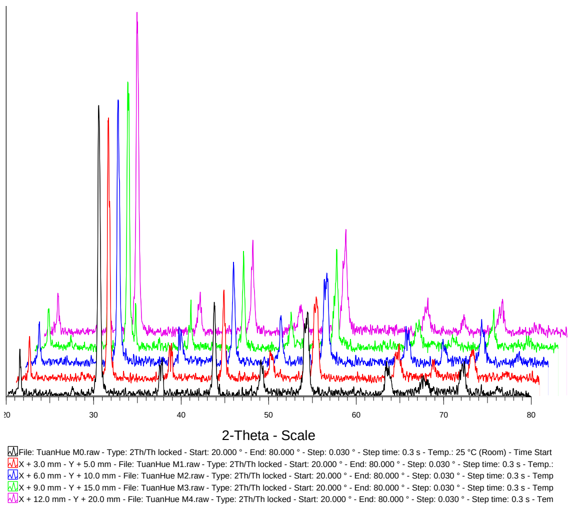

Figure 1. X-ray diffractions diagrams ofM0-a), M1-b), M2-c), M3-d), M4-e)

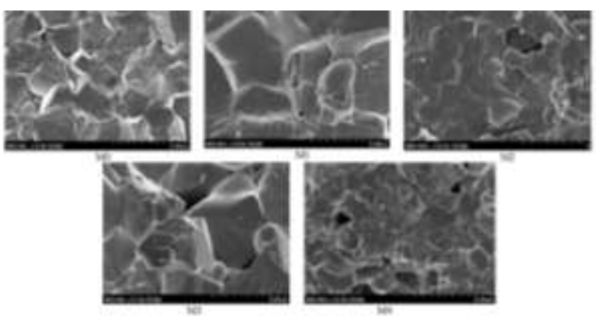

Figure 2. SEM images of M0, M1, M2, M3, and M4 samples of the PZT82.5/17.5-Ta^{5+}

TABLE II. CERAMIC DENSITY OF THE PZT82.5/17.5 –Ta^{5+} COMPOSITIONS

Sample	ρ (g/cm^3)
M0	7.49
M1	7.41
M2	7.48
M3	7.51
M4	7.30

TABLE III. DIELECTRIC CONSTANT $\varepsilon/\varepsilon_0$ AND DIELECTRIC LOSS tgδ OF THE PZT82.5/17.5 –Ta^{5+} COMPOSITIONS

Sample	$\varepsilon/\varepsilon_0$	*tgδ*
M0	367	0.0211
M1	355	0.0232
M2	307	0.0208
M3	348	0.0223
M4	359	0.0247

B. *Effect of Ta^{5+} concentrations on dielectric and ferroelectric properties of the ceramic system of PZT 82.5/17.5 at room temperature*

B.1. Effect Ta^{5+} concentrations on the dielectric properties

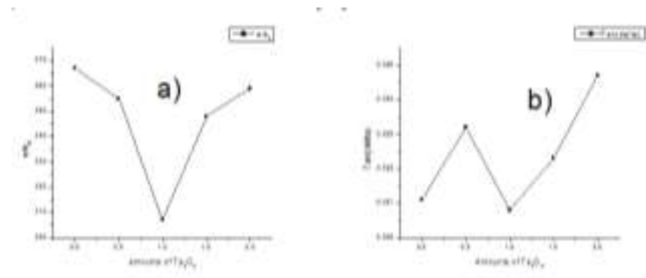

Figure 3. Dependence of the dielectric constant $\varepsilon/\varepsilon_0$ - a), dielectric loss tgδ – b) the PZT82.5/17.5 –Ta^{5+} system measured at room temperature and 1 KHz on Ta_2O_5 concentration

In Table 3 and Figure 3, dependence of dielectric constant $\varepsilon/\varepsilon_0$, dielectric loss tgδ measured at room temperature and 1 kHz presented. The dielectric properties are strongly influenced by Ta^{5+} and very small values. Both $\varepsilon/\varepsilon_0$ and tgδ are of the minimal values at x =1%mol Ta_2O_5 (M2). Here soft Ta^{5+} dopants are replaced instead of Zr^{4+} or Ti^{4+} sites and causing slight distortions of the rhombohedral structure, influencing microstructure of PZT82.5/17.5 compositions. As a result of this, the dielectric properties are changed.

B.2. Effect Ta^{5+} concentrations on the ferroelectric properties: To measure ferroelectric hysteresis loops, author used the Sawyer - Tower scheme and calculated permanent polarization P_r, coercive field E_c. Ferroelectric hysteresis loops and P_r, E_c of M0, M1, M2, M3, M4 samples are shown in Figure 4 and Table 4.

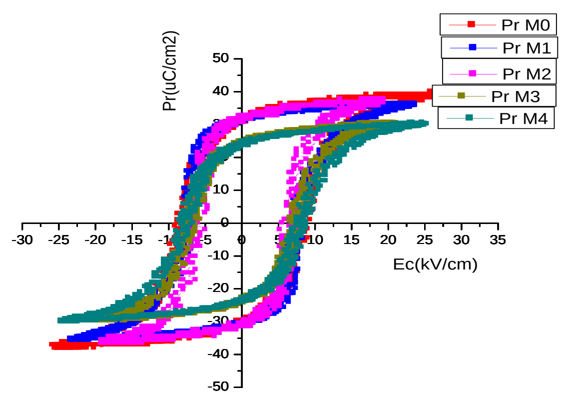

Figure 4. Dependence of the hysteresis loops of the PZT82.5/17.5 –Ta^{5+} system measured at room temperature on Ta_2O_5 concentrations

All samples are of typically rectangular hysteresis loops forms of ferroelectric materials. Permanent polarization P_r = 23.9 – 32.4($\mu C/cm^2$), coercive field E_c = 6.8 – 8.9(kV/cm).

TABLE IV. DEPENDENCE OF E_C AND P_R ON Ta_2O_5 CONCENTRATION

Sample	E_c (kV/cm)	P_r ($\mu C/cm^2$)
M0	8.9	32.4
M1	8.6	31.9
M2	6.8	32.2
M3	7.5	24.0
M4	8.1	23.9

Ta^{5+} strongly effects on ferroelectric hysteresis loops. In Figure 5 dependence of E_c and P_r of the PZT82.5/17.5 $-Ta^{5+}$ system on the Ta_2O_5 are presented. Ceramics of these ferroelectric hysteresis loops can be suitable for ferroelectric memories FERAMS application.

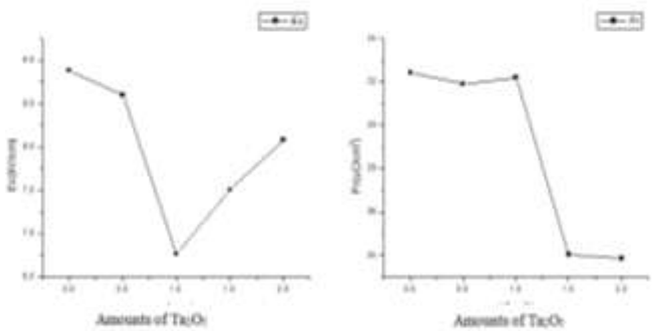

Figure 5. Dependence of E_c –a) and P_r –b) of the PZT82.5/17.5 $-Ta^{5+}$system on the Ta_2O_5 concentration

C. *Effect of Ta^{5+} concentrations on pyroelectric property of the ceramic system of PZT 82.5/17.5 at room temperature*

Pyroelectric currents of the PZT82.5/17.5 -Ta5+ samples are measured by thermodynamic method with Keithley 485 Autoranging Picoammeter.

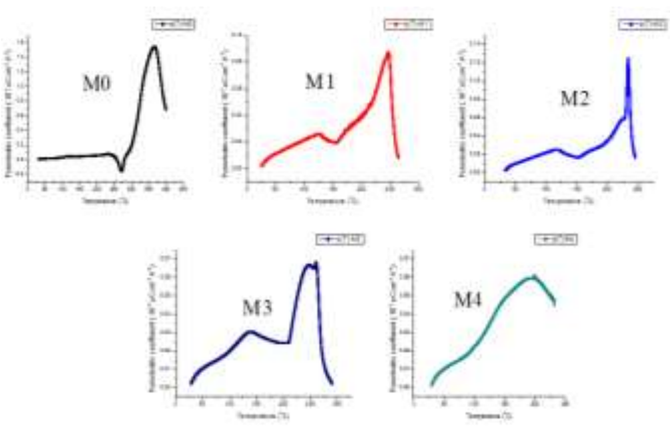

Figure 6. Dependence of pyroelectric coefficients on temperature of M0, M1, M2, M3, M4

Pyroelectric intensity of the samples is calculated. ΔP_s spontaneous polarizations are calculated as follows: $\Delta P = I.R_nC_0/A_0$. Pyroelectric coefficients are calculated by using formula: $\gamma = \Delta P/\Delta T = I.R_nC_0/A_0\Delta T$. Figure 6 shows the dependence of pyroelectric coefficients of PZT82.5/17.5-Ta^{5+} compositions on temperature. In Table 5, the calculated pyroelectric coefficients of 33^0C and maxima of PZT82.5/17.5 $-Ta^{5+}$ ceramic compositions are presented. From Figure 6 and Table 5 we see Ta^{5+} ion concentrations strongly effect on pyroelectric properties of PZT 82.5/17.5 ceramic system.

TABLE V. CALCULATED PYROELECTRIC COEFFICIENTS OF THE PZT 82.5/17.5-TA^{5+} CERAMICS COMPOSITIONS

Sample	Temperature (^{0}K)	Maxima of pyroelectric coefficients γ ($10^{-2}.\mu C.cm^{-2}.K^{-1}$)	Pyroelectric coefficients at 306 ^{0}K ($10^{-3}.\mu C.cm^{-2}.K^{-1}$)
M0	640.0	1.5	0.05
M1	519.9	8.7	4.22
M2	508.0	24.8	4.38
M3	510.0	6.8	4.31
M4	472.3	6.1	3.38

III. CONCLUSIONS

Pyroelectric ceramics of the PZT82.5/17.5 $-xTa^{5+}$ system were successfully synthesized. The Ta^{5+} concentrations (x) have a strong effect on structure, microstructure, density, dielectric ferroelectric, and pyroelectric properties. The improvement by using power ultrasonic wave for processing ceramic powder during 70 minutes was rather good for crystallization and enhanced the quality of the final product. All of the ceramic compositions are perovskite phase, rhombohedral structure with good microstructure of small pores, high ceramic density, and small dielectric properties suitable for pyroelectric application. At x = 1% mol. Ta_2O_5 (M2), we have the best composition: $\rho = 7.48 g/cm^3$, $\varepsilon/\varepsilon_0 = 307$, $tg\delta = 0.021$, $\gamma = 12.4\ x10^{-2}\mu C.cm^{-2}.K^{-1}$, $\gamma = 2.19x10^{-3}.\mu C.cm^{-2}.K^{-1}$ at 306^0K suitable for making ultra-red sensors pyroelectric detectors.

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