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# The Effect of Doping by Sr on the Structural, Mechanical and Electrical Characterization of $La_1Ba_{1-x}Sr_x Ca_2Cu_4O_{8.5+\delta}$

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#### Abstract

The Sr doped La<sub>1</sub>Ba<sub>1-x</sub>Sr<sub>x</sub> Ca<sub>2</sub>Cu<sub>4</sub>O<sub>8.5+ $\delta}$  samples with  $0 \le x \le 0.3$  had been prepared using the solid state reaction. The samples were claimed at 800°C for 3hr, palletized and sintered at 860°C for 20hr in air . Dielectric constant and loss by means of capacitance have been investigated with frequencies in the range of 1kHZ to 1MHZ for our samples at room temperature. Also, Shore hardness has been measured. The dielectric constant and loss decrease slightly with the increase of frequency for all compounds. Additionally, the partial substitution of Sr<sup>+2</sup> into Ba<sup>+2</sup> sites never have effect on the dielectric properties. X-ray diffraction (XRD) analysis showed a tetragonal structure and the as grown La<sub>1</sub>Ba<sub>1-x</sub>Sr<sub>x</sub> Ca<sub>2</sub>Cu<sub>4</sub>O<sub>8.5+ $\delta}$  correspond to the 1124 phase. It was found that the change of the Sr concentrations of all our samples produces a change in a, c and c/a parameters.</sub></sub>

Keywords:  $La_1Ba_{1-x}Sr_x Ca_2Cu_4O_{8.5+\delta}$ , dielectric properties, Shore hardness.

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## Introduction

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High transition temperature T<sub>c</sub> superconductors have generated tremendous excitement because of the potentially significant technological applications. Materials have been discovered that exhibit superconductivity up to temperatures much higher than the boiling point of liquid Nitrogen (77K). Since 1911, when the Dutch physicist Heike Kemerlingh Onnes discovered superconductivity in Mercury at 4.2K [1], the highest observed values of T<sub>c</sub> gradually moved upward. In spite of great efforts to increase T<sub>c</sub>, 23.2K (reported in the intermetallic compound Nb<sub>3</sub>Ge in 1973 by Gavaler [2]), stood as the record until 1986. In that year J.G.Bednorz and K.A.Muller [3] observed that lanthanum barium copper oxide (La-Ba-Cu-O) began its superconducting transition as it was cooled below 35K. This discovery opened the way for all of the subsequent work on high temperature superconductors. Soon after the discovery of superconductivity at 30K in La-Ba-Cu-O system, these materials are extensively studied by the substitution of rare-earth compound to understand the nature of transport phenomena in each system. The exact composition of superconducting phase La<sub>2</sub>- $_{x}Ba_{x}CuO_{4-y}$  (0.1 < x < 0.2) was found by Uchida et al. [4] and Takagi et al. [5]. The structure of  $La_1Ba_{1-x}Sr_xCa_2Cu_4O_{8.5+\delta}$  is shown in figure 1. LBCCO is physically the hardest of the four materials, and with stronger bonds. Neutron scattering experiments, which probe the magnetic structure of the material, are typically limited to study LBCCO because of their requirement for large single crystals. But LBCCO has not been successfully studied with an STM, because so far there has been no successful recipe to obtain an atomically flat surface with tunnel access through an insulating layer to the relevant unperturbed CuO<sub>2</sub> plane. This paper will describe perovskite structure, based on  $La_1Ba_{1-x}Sr_x Ca_2Cu_4O_{8.5+\delta}$  composition, and interpret the mechanic and dielectric properties ,Then discuss how the difference of substitution that would influence  $La_1Ba_{1-x}Sr_x Ca_2Cu_4O_{8.5+\delta}$  based structures of mechanic and dielectric properties.

## **Experimental Technique**

The synthesis of  $La_1Ba_{1-x}Sr_x Ca_2Cu_4O_{8.5+\delta}$  (x=0, 0.1, 0.2 and 0.3) compounds have been prepared by solid state reaction method. We have used appropriate weights of pure powders materials 99% of La<sub>2</sub>O<sub>3</sub>, BaO, SrCo<sub>3</sub>, CaO and CuO as starting materials .They were carefully mixed and ground by using a gate mortar. The mixture was dried in an oven at 200°C, then it is put in farness for calcinations at 800°C during 3hr, then cooled to room temperature. In the second step, the mixture was pressed into disc shaped pellets(1.6 cm) in diameter and (0.2-0.3 cm) thick, using hydraulic press under pressure of  $(9 \text{ ton/cm}^2)$ . The pellets were sintered in air at 860°C for 20hr and then cooled to room temperature. The samples were characterized by X-ray diffractometer. The excess of oxygen content ( $\delta$ ) have been described elsewhere [6,7]. The structure of the prepared sample was obtained by using X-ray diffractometer (XRD). A computer program was established to calculate the lattice parameters a and c this program is based on Cohen's least square method [8]. The frequency dependent dielectric measurements were carried out by using a HP-R2C unit 4274A LCR meter (Hewlett-Packard, USA) in the range of 100 kHz–10 MHz and the Agilent 4275B LCR meter (Agilent Technologies Japan, Ltd.) in the range of 1 kHz–100 kHz. A conventional two –probe technique was used for these measurements .Silver paint was applied to both the surfaces of the sample, and copper leads were fixed to the silver electrode surfaces. By measuring the capacitance (C) and  $(\tan \delta)$  of the samples, the dielectric constant ( $\hat{\epsilon}$ ) and loss factor ( $\epsilon$ ) of the samples were calculated using the following expressions[9]:



Where d is the thickness of the pellet (0.2 cm) ,  $\epsilon_o$  is the permittivity of space ( $\epsilon_o$  =8.85\*10<sup>-12</sup> F/m ) ,and A is the cross-sectional area of the electrode (pellet).The frequency dependent dielectric measurements of La<sub>1</sub>Ba<sub>1-x</sub>Sr<sub>x</sub>Ca<sub>2</sub>Cu<sub>4</sub>O<sub>8.5+\delta</sub> compounds were done in the room temperature . Shore hardness measurements of the samples produced are performed by using a digital microhardness tester (Durometer Shor D ) at room temperature. The values of shore hardness are determined with an average of three readings at different locations of specimen surfaces for La<sub>1</sub>Ba<sub>1-x</sub>Sr<sub>x</sub>Ca<sub>2</sub>Cu<sub>4</sub>O<sub>8.5+\delta</sub> doped with (x=0,0.1,0.2and0.3).

#### **Results and Discussion**

The series XRD spectra of the samples  $La_1Ba_{1-x}Sr_x Ca_2Cu_4O_{8.5+\delta}$  with x varying from 0 to 0.3 are shown in Figure.2. All the samples in the present investigation were subjected to gross structural characterization by X-ray diffraction. The XRD data collected from various samples (samples having various La, Ca, Ba,Cu and Sr concentration) were all polycrystalline and correspond to La-1124 phases. The XRD also shows some impurity phases with vanishingly small concentrations. It could be seen from the spectra that there were two main phases in all samples of the La-base systems, high-T<sub>c</sub> phase (1124), low-T<sub>c</sub> phase(1202) and a small amount of impurity phases of (Ca, Ba)<sub>2</sub>CuO<sub>3</sub>, CaLaO<sub>4</sub> and CuO. The appearance of more than two phases could be related to the stacking faults along the c-axis. The comparison between the relative intensities of XRD patterns for the samples with Sr=0,0.1, 0.2 and 0.3, with the relative intensity of the same reflections of the sample with non Sr shows that all the samples have reflection high intensity, and it decreased by the increase of Sr . The lattice parameters have been estimated using d-values and (hkl) reflections of the observed x-ray diffraction pattern through the software program based on Cohen's least square method, the parameters a, c and c/a are shown in table(1).

The variations in the real part ( $\hat{\epsilon}$ ) and imaginary part ( $\epsilon$ ") of dielectric constant of La<sub>1</sub>Ba<sub>1-x</sub>Sr<sub>x</sub> Ca<sub>2</sub>Cu<sub>4</sub>O<sub>8.5+ $\delta$ </sub> samples as a function of frequency at room temperature are shown in figure.3(a and b) ,we observed a decrease in dielectric constant ( $\hat{\epsilon}$ ) and loss( $\epsilon$ ") with the increase of frequency at room temperature without effect Sr doping. The real part of the dielectric constant ( $\hat{\epsilon}$ ) gives the magnitude of the part of energy stored within the material when it is exposed to the electrical field .The most likely place at which this energy could be stored is within the grains (inter- granular sites). They act like termination ends for the crystal. The imaginary part of the dielectric constant ( $\epsilon$ ") indicates the absorption and the attenuation of energy across the interfaces under an external electric field .Examples of interfaces are grain boundaries, localized defects and localized charge densities at the defect sites and at grain boundaries [9,10]. Figure.4 shows variation of shore hardness of La<sub>1</sub>Ba<sub>1-x</sub>Sr<sub>x</sub> Ca<sub>2</sub>Cu<sub>4</sub>O<sub>8.5+ $\delta$ </sub> with Sr-doping ,in which the hardness decrease with the increase of Sr-content (x=0.0,0.1,0.2,0.3).

#### Conclusion

We have prepared samples of the type  $La_1Ba_{1-x}Sr_x Ca_2Cu_4O_{8.5+\delta}$  with x = 0, 0.1, 0.2 and 0.3 during a short preparation time by solid state reaction. The structure of the La-1124 did not change with the replacement of Ba by Sr ions whereas the lattice parameters were found to be changed. It was observed that dielectric constant and loss decrease slightly with the increase of frequency for all compounds.

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Table No.(1) : Values of lattice parameter, c/a ,oxygen content ( $\delta$ ), ( $\epsilon$ ), ( $\epsilon$ ") and hardnessfor the samples for different compositions of La1Ba1-xSrx Ca2Cu4O8.5+

X	δ(02)	a(A0)	c(A0)	c/a	έ(at1MHz)	ε"(at1MHz)	Hardness Shore
0	0.52	3.789	21.972	5.799	0.955	0.049	91
0.1	0.51	3.785	21.981	5.807	1.031	0.097	89
0.2	0.49	3.773	21.9842	5.827	1.123	0.103	86
0.3	0.537	3.7853	21.9815	5.807	1.572	0.182	78



Figure No.(1): The structure of La<sub>1</sub>Ba<sub>1-x</sub>Sr<sub>x</sub> Ca<sub>2</sub>Cu<sub>4</sub>O<sub>8.5+δ</sub>



Figure No.(2): XRD patterns for the  $La_1Ba_{1-x}Sr_xCa_2Cu_4O_{8.5+\delta}$ samples with x=0, 0.1, 0.2 and 0.3.



Figure No.(3): Variations of (a)dielectric constant and (b)dielectric loss versus frequency for La<sub>1</sub>Ba<sub>1-x</sub>Sr<sub>x</sub> Ca<sub>2</sub>Cu<sub>4</sub>O<sub>8.5+δ</sub> (x=0,0.1,0.2,0.3) at room temperature



Figure No.(4): Variation of Shore hardness with Sr-content for La<sub>1</sub>Ba<sub>1-x</sub>Sr<sub>x</sub> Ca<sub>2</sub>Cu<sub>4</sub>O<sub>8.5+δ</sub>

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# في الخواص التركيبية الميكانيكية والكهربائية للمركب Sr تاثير التطعيم La<sub>1</sub>Ba<sub>1-x</sub>Sr<sub>x</sub> Ca<sub>2</sub>Cu<sub>4</sub>O<sub>8.5+δ</sub>

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## استلم البحث في :4 حزيران 2013 ، قبل البحث في 10 تشرين الاول 2013

#### الخلاصة

حضرت نماذج من المركب 5x = 0.3 للمطعم بالسترنيوم Sr عند 2.0 Sr عند 2.0 La<sub>1</sub>Ba<sub>1-x</sub>Sr<sub>x</sub> Ca<sub>2</sub>Cu<sub>4</sub>O<sub>8.5+δ</sub> باستخدام طريقة تفاعل الحالة الصلبة . تم كلسنة النماذج بدرجة حرارة 800م مدة ثلاث ساعات ,كبست على شكل اقراص وحرقت بدرجة حرارة 800 مدة ثلاث ساعات ,كبست على شكل اقراص وحرقت بدرجة حرارة 800 مدة تلاث ساعات ,كبست على شكل اقراص وحرقت بدرجة حرارة 800 مدة تلاث ساعات ,كبست على شكل اقراص وحرقت بدرجة حرارة 800 مدة تلاث ساعات ,كبست على شكل اقراص وحرقت 1kHZ بدرجة حرارة 800 مدة ثلاث ساعات ,كبست على شكل اقراص وحرقت بدرجة حرارة 800 مدة تلاث ساعات ,كبست على شكل اقراص وحرقت بدرجة حرارة 800 مدة عشرين ساعة في الهواء ، قيس ثابت العزل وفقدان العزل وفقدانه يتناقص ببطء مع الملك 11kHZ في درجة حرارة الغرفة فضلا عن قياس الصلادة . واوضحت النتائج ان ثابت العزل وفقدانه يتناقص ببطء مع التردد لجميع النماذج فضلا على ذلك لا يوجد هناك تاثير واضح عند الاستبدال الجزئي  $x^{+2}$  في مستوى  $x^{+2}$  في المرى التردد لجميع النماذج فضلا على ذلك لا يوجد هناك تاثير واضح عند الاستبدال الجزئي  $x^{+2}$  في مستوى  $x^{+2}$  في حدائص التردد لجميع الماد بينا على الماد عن قياس الصلادة . واوضح عند الاستبدال الجزئي  $x^{+2}$  في مستوى  $x^{+2}$  في الماد بينا الترد لجميع النماذ وفقدانه يتناقص ببطء مع الترد لجميع النماذ وفقدا على ذلك لا يوجد هناك تاثير واضح عند الاستبدال الجزئي  $x^{+2}$  في مستوى  $x^{+2}$  في مستوى  $x^{+2}$  في الترد لجميع النماذ وفقد المهر بائي كما اظهر تحليل حيود الاشعة السينية بان تركيب المركب رباعي الطور 1124 كما وجد ال التغير في تركيز السترنيوم لكل النماذ وينتج منه تغيرا في ثوابت الشبيكة 2x.

الكلمات المفتاحية: La1Ba1-xSrx Ca2Cu4O8.5+6، الخواص العزلية، صلادة شور