SYNTHESIS AND STUDY OF EFFECTS OF SOFT AND HARD DOPANTS ON $Pb(Zr_{82.5}Ti_{17.5})O_3$ PYROELECTRIC CERAMIC SYSTEM

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(Ngày nhận bài: 13/10/2025, ngày nhận bài chỉnh sửa: 17/10/2025, ngày duyệt đăng: 24/10/2025)

ABSTRACT

This article presents experimental studies of the synthesis process and the effect of soft dopant and hard dopant on the physical properties of $Pb(Zr_{82.5}Ti_{17.5})O_3$ pyroelectric ceramic system (PZT 82.5 / 17.5). The samples are synthesized by traditional ceramic technology from the initial oxides of PbO, ZrO_2, TiO_2 (with purity 99%), primary milling during 8h, calcinated at 850°C during 2h. Then the powders of PZT 82.5/17.5 and soft dopant (Ta_2O_5) and hard dopant (Cr_2O_3) are primary milled and weighed in desired ratios, mixed together into samples. Then they are processed by high power ultrasonic field in ethanol during 70 minutes. After that they are dried, pressed at high pressure of 1.2 T/cm^2 by a hydraulic presser. Finally, they are sintered at 1150°C during 2h. All the samples have pure Rhombohedral perovskite phase; high densities, strong pyroelectric coefficients suitable to make ultra-red sensors and detectors.

Keywords: *Pyroelectric ceramics, pyroelectric, dielectric, ferroelectric, polarization*

1. Introduction

$Pb(Zr,Ti)O_3$ (PZT) ceramics is a one of the an advanced new electronic materials of important role in engineering applications because of excellent ferroelectric properties, strong piezoelectric, pyroelectric effects, electro-optical properties. Especially, the ferroelectric ceramic system based on the $Pb(Zr, Ti)O_3$ (PZT) with various dopants is of advanced properties. In recent years, Zr- rich PZT compositions with various dopants are paid a great attention by many materials science researchers because of the strong pyroelectric effect [1–5]. In these papers, authors would to present new experimental results of PZT with soft dopant (PZT82.5/17.5 – x % mol Ta_2O_5, where x = 0, 0.5, 1, 1.5, 2 mol %) and hard dopant (PZT85.2/17.5 – y % mol Cr_2O_3, where y = 0, 0.5, 0.75, 1, 1.25, 1.50, 2 mol %). The effect of Ta^{5+} concentrations and Cr^{3+} concentrations on structure, ferroelectric and pyroelectric properties are presented and discussed.

2. Experimental

Raw materials are oxides PbO, ZrO_2, TiO_2, Cr_2O_3 and Ta_2O_5 with a purity 99%. The pyroelectric ceramics were synthesized by traditional ceramic technology combined with innovation of high power ultrasonic processing during 70 minutes instead of second traditional long time mixing, milling has been used. The ceramic powder of PZT 82.5/17.5 was synthesis by traditional ceramic technology with parameters: primary milling on PM 400/2 device during 8 h,

pressed at 800 kg/cm^2 into disks of Φ = 25 mm, calcinated at 850◦C during 2 h. The powders of PZT 82.5/17.5 and Ta_2O_5 (or Cr_2O_3) are primary milled and weighed in desired ratios, mixed together into a variety of samples M0, T1, T2, T3, and T4 samples (or M0, M1, M2, M3, M4, M5, and M6 samples). Then they are dissolved in ethanol and processed by high power ultrasonic wave from an ultrasonic device of 70W during 70 minutes. After that, they were dried, pressed at high pressure of 1.2 T/cm^2 by hydraulic pressure, they are sintered at 1150˚C during 2 h in a Lenton furnace, firing and cooling of 5˚C/min. After processing and covering Ag electrodes samples are polarized with a DC high voltage of 30 kV/cm during 15 minutes in silicone oil at temperature of 125˚C.

3. Results and discussion

3.1. Effect of dopants concentration on ferroelectric properties of the PZT82.5/17.5 system

3.1.1. Effect of soft dopant concentration on ferroelectric properties

To measure ferroelectric hysteresis loops of the samples, the Sawyer – Tower scheme is used and permanent polarization P_r, coercive field E_c are calculated. Ferroelectric hysteresis loops and P_r, E_c of M0, T1, T2, T3, T4 samples are shown in Figure 1 and in Table 1. From Figure 1 we see all of the hysteresis loops are typical rectangular form characterizing ferroelectric materials and strongly dependent on Ta^{5+} concentration.

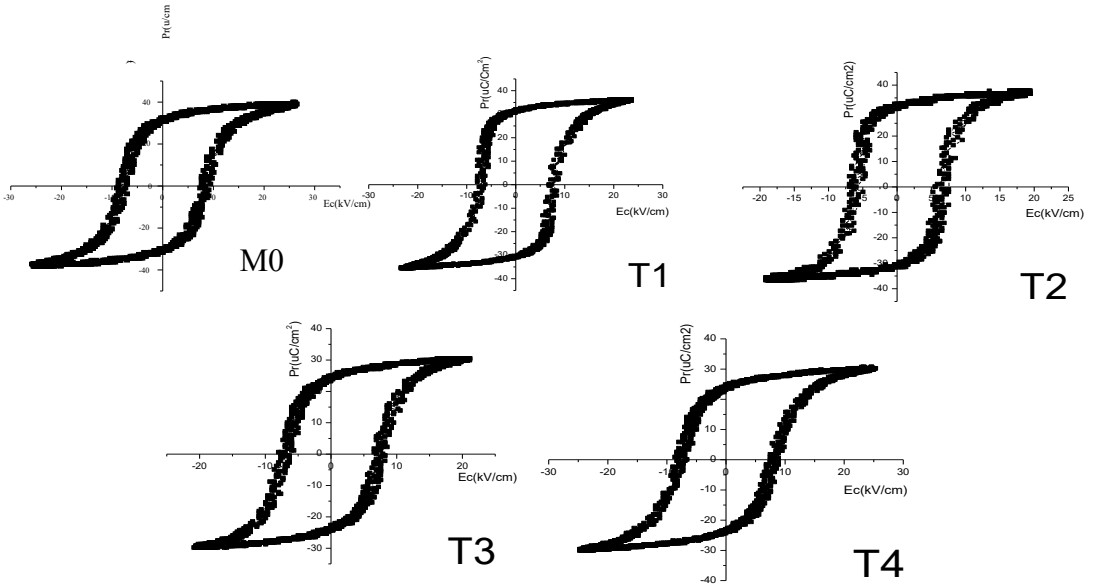


Figure 1: *Dependence of hysteresis loops of PZT82.5/17.5 samples on Ta^{5+} concentration*

In Table 1, it is clear coercive field E_c and permanent polarization P_r are strongly changed under the effect of Ta^{5+} concentration. We see E_c value is decreased when Ta^{5+} concentration increased to x = 1 % mol and gained a

minimum here, then increased when Ta^{5+} increased. We also see that coercive fields are of rather small values E_c = (7.5 – 8.8) kV/cm and permanent polarization is decreased when Ta^{5+} concentration increased. At = 1 % mol the ceramic composition is of E_c = 6.76 kV/cm and P_r = 32.19 μC/cm^2.

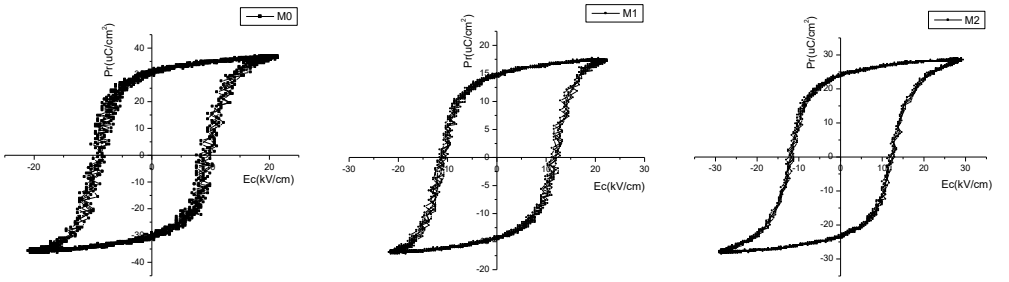
Table 1: *Coercive field E_c, P_r dependent on Ta^{5+} concentration*

Sample	E_c (kV/cm)	P_r (μC/cm^2)
T0=M0	9.50	32.41
T1	8.60	31.90
T2	6.76	32.19
T3	7.50	24.02
T4	8.08	23.852

3.1.2. Effect of hard dopant concentration on ferroelectric properties

In Figure 2, we see all hysteresis loops are of typical rectangular forms characterizing ferroelectric materials and all of hysteresis loops are saturated. Permanent polarization P_r and coercive fields E_c are presented in Table 2. We see E_c is changed not much and of minimum at x = 0% mol (M0), P_r is strongly decreased and of minimum also at y = 0% mol (M0). We see that Cr^{3+} hard dopant concentrations are at of strong effect on ferroelectric properties of the studied ceramic compositions. Generally speaking, P_r values are rather high and E_c values are typical for ferroelectric materials.

P_r/E_c values are high. It is normal in the rhombohedral structure. These ratios are decreased when Cr^{3+} concentrations increased gradually up to x = 2% mol (M6, the ratio nearly equal 1). This can understand Cr^{3+} hard dopant making domain wall mobility increased, dielectric loss energy decreased (surface of ferroelectric hysteresis decreased gradually in the studied concentration region). This fact is reason of decreasing of dielectric loss factor *tanδ* with increasing Cr^{3+} concentration and of minimal value at x = 1.25% mol (M4) as shown in Table 2. Cr^{3+} ion is hard dopant and agrees with radius, electric negativities [RCr^{3+} = 0.64Å, RZr^{4+} = 0.79Å, RTi =0,68Å [3] and electric negativities equal 1.66; 1.33; 1.54 respectively [3] replacing into Zr^{4+} or Ti^{4+} sites.



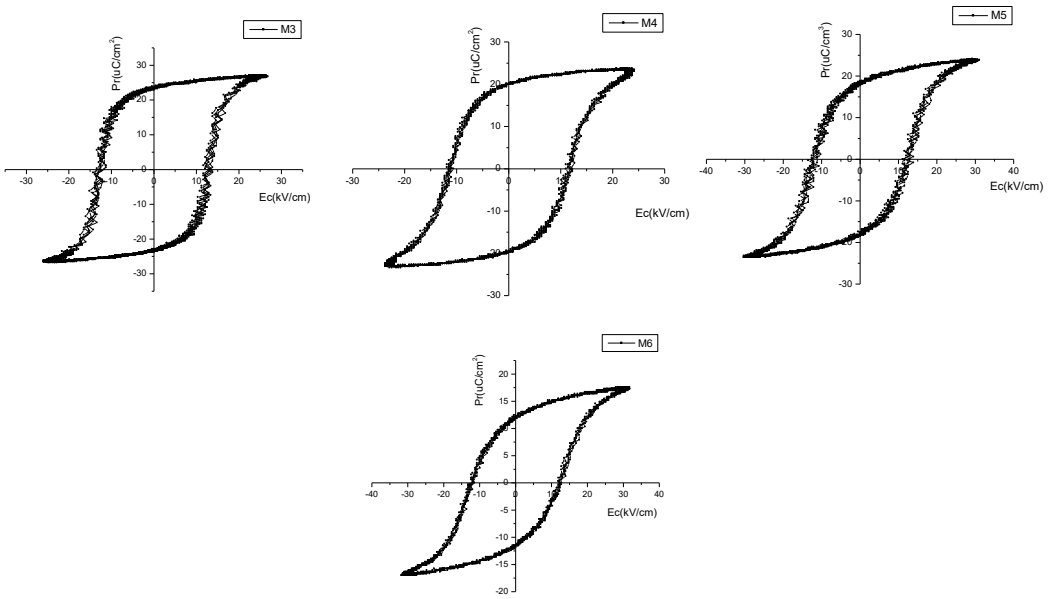


Figure 2: *Ferroelectric hysteresises of M0-M6 samples of the PZT82.5/17.5*

Table 2: *Calculated E_c and P_r values of M0-M6 samples*

Sample	E_c (kV/cm)	P_r (μC/cm^2)
M0	9.5	32.4
M1	11.8	29.6
M2	12.2	23.8
M3	12.7	23.5
M4	11.5	20.0
M5	11.8	18.4
M6	12.4	11.9

3.2. Effect of dopants concentration on phase and structure of the PZT82.5/17.5 system

3.2.1. Effect of soft dopant concentration on phase and structure

From Table 3, we see network parameters a and c are changed with Ta^{5+} concentration. X-ray diffraction diagrams are carried out on D 5000 device and presented in Figure 3. In Figure 3 are presented X-ray diffractions diagrams of M0, T1, T2, T3, T4 samples. From X-ray diagrams we can see all samples M0, T1, T2, T3, T4 are of pure Rhombohedral perovskite phase. It is important to say that parameters of used technology are suitable and good. All peaks in diagrams are not displaced, only intensities are slightly changed. This means that the perovskite phase are not changed, and only lattice parameters slightly changed.

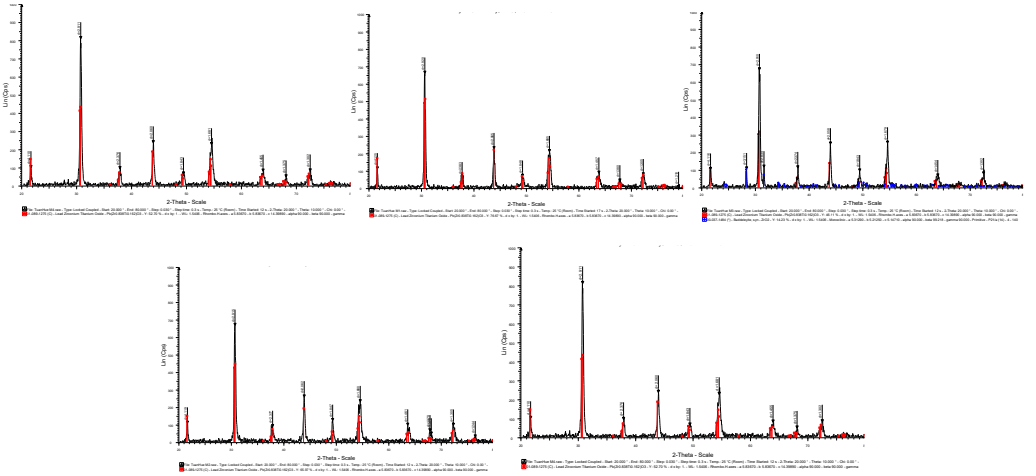


Figure 3: *X- ray diffraction diagrams of T0, T1, T2, T3, T4 samples*

Table 3: *Calculated network parameters a, b, c of T0, T1, T2, T3, T4 samples*

Sample	T0	T1	T2	T3	T4
Parameter a	5.8282	5.8361	5.8258	5.8133	5.8224
Parameter b	5.8282	5.8361	5.8258	5.8133	5.8224
Parameter c	14.3628	14.3684	14.3590	14.3262	14.3290

3.2.2. Effect of hard dopant concentration on phase and structure

In figure 4 a, b, c, d, e, f, g are presented X-ray diffractions diagrams of M0, M1, M2, M3, M4, M5, M6 samples.

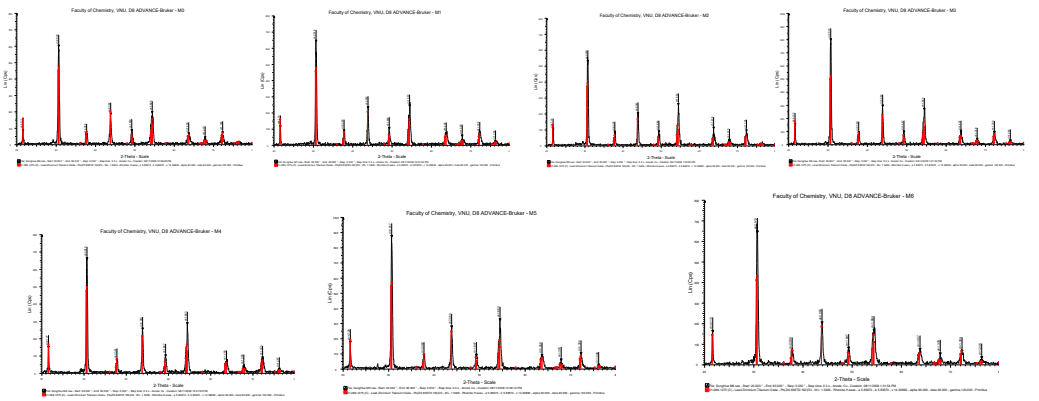


Figure 4: *X-ray diffraction patterns of M0-a, M1-b, M2-c, M3-d, M4-e, M5-f, M6-g samples*

From Figure 4, it is clear that exist only pure perovskite phases and rhombohedral structures in all X- ray diagrams. We also see that the sites of all peaks are not changed, their intensities greatly changed under the effect of Cr^{3+}concentrations. This means the Cr^{3+}concentrations are of strong effect

on structure and microstructure, not of effect on the perovskite phase of the ceramics. This result is revealed clearlier by changes of network parameters presented in Table 4

Table 4: *Calculated network parameters a, b, c of M0, M1, M2, M3, M4, M5, M6 samples*

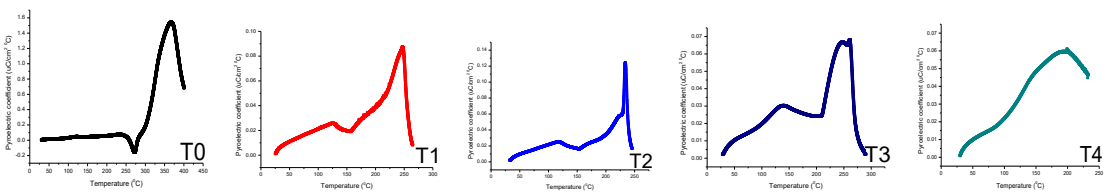
Sample	M0	M1	M2	M3	M4	M5	M6
Parameter a	5.8289	5.8254	5.8218	5.8274	5.8260	5.8272	5.8304
Parameter b	5.8289	5.8254	5.8218	5.8274	5.8260	5.8272	5.8304
Parameter c	14.3611	14.3666	14.3586	14.3578	14.3613	14.3623	14.3655

From Table 4 it is clear parameters a, b, c are strongly changed by the effect of Cr^{3+} concentrations; The perovskite phase and rhombohedral structure remain constant. It is clear that Cr^{3+}concentration makes the ceramics strained rhombohedral structure.

3.3. Effect of dopants concentration on pyroelectric properties of the PZT82.5/17.5 system

3.3.1. Effect of soft dopant concentration on pyroelectric properties

Pyroelectric current intensities of the M0, T1, T2, T3, T4 samples are measured by direct method with Autorange picoamplemeter Keiley 485. Pyroelectric coefficients of the samples are calculated of the sample are calculated. The results are presented in Figure 5 and Table 5. Pyroelectric coefficients are calculated by I_p, ΔP_s, where ΔPs: spontaneous polarizations are calculated as following: $\Delta P = IR_nC_o/A_o$. Pyroelectric coefficients are calculated by the formula: $\gamma = \Delta P/\Delta T = IR_nC_o/A_o\Delta T$. In Figure 5 are shown the dependence of pyroelectric coefficients γ_{max} of PZT82.5/17.5 – x % mol Ta^{5+} compositions on temperature.



a) b) c) d) e)

Figure 5: *Dependence of pyroelectric coefficients γ_{max} on temperature of M0-a), T1-b),T2-c) T3-d),T4-e)*

In Table 5 are presented the calculated pyroelectric coefficients γ_{room} at room temperature (33°C) and maximal measured intensities γ_{max} of PZT82.5/17.5 – x% mol Ta^{5+}ceramic compositions.

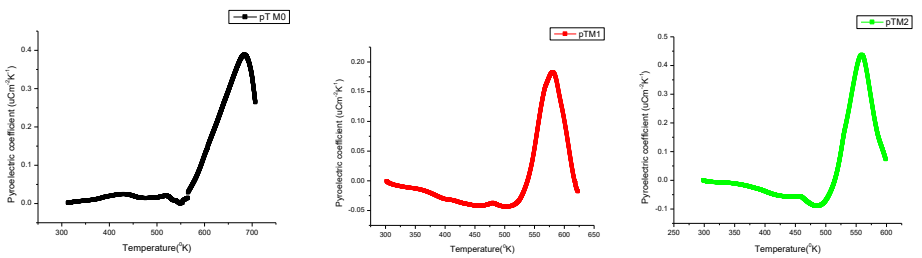
We see Ta^{5+} concentration is of strong effect on pyroelectric properties of the studied. All compositions of PZT82.5/17.5 – x% mol. Ta^{5+}ceramic compositions are of very strong pyroelectric effect. Pyroelectric coefficients γ_{max} of the studied ceramic compositions are very large such as γ_{max} = (6.1 - 12.4).10^{-2}.μC.cm^{-2}.K^{-1} and at room temperature γ_{room} = (2.19 – 5.80).10^{-3}.μC.cm^{-2}K^{-1}. At x = 1 % mol Ta^{5+} maximal pyroelectric coefficient is of the largest value γ_{max} = 12.4 (.10^{-2}.μC.cm^{-2}.K^{-1}). At 0.5 % mol. Ta^{5+}, at room temperature pyroelectric coefficient is of the largest value γ_{room} = 5.8 (.10^{-3}.μC.cm^{-2}K^{-1}). It is very interesting to say that ultra- red sensors and detector are always running near room temperature. That' why the ceramic composition with x = 0.5% Ta^{5+} is very useful in practical applications.

Table 5: *Calculated pyroelectric coefficients of the PZT 82.5/17.5- Ta^{5+} ceramics compositions*

Sample	Temperature K	Maxima of pyroelectric coefficients γ_{max} (10^{-2}.μC.cm^{-2}.K^{-1})	Pyroelectric coefficients γ_{room} at room temperature (10^{-3}.μC.cm^{-2}.K^{-1})
T0	640.0	6.9	4.68
T1	519.9	8.7	5.80
T2	507.0	12.4	2.19
T3	480.5	6.8	4.31
T4	472.3	6.1	3.38

3.3.2. Effect of hard dopant concentration on pyroelectric properties

Pyroelectric intensities of the samples are calculated. The results are presented in figure 6 and table 6. We see that all of the compositions are of very high pyroelectric coefficients with γ = (0.78 - 7.72).10^{-2}μC.cm^{-2}.K^{-1}. At room temperature (306^{o}K), γ_{room} = (0.15 - 0.96).10^{-3}μC.cm^{-2}.K^{-1}. It is clear the Cr^{3+} concentrations are of strong effect on the pyroelectric effect of all compositions of the studied system. The strongest pyroelectric effect is due to the composition containing x = 1.25% mol. Cr_2O_3 (M4). For this ceramic composition γ = 7.72 .10^{-2}μC.cm^{-2}.K^{-1} and at room temperature (306^{o}k) γ_{room} = 0.96. (10^{-3}μC.cm^{-2}.K^{-1})



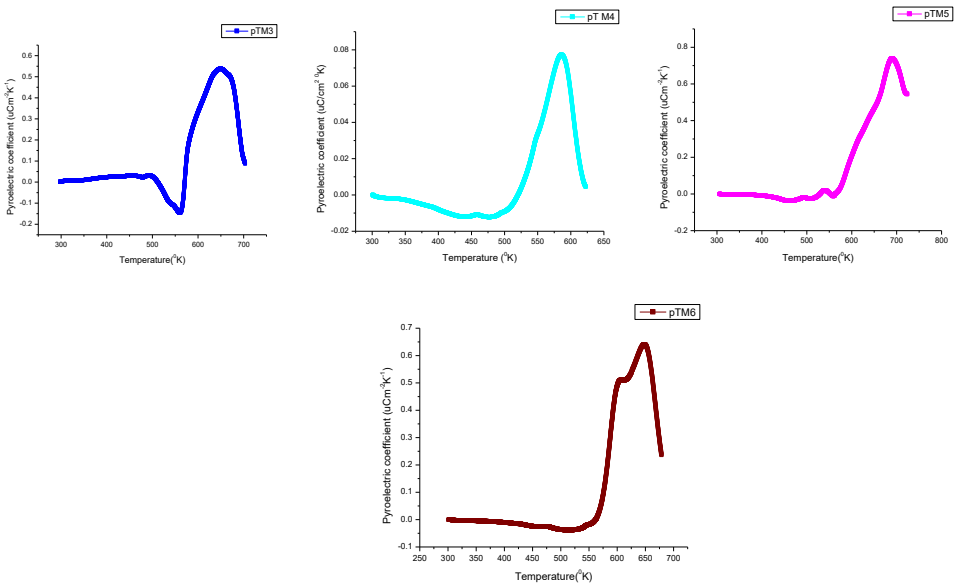


Figure 6: *Pyroelectric coefficients of M0-M6 samples of the PZT82.5/17.5-Cr_2O_3*

Table 6: *Calculated pyroelectric coefficients of the PZT 82.5/17.5- Cr_2O_3 ceramics compositions*

Sample	Temperature K	Maxima of pyroelectric coefficients γ_{max} (10^{-2}.μC.cm^{-2}.K^{-1})	Pyroelectric coefficients γ_{room} at room temperature (10^{-3}.μC.cm^{-2}.K^{-1})
M0	683	0.78	0.37
M1	580	1.83	0.37
M2	559	4.36	0.47
M3	648	5.37	0.42
M4	585	7.72	0.96
M5	690	7.39	0.15
M6	648	6.40	0.19

4. Conclusion

Traditional ceramic technology and improvement in the aid of processing ceramic powders by high power ultrasonic wave in 70 minutes instead of long time milling and mixing are effective. All of the fabricated ceramic compositions are of strong effect on structure and microstructure. Exist pure perovskite phase and rhombohedral structure in all of the samples. The rhombohedral grains in microstructure with light distortion are rather closely arranged agreed with the high ceramic densities of the samples.

The soft dopant Ta^{5+} concentrations have strong effect on structure, ceramic density, electric, ferroelectric and pyroelectric properties of the PZT 82.5/17.5 ceramic system. Ferroelectric hysteresis loops of all of the studied compositions are of typical rectangular

form of ferroelectric materials. The permanent polarization P_r and electric coercive field E_c are strongly dependent on Ta^{5+} concentration and at x = 1% mol the ceramic composition is of E_c = 6.76 kV/cm and P_r = 32.19.μC/cm^2 suitable for fabricating ferroelectric memories FERAMS.

Pyroelectric properties are also strongly dependent on Ta^{5+} concentration. All of the studied compositions are of very large pyroelectric coefficients such as max = (1.5 - 24.8).10^{-2}μCcm^{-2}K^{-1} and at room temperature room = (0.05 - 4.38).10^{-3}μCcm^{-2}K^{-1}. At x = 1 % mol Ta^{5+} maximal pyroelectric coefficient is of the largest value max = 24.8 $\times10^{-2}$μCcm^{-2}K^{-1}, and room temperature pyroelectric coefficient is of the largest value room = 4.38 $\times10^{-3}$μCcm^{-2}K^{-1}. The ceramic composition with x = 1 % Ta^{5+} is possible for practical applications.

At x = 1.25% mol. Cr^{3+} (M4), ceramic has high ceramic densities: ρ = 7.28 g/cm^3. Cr^{3+} concentrations are of strong effect on ferroelectric properties. Ferroelectric hysteresis loops are of typical rectangular form of ferroelectric materials and of high permanent polarizations P_r = (11.9 - 30.4) μC/cm^2, typical electric coercive fields E_c = (9.5 - 12.7) kV/cm. All studied ceramic compositions are of strong pyroelectric effect. At x = 1.25% mol Cr^{3+} (M4) the ceramic composition is of the strongest pyroelectric effect with maximal pyroelectric coefficient max = 7.72 $\times10^{-2}$μCcm^{-2}K^{-1} and at room temperature (306K) room = 0.96×10^{-3}μCcm^{-2}K^{-1}, P_r = 20.0 μC/cm^2, E_c = 11.5 kV/cm. At x = 1.25% mol. (M4) it is suitable to fabricate pyroelectric ceramics for application in the field of ultra-red sensors and detectors [6-8].

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TỔNG HỢP VÀ NGHIÊN CỨU ẢNH HƯỞNG CỦA TẠP MỀM VÀ TẠP CỨNG LÊN GỐM HỎA ĐIỆN $Pb(Zr_{82.5}Ti_{17.5})O_3$

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(Received: 13/10/2025, Revised: 17/10/2025, Accepted for publication: 24/10/2025)

TÓM TẮT

Bài báo trình bày các nghiên cứu thực nghiệm về quy trình tổng hợp, ảnh hưởng của tạp mềm và tạp cứng đến tính chất vật lí của hệ gốm hỏa điện $Pb(Zr_{82,5}Ti_{17,5})O_3$ (PZT 82,5 / 17,5). Các mẫu được tổng hợp bằng công nghệ gốm truyền thống từ các oxit ban đầu PbO, ZrO_2, TiO_2 (độ tinh khiết 99%), được nghiền sơ bộ trong 8 giờ và nung sơ bộ ở 850^{o}C trong 2 giờ. Sau đó, bột PZT 82,5/17,5 cùng tạp mềm (Ta_2O_5) và tạp cứng (Cr_2O_3) được nghiền sơ bộ và cân theo tỉ lệ mong muốn, trộn đều thành mẫu. Tiếp theo, chúng được xử lí bằng sóng siêu âm công suất cao trong etanol trong 70 phút. Sau đó, chúng được sấy khô, ép ở áp suất cao 1,2 T/cm^2 bằng máy ép thủy lực. Cuối cùng, chúng được thiêu kết ở 1150^{o}C trong 2 giờ. Tất cả các mẫu đều có pha perovskite mặt thoi tinh khiết; mật độ cao, hệ số hỏa điện mạnh, phù hợp để chế tạo cảm biến và đầu dò hồng ngoại.

Từ khóa: *Gốm hỏa điện, hỏa điện, điện môi, sắt điện, phân cực*