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# Synthesis and Study of effect of $Cr^{3+}$ concentration on Physical properties and pyroelectric property of the $Pb(Zr_{0.825}Ti_{0.175})O_3$ ceramic system

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***Abstract*— In this paper, the effects of $Cr^{3+}$concentrations on some physical properties and pyroelectric properties of the ceramic system of $(1-x)Pb(Zr_{0.825}Ti_{0.175})O_3 – xCr_2O_3$, where x = 0; 0.50; 0.75; 1.00; 1.25; 1.50; 2.00% mol have been presented. Experimental results indicated that $Cr^{3+}$ concentrations are of great effect on the mentioned above physical properties of the ceramics. X-ray diffraction diagrams indicated that exist pure perovskite phases with rhombohedral structure in all of ceramic compositions of the system. From SEM images we can see that rhombohedral grains of 2 μm size closely arranged with small pores. Besides, ceramic densities, dielectric constants, dielectric loss factor are presented with respective values of $\rho = 7.48$ g/cm$^3$, $\varepsilon/\varepsilon_0 = 343$, $\tan\delta = 0.03$ for the optimal $Cr_2O_3$ concentration of 1.25% mol. $Cr^{3+}$ concentrations are of very strong effect on structure, microstructure and electric property of the studied system. The electric conductivity are of very small values $\sigma = 2.96.10^{-18}\Omega^{-1}$ cm. Hysteresis loops are of typical rectangular form characterizing ferroelectric materials with permanent polarization $P_r$ = (11.9 – 30.4) μC/cm$^2$ and coercive field $E_c$ = 9.5 – 12.4 kV/cm; Pyroelectric effects are very strong in all compositions of the studied system with maximal pyroelectric coefficients $\gamma_{max}$ =(0.78 – 7.72 ).$10^{-2}$ μC.cm$^{-2}$.K$^{-1}$, pyroelectric coefficients at room temperature (306$^0$K) $\gamma_{room}$ = (0.15 – 0.94).$10^{-3}$ μ C.cm$^{-3}$.K$^{-1}$.**

***Keywords*—PZT, Zr–rich PZT ferroelectric ceramics, pyroelectric, polarization***

## I. Introduction

$Pb(Zr,Ti)O_3$ (PZT) ceramics is one of the most frequency studied ferroelectric materials because of excellent ferroelectric properties, strong piezoelectric, pyroelectric effects, and electro-optical properties. In recent years, have been many published papers [2-9] pointing out that in the Zr- and Ti-rich of PZT compositions there are not only good ferroelectric, piezoelectric effects, but also very strong pyroelectric effect. In this paper author would to present new experimental results of $Pb(Zr_{0.825}Ti_{0.175})O_3 – xCr_2O_3$, where x = 0; 0.50; 0.75; 1.00; 1.25; 1.50; 2.00 % mol. Effects of $Cr^{3+}$ concentrations on structure, microstructure, electric, dielectric, ferroelectric, pyroelectric properties and improvement of technology have been presented and discussed.

## II. Experimental

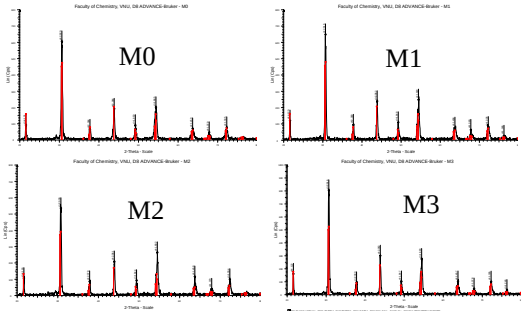
### A. *Synthesis*

The ferroelectric ceramic systems of the PZT- $xCr_2O_3$ systems, where x = 0; 0.50; 0.75; 1.00; 1.25; 1.50; 2.00 % mol. called M0, M1, M2, M3, M4, M5, M6 respectively are fabricated and studied. Raw materials are oxides PbO, $ZrO_2$, $TiO_2$, and $Cr_2O_3$ with purity 99% .The ferroelectric ceramics are synthesized by traditional ceramic technology. The innovation of high power ultrasonic processing for about 70 minutes in stead of second traditional long time mixing, milling has been used. The ceramic powder of $Pb(Zr_{0.825}Ti_{0.175})O_3$ are fabricated by traditional ceramic technology with parameters: primary milling on PM 400/2 device during 8h, pressed at 800kG/cm$^2$ into disks of Φ = 25mm, calcinated at 850$^0$C during 2h. The powders of $Pb(Zr_{0.825}Ti_{0.175})O_3$ and $Cr_2O_3$ are primary milled and weighed in desired ratios, mixed together into six types of M0, M1, M2, M3, M4, M5, M6 samples. Then they are processed by high power ultrasonic field during 70 minutes. After that they are dried, pressed at high pressure of 1.2 T/cm$^2$ by hydraulic presser. Processing and covering Ag electrodes samples are polarized with DC high voltage of 30 KV/cm during 15 minutes in silicone oil at temperature of 125$^0$C. Ceramic densities of the studied compositions are of $\rho = (7.22 – 7.48)$ g/cm$^3$.

### B. *The effect of $Cr^{3+}$ concentrations on phase and structure*

X-ray diffraction diagrams are carried out on D 5000 device and presented in Figure 1.

Figure 1 indicated that there are only pure perovskite phases and rhombohedral structures in all X- ray diagrams. We also see that 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 the effect on perovskite phase of the ceramics. This result is fostered by changes of network parameters presented in Table I.

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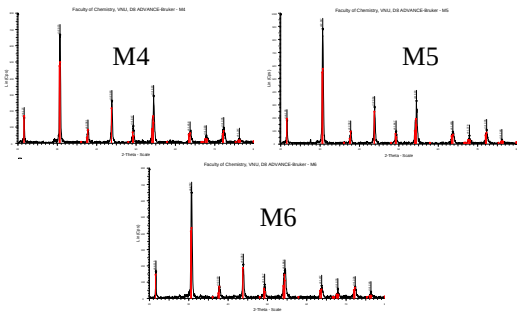


Figure 1. X-ray diffractions diagrams of M0, M1, M2, M3, M4, M5, M6 samples.

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

TABLE I. CALCULATED NETWORK PARAMETERS a, b, c OF M0, M1, M2, M3, M4, M5, M6 SAMPLES

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

## C. The effect of $Cr^{3+}$ concentrations on microstructure

SEM images of the samples are carried out on Hitachi S-4800 device and presented in Figure 2. From Figure 2 it is clear that $Cr^{3+}$ concentrations are of strong effect on microstructure of all of the ceramic compositions. This means that $Cr^{3+}$ concentration is of large effect on solid phase diffusion during sintering process. In the M0 and M6 samples, grains are placed closely with small pores.

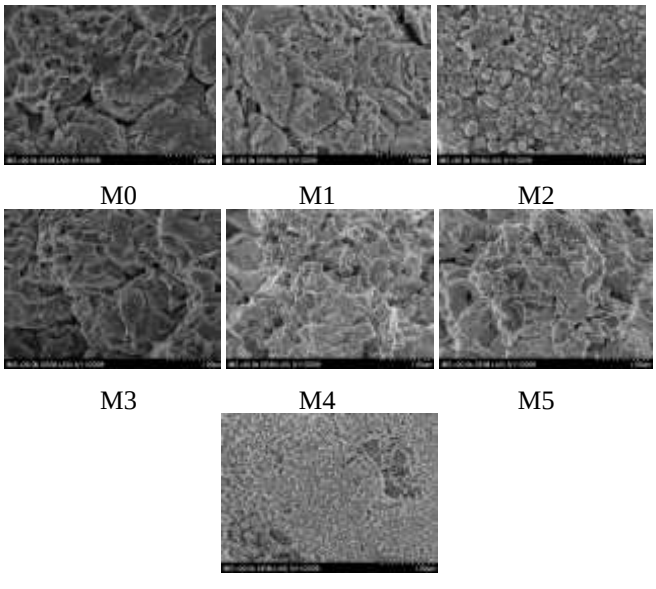


Figure 2. SEM images of M0, M1, M2, M3, M4, M5, M6 samples

## D. The effect of $Cr^{3+}$concentrations on ceramic density

Densities of the ceramics are measured by Archimedes method and digital balance AB204. The measured results are presented in Table II.

TABLE II. CERAMIC DENSITIES OF M0, M1, M2, M3, M4, M5, M6 SAMPLES

| Sample | ρ (g/cm$^3$ ) |
|---|---|
| M0 | 7.48 |
| M1 | 7.28 |
| M2 | 7.22 |
| M3 | 7.25 |
| M4 | 7.28 |
| M5 | 7.29 |
| M6 | 7.48 |

We have seen that ceramic densities of all samples are strongly changed under the effect of the $Cr^{3+}$ concentrations. It is agreed with changes of their microstructure above mentioned and M0, M6 are of the highest densities (ρ = 7.48 g/cm$^3$).

## E. Effect of $Cr^{3+}$concentrations on electric conductivity

We have used the highly automatized TESTER RLC HIOKI 3532 to determine imagine part $\varepsilon''$ of dielectric constant at room temperature and 1KHz. The electric conductivities σ have been calculated using formula $\sigma(\omega) = \omega\varepsilon_0\varepsilon''(\omega)$ [2].

The results are shown in Table III. In Table III electric conductivities of M0, M1, M2, M3, M4, M5, M6 samples are shown. We see electric conductivity of all of the samples are strongly on the $Cr^{3+}$ concentration and of very small values (σ = 0.3 – 3.72).$10^{-17}$ $\Omega^{-1}$ m$^{-1}$. This means that the ceramic compositions are good dielectrics (electric resistances are very high).

TABLE III. ELECTRIC CONDUCTIVITIES OF THE SAMPLES

| Sample | Electric conductivity σ (.$10^{-17}$ $\Omega^{-1}$ m$^{-1}$) |
|---|---|
| M0 | 0.62 |
| M1 | 2.87 |
| M2 | 1.15 |
| M3 | 1.30 |
| M4 | 0.29 |
| M5 | 3.72 |
| M6 | 1.28 |

## F. The effect of $Cr^{3+}$concentrations on dielectric properties

To determine dielectric properties at room temperature, we have used highly automatized TESTER RLC HIOHI 3532 to measure electric capacity C at 1 KHz at room temperature. Using formula is $\varepsilon = \frac{144Ct.10^9}{d^2}$, where C: electric capacity *(F)*, S: surface *($m^2$)*, d: diameter of sample *(m)*, t: thickness of sample (m) to calculate dielectric constant $\varepsilon/\varepsilon_0$ and dielectric loss factor $\tan\delta = \varepsilon''/\varepsilon'$ at room temperature [2]. The results are shown in Table IV and Figure 3.

TABLE IV. DIELECTRIC CONSTANTANS $\varepsilon/\varepsilon_0$ AND DIELECTRIC LOSS FACTOR tanδ

| Sample | $\varepsilon/\varepsilon_0$ | tanδ |
|---|---|---|
| M0 | 690 | 0.04 |
| M1 | 565 | 0.18 |
| M2 | 493 | 0.09 |
| M3 | 461 | 0.11 |
| M4 | 343 | 343 |
| M5 | 439 | 439 |
| M6 | 554 | 554 |

From Table IV and Figure 3 we see that dielectric constant $\varepsilon/\varepsilon_0$ is strongly dependent on $Cr^{3+}$ concentrations. Dielectric constant $\varepsilon/\varepsilon_0$ is of minimum at x = 1.25% mol $Cr_2O_3$ (M4). It is also clear that dielectric dissipation tanδ is changed under effect of $Cr^{3+}$concentrations and is of minimum also at x =1.25% mol $Cr_2O_3$ (M4). At this concentration M4 sample is of $\varepsilon/\varepsilon_0$ = 343 and tanδ = 0.03. We see $\varepsilon/\varepsilon_0$ and tanδ are the smallest values at this concentration. This concentration of the ceramics is chosen to fabricate pyroelectric ceramics for application.

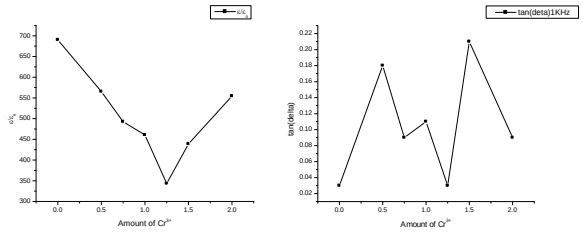


Figure 3. Dependence of $\varepsilon/\varepsilon_0$ and tanδ on $Cr^{3+}$ concentration

## G. The effect of $Cr^{3+}$ concentration on ferroelectric properties of the $Pb(Zr_{0.825}Ti_{0.175})O_3$ system

Using Sawyer–Tower scheme to measure ferroelectric hysteresises of the sample [1]. And results are shown in Figure 4

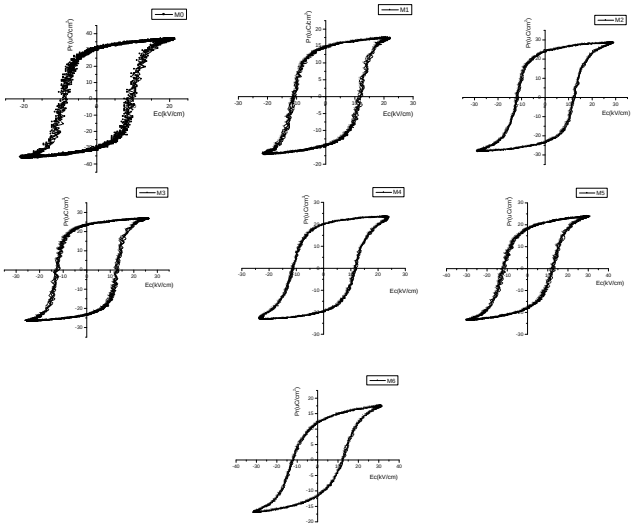


Figure 4. Ferroelectric hysteresis loops of M0-M6 samples

Here we observe 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 V. $E_c$ is changed not much and of minimum at x = 0%mol (M0), $P_r$ is strongly decreased and of minimum also at x = 0% mol (M0). That's why $Cr^{3+}$ hard dopant concentrations are of strong effect on ferroelectric properties of the studied ceramic compositions.

TABLE V. CALCULATED $E_c$ AND $P_r$ VALUES OF M0-M6 SAMPLES

| Sample | $E_c$(kV/cm) | $P_r$(μC/cm$^2$) |
|---|---|---|
| $M_0$ | 9.5 | 30.4 |
| $M_1$ | 11.8 | 29.6 |
| $M_2$ | 12.2 | 23.8 |
| $M_3$ | 12.7 | 23.5 |
| $M_4$ | 11.5 | 20.0 |
| $M_5$ | 11.8 | 18.4 |
| $M_6$ | 12.4 | 11.9 |

In summary, $P_r$ 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, but these ratios are decreased when $Cr^{3+}$ concentrations increased gradually up to x = 2% mol. (M6), where the ratio nearly equal 1. This can understadable because $Cr^{3+}$ hard dopant made domain wall mobility increased, dielectric loss energy decreased (surface of ferroelectric hysteresis decreased gradually in the studied concentration region). This fact is a reason for decrease in dielectric loss factor tanδ with increasing $Cr^{3+}$ concentration and of minimal value at x = 1.25% mol (M4) as shown in Table V. $Cr^{3+}$ ion is hard dopant and agreed with radius [$R_{Cr}^{3+}$ = 0.64Å, $R_{Zr}^{4+}$ = 0.79Å, $R_{Ti}$ =0,68Å$^0$ [3] and electric negativities equal 1.66; 1.33; 1.54 respectively [1]] replacing into $Zr^{4+}$ or $Ti^{4+}$ sites.

## H. The effect of $Cr^{3+}$ concentration on pyroelectric properties of the $Pb(Zr_{0.825}Ti_{0.175})O_3$ system

Pyroelectric current intensities of the PZT82.5/17.5 – $Cr^{3+}$ are measured by direct method with Auto range picoampemeter Keiley 485. Pyroelectric intensities of the samples are calculated. The results are presented in Figure 5 and Table VI.

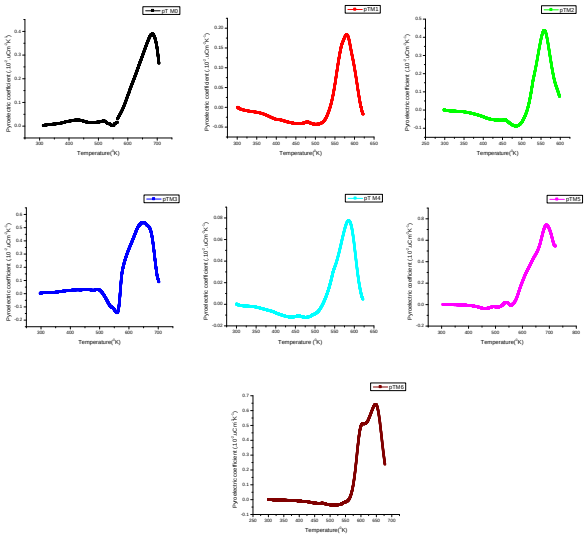


Figure 5. Pyroelectric coefficients of M0-M6 samples

We see that all of the compositions are of very high pyroelectric coefficients with $\gamma_{max}$ = (0.78-7.72).$10^{-2}$μC.cm$^{-2}$.K$^{-1}$. At room temperature (306$^0$K) $\gamma_{room}$ = (0.15-0.96).$10^{-3}$ .μC.cm$^{-3}$.K$^{-1}$.

TABLE VI. MAXIMAL PYROELECTRIC COEFFICIENTS AND PYROELECTRIC COEFFICIENTS AT ROOM TEMPERATURE OF THE M0-M6 SAMPLES

| Sample | Maximal pyroelectric coefficients $\gamma$max (. $10^{-2}$μC.cm$^{-2}$.K$^{-1}$) | Pyroelectric coefficients at 306K $\gamma_{room}$ ($.10^{-3}$μC.cm$^{-3}$.K$^{-1}$) |
|---|---|---|
| M0 | 0.78 (683$^0$K) | 0.37 |
| M1 | 1.83(580$^0$K) | 0.37 |
| M2 | 4.36(559$^0$K) | 0.47 |
| M3 | 5.37(648$^0$K) | 0.42 |
| M4 | 7.72(585$^0$K) | 0.96 |
| M5 | 7.39(690$^0$K) | 0.15 |
| M6 | 6.40(648$^0$K) | 0.19 |

It is clear that 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 $\gamma_{max}$ =7.72.$10^{-2}$μC.cm$^{-2}$.K$^{-1}$ and at room temperature (306$^0$K) $\gamma_{room}$ = 0.96.$10^{-3}$μC.cm$^{-3}$.K$^{-1}$.

## III. CONCLUSION

Traditional ceramic technology and improvement in the aide of processing ceramic powders by high power ultrasonic wave for 70 minutes in stead of long time milling and mixing are effective. All of the fabricated ceramic compositions are of rather high ceramic densities (ρ = 7.22 – 7.48 g/cm$^3$).

$Cr^{3+}$ concentrations are of strong effect on structure and microstructure. Exist pure perovskite phase and rhombohedral structure in all of the samples. The rhombohedral grains of microstructure with light distortion are rather closely arranged agreed with the high ceramic densities of the samples.

All of the ceramic compositions are of very low electric conductivities σ = (0.29 - 3.72). $10^{-17}$ Ω$^{-1}$ m$^{-1}$ and very good dielectrics.

Dielectric properties are strongly dependent on $Cr^{3+}$ concentration and of rather small values such as $\varepsilon/\varepsilon_0$ = 343 – 690, tanδ = 0.04 – 0.21. At x = 1.25% mol. $Cr^{3+}$ (M4) the ceramic composition is of minimal dielectric constant and dielectric loss factor $\varepsilon/\varepsilon_0$ = 343, tanδ = 0.04 suitable for pyroelectric application. At this concentration the other parameters of the ceramics are: ρ = 7.28 g/cm$^3$, σ = 0.29.$10^{-17}$ Ω$^{-1}$ m$^{-1}$.

The hard $Cr^{3+}$ dopant concentrations are of strong effect on the solid phase diffusion during sintering of the ceramics. Ceramic densities are rather high ρ = (7.22 – 7.48)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 $\gamma_{max}$ = 7.72.$10^{-2}$μC.cm$^{-2}$.K$^{-1}$ and at room temperature (306$^0$K) $\gamma_{room}$ = 0.96. 10-3μC.cm$^{-3}$.K$^{-1}$, $P_r$ = 20.0μC/cm$^2$, $E_c$ = 11.5kV/cm, at x = 1.25% mol. (M4) is suitable to fabricate pyroelectric ceramics for application in the field of ultra-red sensors and detectors.

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