

Studying The Dielectric and Structural Properties of $Ba_xSr_{1-x}TiO_3$ (BST) Ferroelectric System Prepared by Using Oxalic Acid Route

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Abstract

$Ba_xSr_{1-x}TiO_3$ (BST) ferroelectric nano, poly crystalline systems were processed with three concentrations ($x = 0.5, 0.7$ and 0.9) using a technique known as oxalic acid route. The XRD spectra were analyzed, and used Scherer formula to estimate the crystallite size of the products, which reached to 15.4 nm at $x = 0.5$. It is found that increasing of Sr^{2+} cations help to decrease the crystallite size of $Ba_xSr_{1-x}TiO_3$ system and the tetragonality c/a increases when the crystallite size increases. In physical tests we conclude that the oxalic acid method is a good method to prepare a BST ferroelectric phase with high density ($5.05, 5.5$ and 5.45) gm/cm^3 , and small porosity ($16, 8,$ and 11) % for ($x = 0.5, 0.7$ and 0.9) respectively.

Keywords: ferroelectric, polar materials, BST

دراسة الخصائص الكهربائية والتركيبية للنظام الفيروكهربائي $Ba_xSr_{1-x}TiO_3$
(BST) المحضر بطريقة حامض الاوكزاليك

الخلاصة

تم تحضير مادة فيروكهربائية نانوية ذات النظام متعدد التبلور $Ba_xSr_{1-x}TiO_3$ (BST) وبثلاثة تراكيز هي ($x = 0.5, 0.7$ and 0.9) باستخدام طريقة الحامض الاوكزاليك. تم تحليل طيف حيود الاشعة السينية XRD للنماذج وبتطبيق معادلة شيرر يمكن حساب حجم الـ crystallite. وفي هذا البحث بلغ حجم الـ crystallite القيمة 15.4 نانومتر عند التركيز $x = 0.5$, كما وجد أن زيادة تركيز ايونات السنترونيوم في النظام (BST) يساعد في أنقاص حجم الـ crystallite ولوحظ أن زيادة الاستطالة c/a مع ازدياد حجم الـ crystallite. ومن خلال الاختبارات الفيزيائية تم الاستنتاج بان طريقة الحامض الاوكزاليك طريقة جيدة لتحضير مادة BST الفيروكهربائية بكثافة عالية ($5.05, 5.5,$ and 5.45) gm/cm^3 , ومسامية قليلة ($16, 8,$ and 11) % للتراكيز ($x = 0.5, 0.7$ and 0.9) على التوالي.

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Introduction:

Ferroelectrics are polar materials. They exhibit spontaneous polarization even in the absence of external electric field and their spontaneous polarization can be switched by subjecting the material to electric field [1-3]. Ferroelectrics also possess domains, exhibit hysteresis loops, and show Curie-Weiss behavior near their phase transition temperature T_C [4]. The applications of ferroelectric materials cover a broad range based on their dielectric piezoelectric, pyroelectric, electro-optic and ferroelectric specialty properties. A huge leap in the research on ferroelectrics leading to the wide spread use of ferroelectric ceramics in capacitor applications and piezoelectric transducer devices, since then many other ferroelectrics (like Barium titanate BT, Barium Zirconium titanate BZT, Lead Zirconium titanate PZT, and BST) have been developed and utilized for variety of applications [5-6]. BST (Barium strontium titanate) is a ferroelectric solid solution of $BaTiO_3$ and $SrTiO_3$, which prepared by using sol-gel and Ceramic methods,[7,8]. BST structure belongs to perovskite family which has the general formula ABO_3 . The spontaneous polarization in $Ba_xSr_{1-x}TiO_3$ ferroelectric states usually attributed to the distortion of both cation and anion of sub lattices. Its structure dependent on T_C (Curie temperature) in other words if the temperature above T_C it has a cubic symmetry (paraelectric phase) figure (1-a), while at temperature below Curie temperature BST exhibit tetragonal symmetry (polar phase)

fig. (1-b), [9-12]. In $Ba_xSr_{1-x}TiO_3$ system, dielectric constant reached to 19000 for ($x = 0.7$) with sintering temperature $1350^\circ C$ for 6h by using a solid state reaction sintering processing, and the grain size (8.77–14.70 μm) [10]. While dielectric constant reached to (700, 650, 500) for ($x = 0.9, 0.75$ and 0.5) respectively, using a conventional process with sintering temp $1300^\circ C$ for 2hr and crystallite size (3.89-8.03 nm) [7].

Experimental:

In order to obtain BST powders, the first step is preparing an aqueous solution contains (4.88) gm of ($BaCl_2 \cdot 2H_2O$) and (5.33) gm of ($SrCl_2 \cdot 6H_2O$) by initially boiling distilled water for at least 20 minutes. The water was maintained under stirring by using a magnetic stirrer. After dissolving, the solutions filtered to remove any precipitates. Then TiO_2 powder dissolves with distilled water and adds to the solution which previously described [the initial ratio of (Ba + Sr) relative to (Ti) molar weight must be equal to (1.1) to get a single phase of BST systems], at last one mole of oxalic acid adds the solution. The reaction continues till getting resin and viscose precipitates by adjusting pH using NH_4OH . The resultant was washed by distilled water to remove the residual Ba^{+2} and Sr^{+2} cations. The precipitate dried in a dry oven at $100^\circ C$ for 6 hours, ground, pressed to pellets with (10 mm) in diameter and thickness of (2-3 mm), and sintered at ($800^\circ C, 1000^\circ C, 1100^\circ C$) for (1.5, 2.5, 4) hour for each sintering temperature.

Result and Discussion:

The full shrinkage determines the fit sintering temperature (1100 °C) and soaked time (4hr) to BST pellets. Figure (2-(a, b, c)) illustrated the XRD patterns of ($Ba_xSr_{1-x}TiO_3$) pellets for the three concentrations ($x = 0.5, 0.7$ and 0.9) respectively, which prepared at 1100 °C for 4h. It is clearly observed that there is no XRD peaks correspond to TiO_2 (not detected), which indicated complete reaction of TiO_2 powder under preparing conditions. The phase examination was built by comparing between that the XRD spectra of this investigation (2θ , d-spacing and miller indices) (where the θ range for all specimens about ($2\theta - 50^\circ$) with XRD patterns of 1997 JCPDS – International center for diffraction Data .It is found that ultra fine powders, poly crystalline, tetragonal $Ba_xSr_{1-x}TiO_3$ structure has been obtained from this process. The analysis demonstrates the reflection from planes (100), (110), (111), (200) for each concentration. The major peak of the high crystallinity lies in the angle $2\theta = 31.74^\circ$ of the XRD standard pattern was shifted to ($31.49^\circ, 31.56^\circ$ and 31.690°) for different concentrations (with $x = 0.5, 0.7$ and 0.9) respectively, this change is induced due to the effect of adding Sr^{+2} cations in the crystal lattice.

Table (1) gives the crystallite grain size, and the tetragonality c/a of the resultant powders. It is clear from this table that increasing of Sr^{+2} cations help to decrease the grain size of $Ba_xSr_{1-x}TiO_3$ systems, while it is found that the tetragonality c/a increases when the crystallite size increases.

Figure (3) show a micrographs of BST pellets carried out by using optical microscope (type: A. Cruss, Optronic Germany) with digital camera. It is clearly observed in this photo that an ultra fine microstructure with sub micrometer grains. The figure also implies the absence of abnormal grain growth, actually, relatively little normal grain growth is observed. This demonstrates the value of pressing and sintering for achieving high densities while creating ultra fine grain sizes. Table (2) shows the apparent density of the products which is high reach's to 5.5gm/cm^3 for pellet sintered at 1100°C for 4hr of BST, and close to theoretical value is 5.7 gm/cm^3).

This indicates that it is possible to produce BST ceramics with high density by using oxalate process; while the porosity is small 8%. We should mention that it is so important to reach a high density because of the significant dependent of the polarization properties on it. Table (3) demonstrates the dielectric strength of BST ceramic pellets subjected to break down voltage of (1kV/mm) and (2kV/mm). This table implies that the dielectric strength of BST ceramics increases when Sr^{+2} cations is increased in proportion equal to (0.2wt %), but this increment is not continuous, because the dielectric strength decreased with grandly increased of Sr^{+2} cation. The amount of dielectric strength for the prepared BST is the same to semiconductors; this result indicates that it is possible of BST to have semiconductor properties. Also the amount of dielectric strength for the three concentrations under slow rise

is less than the dielectric strength of high break down voltage that is due to the dielectric temperature, the slow rising of the breakdown voltage gives a sufficient time to rise the dielectric temperature and that will be helpful in hastening the ceramics to break down.

Figure (4) shows the lower crystal symmetry ferroelectric phase undergo transformation to a higher crystal symmetry paraelectric phase when the heating increased above a Curie temperature, and the decreases of Curie temperature to (95 oC, 32 oC and is less than -15 oC) with increase the Sr⁺² cations. in this investigation the dielectric constant reach to (500, 700) for Ba_{0.9} Sr_{0.1} TiO₃ , Ba_{0.7} Sr_{0.3} TiO₃ .

The lower dielectric constant in the resent investigation caused by the effect of the ultra fine crystalline grain size (15.4, 43.65, 42.13) nm, where size less than 1 μ m had a single domain forms inside each grain and for that the movement of domain walls are restricted by the grain boundaries, while fine and coarse grain size > 1 μ m had a multiple domains in a single grain. The motion of its walls increases the dielectric constant. The broadening of the dielectric peaks in figure(4) caused when domains orientation is random which will tend to broaden the ferroelectric transition(that means a much lower temperature dependency of the dielectric constant, in other words, a better temperature stability of dielectric constant), and that happened in ultra fine grain size (< 0.200 nm). Temperature increases affected on the density and leads to perturb the alignment of permanent dipoles as

a result of the thermal vibration of the atoms, for these reasons polarization mechanisms contributions decreased. This affect of temperature increases demonstrates clearly at Figure (5) and Figure (6), which shows the loss factor and quality behavior respectively with temperature increases. Figure (5) illustrates the loss factor ($\tan \delta$) vs. temperature for the three concentrations. The loss factor ($\tan \delta$) reached to (0.175, 0.19 and 0.2) at Curie temperature. The loss in energy is caused by heating there is only one mechanism of polarization "orientation" which contributes in the polarization (while the others decrease as a result of decreasing the density with high temperature till Curie temperature).

At Curie temperature, the contribution of orientation dipoles was over due to the thermal vibration and that leads to perturb the alignment. This explains why the high loss factor takes a part at Curie temperature. The last part of dielectric loss factor peaks comes from the contribution of the residual polarization mechanisms which decreases with temperature. Above Curie temperature the material is in cubic symmetry so there is no energy dissipation that associated with charge polarization.

The previous reasons are also affected the quality factor Q, figure (6) demonstrated those effects for Ba_xSr_{1-x}TiO₃ systems. Above Curie temperature, the material was in paraelectric state (that mean a cubic symmetry) so there is no energy dissipation that associated with charge polarization.

Figure (7) illustrates the resistivity for each concentration affected by heating. When a tetragonal undergoes transition to cubic symmetry by heating, the resistivity undergoes from low resistivity below Curie temperature to high resistivity above Curie temperature, and that is because of inhibition the dipoles in paraelectric state. In fig. (8) and fig. (9) the dielectric constant and the $(\tan\delta)$ respectively become almost constant for frequency range (103Hz-105 Hz). The dielectric constant reach (590, 490 and 298) for $Ba_{0.5}Sr_{0.5}TiO_3$, $Ba_{0.7}Sr_{0.3}TiO_3$ and $Ba_{0.9}Sr_{0.1}TiO_3$ at 1kHz respectively, and it is almost constant over a wide range of frequencies. It is clearly observed that for frequency range (103Hz-105 Hz) the external field has a large effect on charges and dipoles movement, In other words the three kinds of polarization mechanisms (orientation, Ionic and electronic) obey the external electric field orientation at that range, and contribute in the polarization.

Conclusions

The oxalic acid method was applied for synthesis $Ba_xSr_{1-x}TiO_3$ (BST) ferroelectric and poly crystalline pellets under sintering temperature 1100 °C for 4hour. BST Systems were processed with three concentrations ($x = 0.5, 0.7$ and 0.9). Increasing of Sr^{+2} cations help to decrease the Curie temperature to (-15 °C) and crystallite size to (15.4 nm) of $Ba_xSr_{1-x}TiO_3$ systems at $x = 0.5$. While the tetragonality c/a of the tetragonal component decreases

with decreasing the crystallite size by adding more Sr^{+2} ions.

Each ultra fine BST crystallite grains and the high density will reach's to 5.5gm/cm³ are due to significant dependent of the polarization properties on it. The low amount of dielectric strength for the prepared BST indicates that it is possible of BST to have semiconductor properties. The dielectric constant and the $(\tan\delta)$ respectively become almost constant for frequency range (103Hz-105 Hz).

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Table (1): The Crystallite Sizes, a, c, c/a and V for the three concentration.

$Ba_xSr_{1-x}TiO_3$	C.S (nm)	c (Å°)	a (Å°)	c/a	V(Å°)^3
$Ba_{0.5}Sr_{0.5}TiO_3$	15.4	3.971	3.944	1.007	61.769
$Ba_{0.7}Sr_{0.3}TiO_3$	34.65	3.979	3.936	1.01	61.643
$Ba_{0.9}Sr_{0.1}TiO_3$	42.13	3.988	3.91	1.02	60.969

Table (2): The App. density, bulk density and the porosity for BST Pellets sintered for 4hr at 1100 °C.

BST Systems	App. density (gm/cm ³)	Bulk density (gm/cm ³)	App. Porosity (%)
$Ba_{0.5}Sr_{0.5}TiO_3$	5.05	4.62	0.16
$Ba_{0.7}Sr_{0.3}TiO_3$	5.5	5.1	0.08
$Ba_{0.9}Sr_{0.1}TiO_3$	5.45	4.9	0.11

Table (3): The dielectric strength for BST pellets sintered for 4hr at 1100°C.

BST Systems	E_b (kV/mm)	
	1kV/ mm	2 kV/ mm
$Ba_{0.5} Sr_{0.5} TiO_3$	2.52	2.68
$Ba_{0.7} Sr_{0.3} TiO_3$	3.18	5.19
$Ba_{0.9} Sr_{0.1} TiO_3$	3.03	4.7

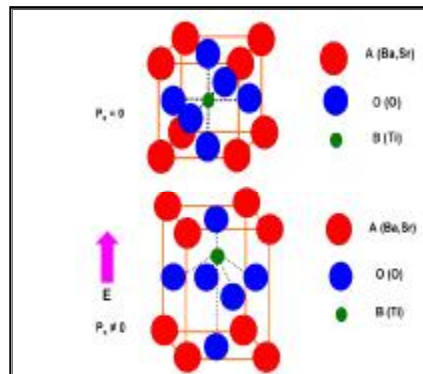


Figure (1): the perovskite structure of BST ferroelectric at (a) $T > T_c$, (b) $T < T_c$, [10]

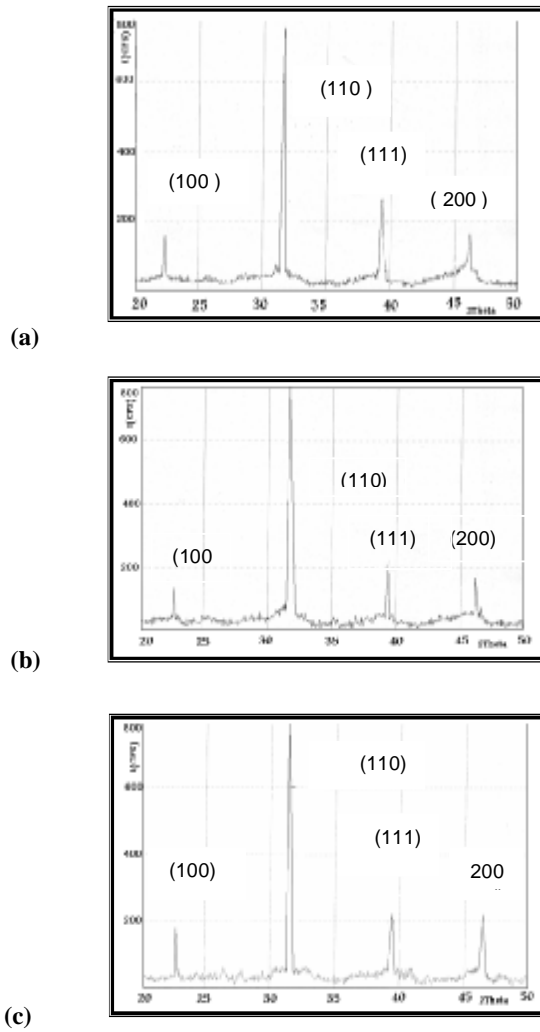
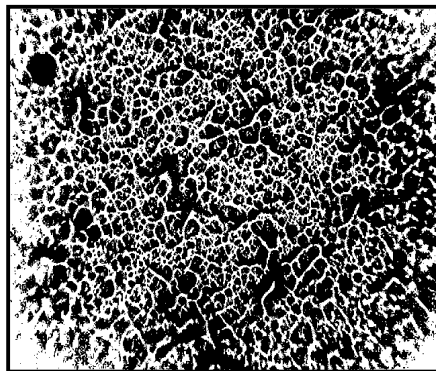
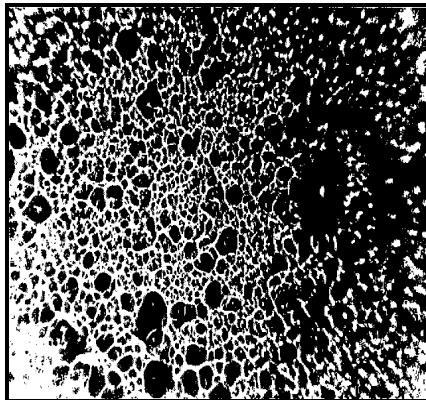


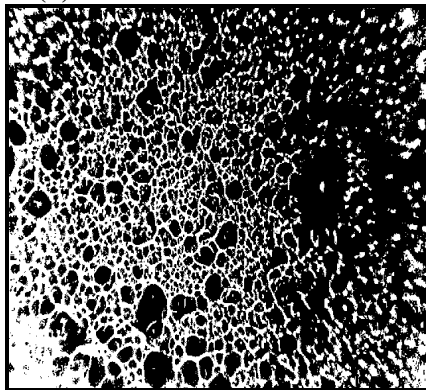
Figure (2): XRD spectrum for (a) $Ba_{0.5}Sr_{0.5}TiO_3$
(b) $Ba_{0.7}Sr_{0.3}TiO_3$ (c) $Ba_{0.9}Sr_{0.1}TiO_3$



(a)

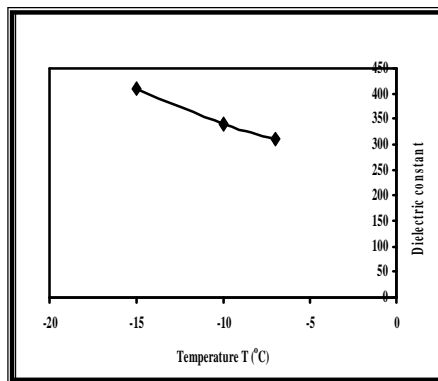


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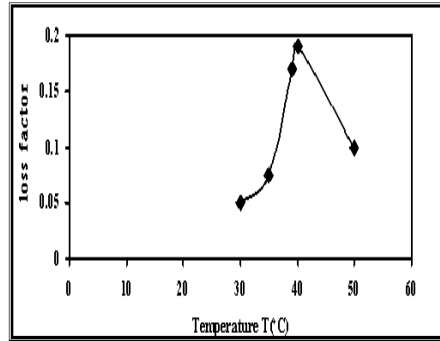


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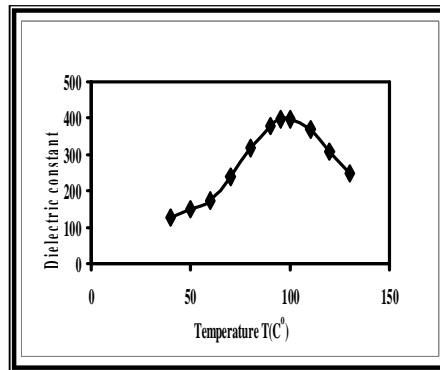
Figure (3): Micrographs of (a) $Ba_{0.5}Sr_{0.5}TiO_3$, (b) $Ba_{0.7}Sr_{0.3}TiO_3$, (c) $Ba_{0.9}Sr_{0.1}TiO_3$, X=600



(a)

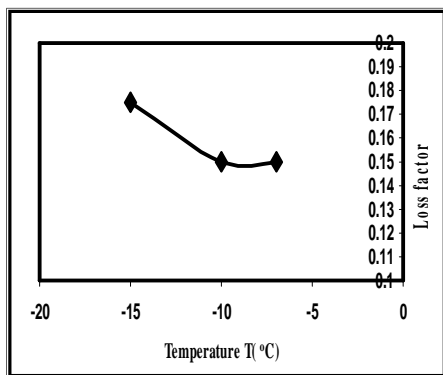


(b)

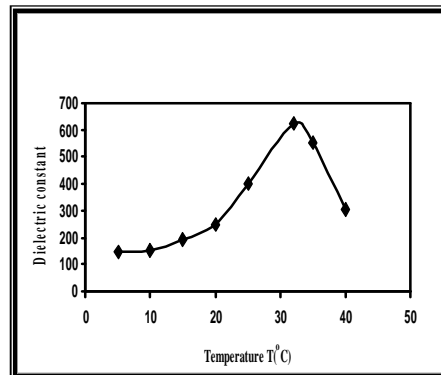


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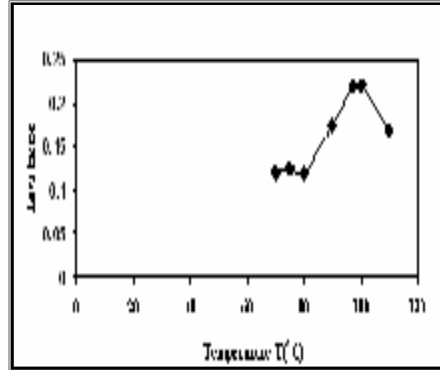
Figure (4): demonstrated dielectric constant vs. temperature for (a) $Ba_{0.5}Sr_{0.5}TiO_3$, (b) $Ba_{0.7}Sr_{0.3}TiO_3$ (c) $Ba_{0.9}Sr_{0.1}TiO_3$ sintered at 1100 C° for 4hour.



(a)

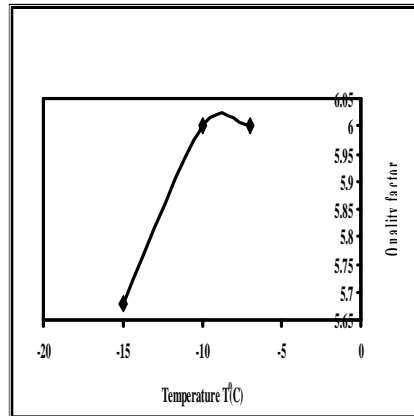


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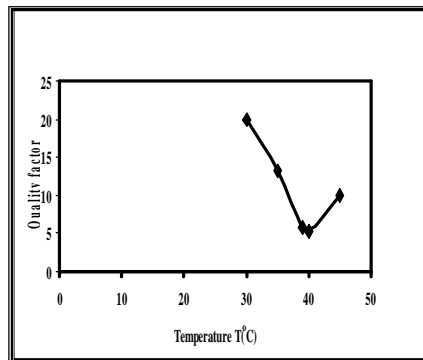


(c)

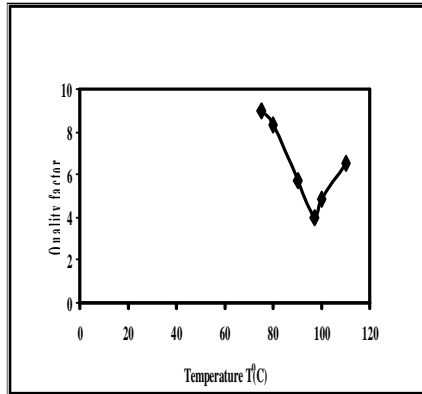
Figure (5): The quality factor vs.-temperature for (a) $Ba_{0.5}Sr_{0.5}TiO_3$ (b) $Ba_{0.7}Sr_{0.3}TiO_3$ (c) $Ba_{0.9}Sr_{0.1}TiO_3$ systems sintered at 1100 °C for 4hour



(a)

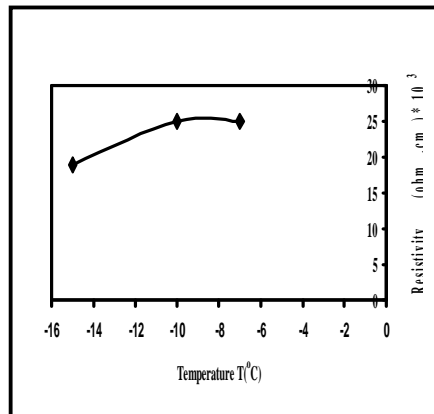


(b)

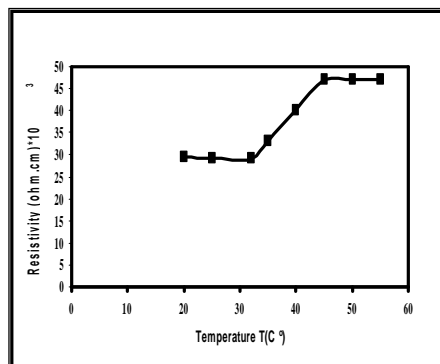


(c)

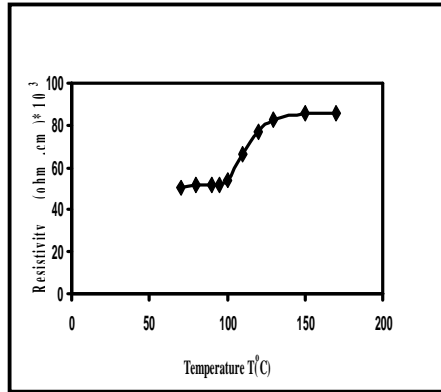
Figure (6): The loss factor vs.-temperature for (a) $Ba_{0.5}Sr_{0.5}TiO_3$ (b) $Ba_{0.7}Sr_{0.3}TiO_3$ (c) $Ba_{0.9}Sr_{0.1}TiO_3$ systems sintered at 1100 °C for 4hour



(a)



(b)



(c)

Figure (7): (c) The resistivity vs.-temperature of (a) $Ba_{0.5}Sr_{0.5}TiO_3$, (b) $Ba_{0.7}Sr_{0.3}TiO_3$ (c) $Ba_{0.9}Sr_{0.1}TiO_3$ systems sintered at 1100 °C for 4hour

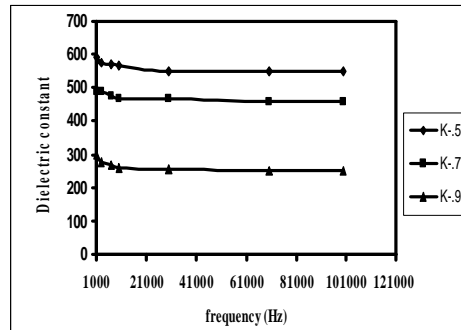


Figure (8): The dielectric constant vs.frequency sintered at 1100 °C for 4hour

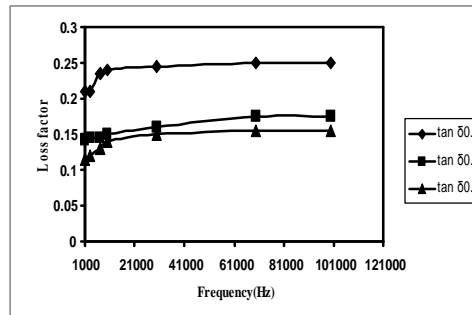


Figure (9): The loss factor vs. frequency sintered at 1100 oC for 4hour