

PREPARATION AND STUDYING THE PHYSICAL AND ELECTRICAL PROPERTIES OF BARIUM TITANATE DOPED WITH STRONTIUM AND EUROPIUM⁺

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Abstract

Barium titanate (BaTiO_3) have been prepared by mixing equimolares of titanium dioxide (TiO_2) and barium carbonate. Identification of the calcined powder achieved by using X-ray diffraction technique to know the purity of the powder and the crystal phase. Sintering is done at different temperature (1100°C , 1200°C , 1300°C). The best sintering temperature is 1300°C , it gives the higher bulk density (5.36g/cm^3), minimum percentage porosity (6%), and maximum linear shrinkage (18%).

The prepared barium titanate doped with different ratios of rare earth oxides {Strontium oxide (SrO) and Europium oxide (Eu_2O_3)}.

It appears that the addition of these oxides in ratio of (0.3%) gives an increase in density to reach a maximum value of (5.56g/cm^3 for SrO and 5.53g/cm^3 for Eu_2O_3), and reduction in porosity to reach a minimum value of (5% for SrO and 4.5% for Eu_2O_3).

The oxide addition leads to increase the dielectric constant to reach a maximum value (2775.3 for Eu_2O_3 and 3867.5 for SrO), then decreases with increasing the oxides concentration at temperature (30°C) and frequency 1kHz.

Addition of (SrO) and (Eu_2O_3) at ratio 0.3% leads to decreasing the electrical resistivity to reach a minimum value (0.78×10^{10}) for Eu_2O_3 and 0.69×10^{10} for SrO then increased with increasing the oxide concentration at 30°C .

Keywords:

Electrical properties of barium titanate, Doping of barium titanate with rare earth elements, Piezoelectric materials.

المستخلص

حضرت مادة تيتانات الباريوم BaTiO_3 بواسطة الخلط المتوازن لمركبي ثنائي اوكسيد التيتانيوم (TiO_2) وكاربونات الباريوم (BaCO_3) بنسبة مولية {1:1}. استخدمت تقنية حيود الاشعة السينية لتحديد نقاوة المسحوق الناتج بعد الكلسنة الاولى ومعرفة الطور البلوري. تم التليد بعدة درجات حرارية (1100°C , 1200°C , 1300°C). وجد ان افضل درجة حرارة تليد هي 1300°C حيث اعطت اكبر كثافة (5.36g/cm^3) واكبر انكماش خطي (18%) وادنى مسامية (6%).

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شويبت مادة تيتانات الباريوم المحضرة بنسب مختلفة من الاكاسيد النادرة مثل اوكسيد السترونشيوم (SrO) واوكسيد اليتريوم (Eu_2O_3) .
 اتضح من النتائج ان اضافة نسبة (0.3%) من كلا الاوكسيدين اعطى زيادة في الكثافة وصلت الى (5.53g/cm^3) في حالة (Eu_2O_3) و (5.56g/cm^3) في حالة (SrO) وأدنى مسامية 4.5% في حالة (Eu_2O_3) و 5% في حالة (SrO) .
 أدت الزيادة الى رفع قيمة ثابت العزل الكهربائي النسبي لتصل إلى اكبر قيمة (2775.37) في حالة (Eu_2O_3) و 3867,56 في حالة (SrO) ثم تقل مع زيادة تركيز المادة المشوبة عند درجة حرارة (30°C) وتردد 1kHz.
 اضافة اوكسيد السترونشيوم (SrO) واوكسيد اليتريوم (Eu_2O_3) بنسبة 0.3 ادت الى نقصان الممانعة الكهربائية لتصل الى ادنى قيمة لها (0.78×10^{10}) في حالة (Eu_2O_3) و (0.69×10^{10}) في حالة (SrO) ثم تزداد مع زيادة تركيز المشوبة عند درجة حرارة (30°C) .

Introduction

Piezoelectricity is an electrical polarization produced by mechanical strain in certain crystals. The polarization is proportional to the amount of strain. The reverse also is true: an electrical polarization will induce a mechanical strain in the piezoelectric crystals. The ceramic piezoelectric materials may be made in any chosen direction by a poling treatment that involves exposing it to a strong electric field. When the electric field is removed, the dipoles remain locked in an alignment, giving the ceramics material a permanent polarization and permanent piezoelectricity. This poling treatment is usually the final stage in manufacture of piezoelectric ceramic component [1]. The beginning of twentieth century gave birth to most classic applications of piezoelectrics such as barium titanate (BaTiO_3) and lead zirconium titanate (PZT).

Some or all-piezoelectric materials are also ferroelectric materials. Ferroelectric materials are an important class of functional materials for research and applications, since they exhibit interesting properties such as high dielectric permittivity [2], and spontaneous polarization that can be reversed in direction by application of realizable electric field over some temperature range. Most ferroelectric materials have a Curie temperature (T_c), below which they are polar and above which they are not. The direction of permittivity often has a peak at (T_c), the large permittivity values that are characteristics of ferroelectric materials are greatly exploited in many applications, most widely in the multilayer-capacitor industry. Applying a large alternating electric field causes the polarization to reverse, and this gives rise to the ferroelectric hysteresis loop, relating the polarization (P) to the applying electric field (E) [3]. Barium titanate (BaTiO_3) has been introduced for applications in ultrasonic transducers, more recently. It is expected that the applications of piezoelectric ceramics will continue to extended into a broader range of industries as new piezoelectric materials are created [4].

Choi and Tuller [5] studied the electrical properties on the compound ($\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$) at ($x=0.2, 0.3$, and 0.4% mole), they showed that the dielectric constant (ϵ_r') increases with increasing (SrO) concentration until reaching a maximum value at (2420) at ($x=0.2\%$ mole), then the dielectric constant (ϵ_r') decreases with increasing (SrO) concentration in the compound, and the dissipation factor ($\tan\delta$) decreases with increasing (SrO) concentration at (25°C) and (1kHz).

Syamaprasad [6] studied the dielectric constant (ϵ_r') and dissipation factor ($\tan\delta$) for compound ($\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$) at ($x=0, 0.1, 0.2, \dots 1\%$ mole), the dielectric constant (ϵ_r') increases until reaching a maximum value of (2510) at ($x=0.2\%$ mole), then the

dielectric constant (ϵ_r') decreases with increasing (SrO) concentration, and the dissipation factor ($\tan\delta$) decreases with increasing (SrO) concentration at (25°C) and (1kHz).

Wechsler and Kirby [7] studied the effect of Strontium oxide (SrO) concentration in the compound ($\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$) at ($x=0.1, 0.2, 0.3, 0.4, \dots 0.7\%$ mole), they showed the Curie temperature (T_c) decreases with increasing of Strontium oxide (SrO) concentration (x).

Benguigui and Bethe [8] studied the effect of diffused phase transitions in the compound ($\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$) at ($x=0.39, 0.26, \text{ and } 0.24\%$ mole), they showed the polarization increases at decreasing of the temperature, and the dielectric constant (ϵ_r') increases with increasing of Strontium oxide (SrO) concentration (x).

Molokhia et. al. [9] studied the dielectric constant (ϵ_r') and the dissipation factor ($\tan\delta$) for Barium titanate (BaTiO_3) doped with ytterbium oxide (Yb_2O_3), in different concentrations (0 to 6% mole), they showed the dielectric constant (ϵ_r') of Barium titanate (BaTiO_3) decreases from (4000) at Curie temperature (T_c), to (500) by adding (6 % mole) of ytterbium oxide (Yb_2O_3), the grain size decreases from (25.7 μm) for indoped Barium titanate (BaTiO_3), to (1.9 μm) by adding (6% mole) of ytterbium oxide (Yb_2O_3), and the curie temperature (T_c) decreases to the room temperature through the structure transformed from tetragonal to cubic at room temperature.

Experimental Work

The raw materials {Barium carbonate (BaCO_3) and Titanium dioxide (TiO_2)} were weighed out in (1:1) molar ratio according to chemical equilibrium equation(1);

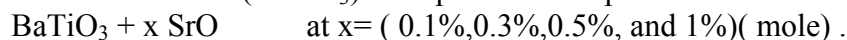


Mixing and grinding the raw materials achieved by using an agate ball mill (Spes, USA) for period (12hrs).

The prepared mixture have been putted in a fused alumina crucible and calcined at (1200°C) for (10hrs) , in an electrical furnace (carbolite muffle furnace) made in England.

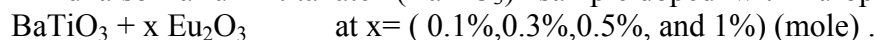
The calcined powder then ground by an agate ball mill (Spes, USA) then sieved by a special screen to get on the particle sizes less than (38 μm) . The powder then pressed by using hydraulic press (Herzog) in a disc shape {with a diameter (1cm), and thickness (2-3 mm)}, the pressure used is (5ton/ cm^2) for (2min). The (1wt %) of (polyvinyl alcohol) was used as a binder during pressing [10].

Barium titanate (BaTiO_3) sample was doped with Strontium oxide (SrO) as:



Where x is the concentration of SrO .

And also Barium titanate (BaTiO_3) sample doped with Europium trioxide (Eu_2O_3) as:



Where x is the concentration of Eu_2O_3 .

The pellets then sintered at a temperature (1300°C) for (8hrs).

The density of pure barium titanate as shown in literatures is (6.02 gm/cm^3), [6,11].

Results and Discussion

1-Table (1) shows the X-ray diffraction results for prepared Barium titanate (BaTiO_3) which shows a good improvement in the growth of Barium titanate (BaTiO_3) phases with good purity, and gives the ideal peaks for tetragonal Barium titanate (BaTiO_3).

Table (1) X-ray diffraction results for Barium titanate (BaTiO_3)

2 θ (deg)	d (A $^\circ$)	ASTM d(A $^\circ$)	hkl
22.2	3.998	3.99	100
31.6	2.822	2.825	110
39.0	2.306	2.314	111
45.4	1.991	1.997	200
51.2	1.781	1.786	210
56.3	1.631	1.634	211

The linear shrinkage (L.Sh.%) increases by increasing the sintering temperature, due to the packing of the grains, which reduces the pores. The best result is found at (1300°C) for (8hrs), reaching a maximum value (21% for SrO, and 20.5% for Eu₂O₃) at (0.3%), then the linear shrinkage (L.Sh.%) decreases because of inhibition of the grain growth, which inhibits grains packing and behaves as an impurity.

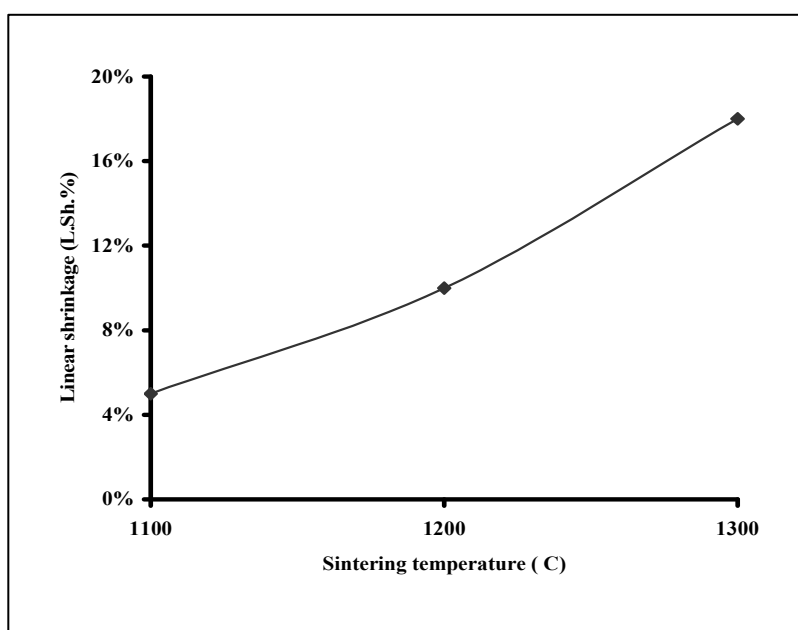


Figure (1) the variation of a linear shrinkage (L.Sh.%) with sintering temperature (°C) for undoped Barium titanate pellets (BaTiO₃) at (8hrs).

3-Figure (2) shows the variation of bulk density with sintering temperature for indoped Barium titanate (BaTiO₃) at (8hrs), which has a maximum value of (5.36 gm/cm³) at sintering temperature (1300°C), that mean it has a minimum porosity.

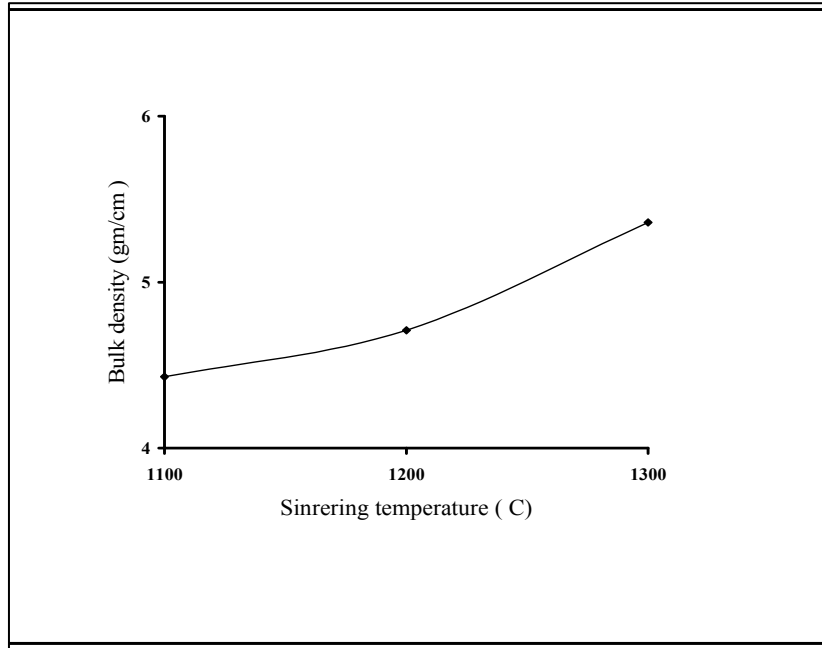


Figure (2) the variation of a bulk density (gm/cm³) with sintering temperature (°C) for indoped Barium titanate (BaTiO₃) at (8hrs).

Figure (3) shows the bulk density increases with increasing the dopant materials (SrO and Eu₂O₃) concentration, which has a maximum value of (5.56 gm/cm³ for SrO {92.3% of the theoretical}, and 5.53 gm/cm³ for Eu₂O₃ {91.8% of the theoretical} at (0.3%), which has a minimum porosity, and minimum resistivity, then the bulk density decreases with increase of dopant materials (SrO and Eu₂O₃) concentration, that means the grain growth increases with the increasing in (SrO and Eu₂O₃) addition to (0.3%), then inhibition is happened in the grain growth after increase in the dopant material (SrO and Eu₂O₃) concentration.

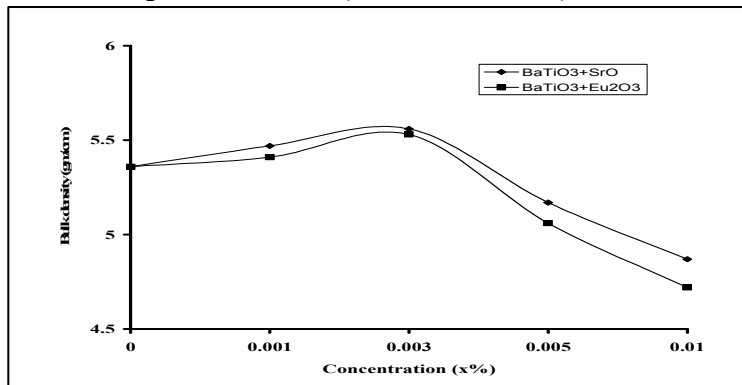


Figure (3) the variation of a bulk density (gm/cm³) with concentration (x%) for undoped and doped Barium titanate (BaTiO₃) pellets at (1300°C) and (8hrs).

3- Figure (4) shows that the porosity decreases with increase in sintering temperature for period time (8hrs) because of the increase in grain growth and grains packing for indoped Barium titanate (BaTiO₃).

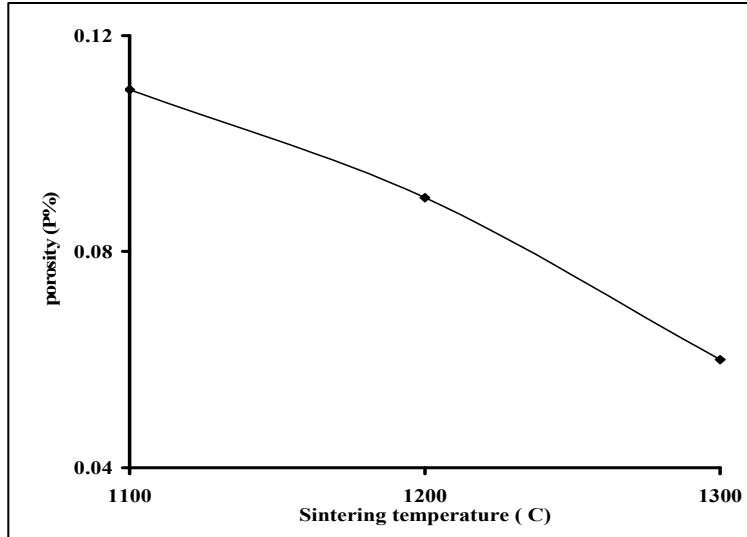


Figure (4) the variation of porosity with sintering temperature (°C) for indoped Barium titanate (BaTiO₃) at (8hrs).

Figure (5) shows the porosity decreases with increase in dopant materials (SrO and Eu₂O₃) concentration, that means increase in grain growth and grains packing to reach a minimum value of (5% for SrO and 4.5% for Eu₂O₃) at (0.3%), then increases with increase in dopant materials (SrO and Eu₂O₃) concentration, that means the grain growth inhibited and grains packing behaves as impurity.

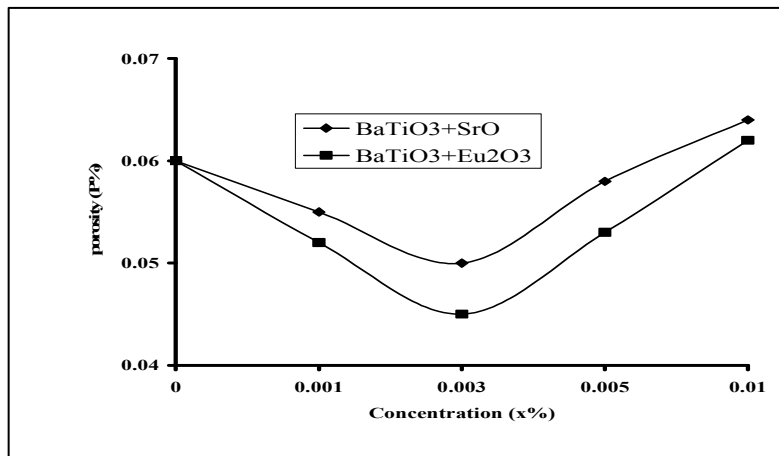


Figure (5) the variation of porosity with concentration for indoped and doped Barium titanate (BaTiO₃) at (1300°C) and (8hrs)

- 4- The dielectric constant for undoped and doped Barium titanate (BaTiO₃) at (30°C), and temperature (30°C-150°C) at (1kHz) is calculated by measuring (C_p) using (LCR meter) as shown in the equation (2).

$$\epsilon_r' = C_p d / \epsilon_0 a \dots\dots\dots (2)$$

Where: ϵ_r' : is the relative permittivity (dielectric constant), dimensionless value
 ϵ_0 : is the vacuum permittivity (8.854×10^{-12} F/m), a : is the cross-sectional area (m²),
 and d : is the thickness (m).

The dielectric constant for conventional coars grained barium titanate is 1200, [12].

Figure (6) shows the variation of a dielectric constant with concentration at frequency (1kHz) and temperature (30°C) for doped Barium titanate (BaTiO₃) by the dopant materials (SrO, and Eu₂O₃), it shows increasing in the dielectric constant as a result of increasing in grain growth, increasing in density, and decreasing in porosity to reach a

maximum value (3867.56 for SrO, and 3985.37 for Eu_2O_3) at dopant materials (SrO, and Eu_2O_3) concentration (0.3%), then the dielectric constant decreases with increase in dopant materials (SrO, and Eu_2O_3) concentration as a result of grain growth inhibition for these samples.

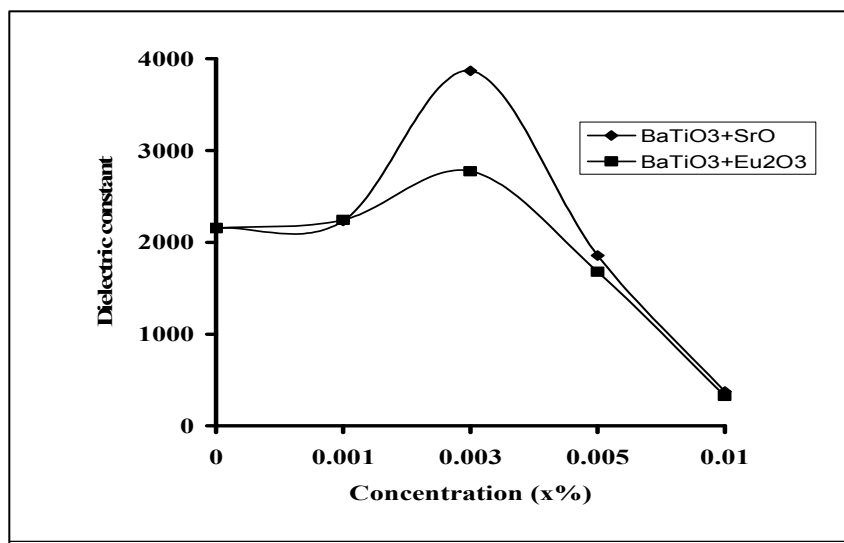


Figure (6) the variation of dielectric constant (ϵ_r') with concentration for doped Barium titanate (BaTiO_3) at (1kHz) and (30°C)

Figure (7) shows the variation of dielectric constant with temperature for Barium titanate (BaTiO_3) doped by SrO at (1kHz), it appears that (0.1%) addition leads to dielectric constant having (7342.31) by shifting the Curie point (T_c) at (10°C) toward (110°C), (0.3%) addition leads to increasing in a dielectric constant to reach (9821.71) by shifting the Curie point (T_c) at (10°C) toward (110°C), (0.5%) addition leads to decreasing in a dielectric constant about (0.1%, and 0.3%) to reach (4534.05) by shifting Curie point (T_c) at (10°C) toward (110°C), and the (1%) addition leads to decrease in a dielectric constant about (0.1%, 0.3%, and 0.5%) to reach (713.02) by shifting the Curie point (T_c) at (10°C) toward (110°C).

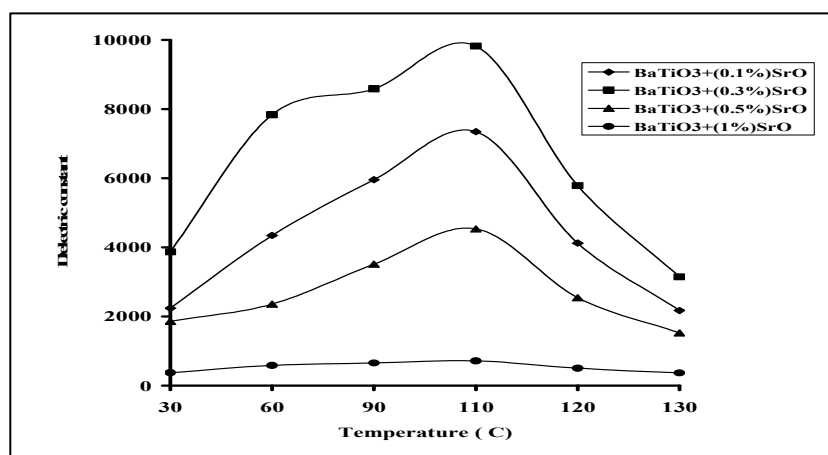


Figure (7) the variation of dielectric constant with temperature ($^{\circ}\text{C}$) for Barium titanate (BaTiO_3) doped by (SrO) at (1kHz).

Figure (8) shows the variation of dielectric constant with temperature for Barium titanate (BaTiO_3) doped by Eu_2O_3 at (1kHz), it appears that (0.1%) addition leads to dielectric constant having (7832.82) by shifting the Curie point (T_c) at (10°C) toward (110°C), (0.3%) addition leads to increasing in a dielectric constant to reach (8979.17) by shifting the Curie point (T_c) at (10°C) toward (110°C), (0.5%) addition leads to decreasing in a dielectric constant about (0.1%, and 0.3%) to reach (4949.27) by shifting Curie point (T_c) at (10°C) toward (110°C), and the (1%) addition leads to a decrease in a dielectric constant about (0.1%, 0.3%, and 0.5%) to reach (622.68) by shifting the Curie point (T_c) at (10°C) toward (110°C).

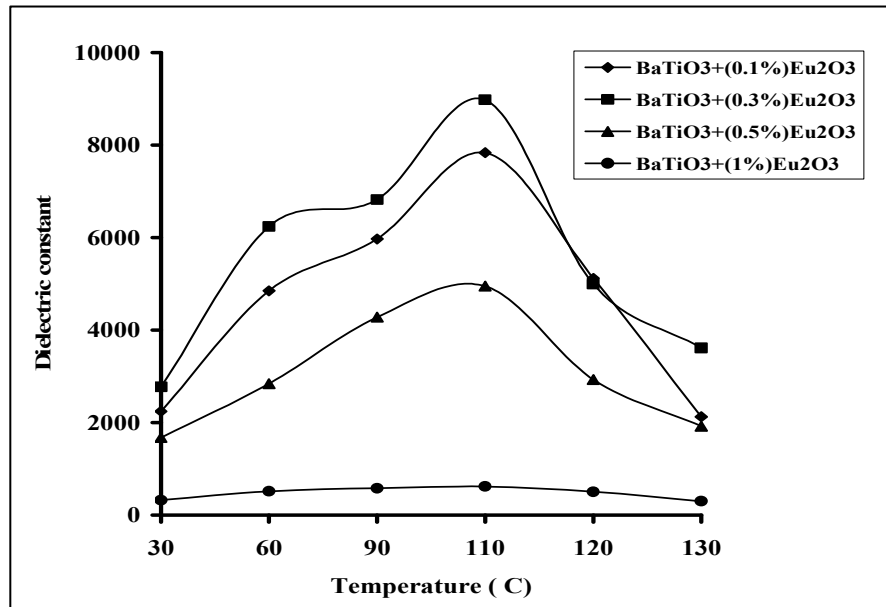


Figure (8) the variation of dielectric constant with temperature ($^{\circ}\text{C}$) for Barium titanate (BaTiO_3) doped by (Eu_2O_3) at (1kHz).

Figures (6), and (7) show the maximum value of dielectric constant at (0.3%) then it decreases by shifting the Curie point (T_c) to (10°C) toward (110°C), for this reason presence impurities leads to change in crystalline structure of Barium titanate (BaTiO_3), that accelerates the tetragonal-to-cubic transition at (110°C), at increasing in dopant materials (SrO , and Eu_2O_3) concentration to (0.5%) leads to the dielectric constant decrease because of the dopant materials behave as impurities. That leads to crystalline defects in the crystalline structure and affects (c/a) values of Barium titanate (BaTiO_3) crystalline lattice.

Table (2) shows that the electrical resistivity decreases with increase in a temperature of Barium titanate (BaTiO_3), and Barium titanate (BaTiO_3) doped by dopant materials (SrO and Eu_2O_3), as a result found the anomalous grain growth and formation of semiconducting grains, which is accompanied by an oxygen release proportional to the amount of the dopant materials present in this samples.

Table (2) the variation of electrical resistivity with temperature for indoped and doped Barium titanate (BaTiO₃).

<u>Samples</u>	<u>Electrical resistivity ($\times 10^{10} \Omega.cm$)</u>					
<u>Temperatures (°C)</u>	30°C	60°C	90°C	110°C	120°C	130°C
BaTiO ₃	6.32	4.73	2.86	1.94	1.65	0.27
BaTiO ₃ +SrO(0.1%)	4.32	3.85	2.73	1.75	1.20	0.75
BaTiO ₃ +SrO(0.3%)	0.69	0.32	0.21	0.16	0.11	0.06
BaTiO ₃ +SrO(0.5%)	7.25	5.24	3.25	2.61	2.42	2.30
BaTiO ₃ +SrO(1%)	10.11	9.32	7.26	6.82	5.35	4.23
BaTiO ₃ +Eu ₂ O ₃ (0.1%)	4.93	3.02	2.11	1.72	1.14	0.92
BaTiO ₃ +Eu ₂ O ₃ (0.3%)		0.49	0.28	0.20	0.17	0.08
BaTiO ₃ +Eu ₂ O ₃ (0.5%)	8.15	0.78	4.02	2.82	2.54	2.38
BaTiO ₃ +Eu ₂ O ₃ (1%)	11.24	10.05	8.13	7.27	6.18	4.86

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