

Investigating Effect of Ca Content on Electrostatic Potential Energy (EP), Critical Temperature (T_c) and Structure Parameters on $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ Superconductor

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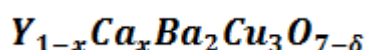
(Received 28 / 11 / 2013 ; Accepted 10 / 3 / 2014)

ABSTRACT

In this paper the effect of Ca content in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ and the relation between electrostatic potential energy, critical temperature (T_c), lattice parameters (a_{pa}), volume lattice parameter (V_{pa}), orthorhombicity, and the hole concentration is investigated by applying the ionic model to calculate the change in the electrostatic potential due to increasing the Ca content in the compound in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$. It is found that Ca^{2+} substitution for Y^{3+} leads to increase EP caused by increased ion volume and decrease of charge, this explains changes of superconducting structure parameters such as: lattice parameter (a_{pa}), volume lattice parameter (V_{pa}), orthorhombicity. Furthermore (T_c) decreases with increasing Ca content due to increase of EP which leads to change of the crystal structure and thus decreasing oxygen content and as a result decreasing of (T_c). Finally considering all above effects the increase of EP will increase the superconducting current.

Keywords: Electrostatic potential energy, Ca content, superconductor compounds.

استقصاء تأثير محتوى الكالسيوم على EP و (T_c) ومعلم التركيب للمركب الفائق التوصيل



المخلص

في هذا البحث تمت دراسة تأثير محتوى الكالسيوم في المركب $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ والعلاقة بين الجهد الكهروستاتيكي (T_c)، والمعلم الشبكي، والصفة المعينية متعامدة المحاور و معلم الحجم وتأثيره على تركيز الفجوات. وذلك بتطبيق النموذج الأيوني لاحتساب التغير للجهد الكهروستاتيكي بسبب زيادة محتوى الكالسيوم في $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$. ولقد وجد أن إبدال Ca^{2+} محل Y^{3+} يؤدي إلى زيادة الجهد الكهروستاتيكي بسبب زيادة الحجم الايوني و نقصان الشحنة. وهذا يفسر التغير في المعالم التركيبية فائقة التوصيل مثل: المعلم الشبكي (a_{pa})، المعلم الحجمي والصفة المعينية متعامدة المحاور. ولوحظ أيضا نقصان (T_c) مع زيادة محتوى الكالسيوم وذلك بسبب زيادة الجهد الكهروستاتيكي والذي أدى ارتخاء التركيب البلوري وبالتالي نقصان محتوى الأوكسجين وهذا أدى إلى نقصان (T_c). إن زيادة الجهد الكهروستاتيكي أدى إلى زيادة التركيز الإجمالي للفجوات وهذا أدى إلى ازدياد التيار الفائق التوصيل في الموصل الفائق بالرغم من تناقص (T_c).

الكلمات الدالة: طاقة الجهد الكهروستاتيكي، تركيز الكالسيوم والمركبات الفائق التوصيل.

INTRODUCTION

Ever since Y_{123} the first discovery in 1986 an enormous work has done toward experimental and theoretical investigation about structure and conduction in this compound. However, till now researches are active in this field (Wu *et al.*, 1998), (Sedky and Abu-Ziad, 2010). In spite of the great efforts spent by researches in order to explain conduction in Y_{123} , till now there is no agreement about model for conduction in Y_{123} compound. Efforts on substitution in high temperature superconductors (HTSC) from their initial discovery lead to great improvement in (T_c) and to the discoveries of new high temperature superconductors, HTSC (Zhao, 2005), (McCormack and de Fontaine., 1992).

Substitution of Ca^{2+} instead of Y^{3+} ion in $YBa_2Cu_3O_{7-\delta}$, with comparable ionic radii, with amount of Ca^{2+} content (0 to 0.3), has the effect of increase of superconducting current in the compound; however, the transition temperature decreases (Naqib *et al.*, 2009), (Schlachter *et al.*, 1999). On the other side, substitution of Ca^{2+} in $YBa_2Cu_3O_{7-\delta}$ does not change the average valence of Cu ion, but the amount of oxygen deficiency δ increases linearly with Ca content (Iguchi *et al.*, 1988). Ca^{2+} substitution for Y^{3+} increases the overall hole concentration. Hole doping is very low for highly oxygenated samples, while it is quite significant for oxygen deficient samples (Liyanawaduge *et al.*, 2012). Introducing calcium residue in CuO_2 planes, lead to a competition mechanism of the hole density in CuO_2 planes between Ca doping and oxygen depletion (Jian *et al.*, 1998).

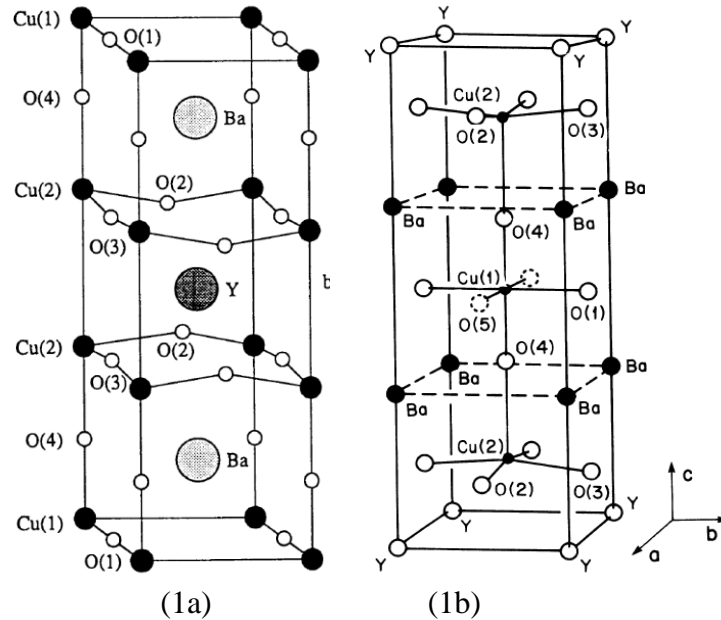
Great efforts till now try to study effects of substitution of Ca^{2+} in Y_{123} on the properties like the lattice parameters orthorhombicity, and (T_c) in superconductor $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ (Giri *et al.*, 2005), (Han *et al.*, 2001).

The purpose of this research is to apply the ionic model to calculate the change in the electrostatic potential due to increasing the Ca content in the compound in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ and to prove that there is a relation between changing EP and Ca content using real experimental data (Khosroabadi *et al.*, 2002), (Han *et al.*, 2001), (Baetzold, 1988) about change in lattice parameters and oxygen content in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$.

THEORETICAL

The substitution of different amounts of atoms of Ca in the superconductor $Y_1Ca_xBa_2Cu_3O_{7-\delta}$ on the structure of it (Iguchi *et al.*, 1988), (Giri *et al.*, 2005), (Han *et al.*, 2001), greatly studied. It may be noticed that the lattice constant (a_{pa}) increases with increasing Ca^{2+} content while lattice constant b and c changes slightly. On the other hand, the addition of Ca^{2+} at Y^{3+} site decreases slightly the difference between a and b parameters and thus reduces the orthorhombicity $(a-b)/(a+b)$ of Y_{123} phase, also, (T_c) decreases with increasing Ca content this was also confirmed by AC susceptibility (Giri *et al.*, 2005), from the references (Iguchi *et al.*, 1988), (Giri *et al.*, 2005), (Han *et al.*, 2001) there are some data about the effect of addition of Ca to the superconductor $Y_1Ca_xBa_2Cu_3O_{7-\delta}$ on the (T_c) and (a, b, c) lattice parameters. In this research the first step is to find a relation between EP, (T_c) and the lattice parameters. Also the relation between EP and orthorhombicity, volume parameter with increasing Ca must be found. To do the above steps first of all we calculate the distance between the Yttrium ion to all the other ions in the $Y_1Ca_xBa_2Cu_3O_{7-\delta}$ compound as seen in the figures (1a, 1b) also it is important to consider the change in the distances between ions by the addition of Ca in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$, then calculation of the electrostatic potential energy was done by using equation (1). From above calculation EP has been found for every content of Ca from (0 to 0.3). The crystal model of the unit cell of $YBa_2Cu_3O_{7-\delta}$ is shown in figure 1a, and figure 1b: shows the same crystal, but the

crystal of $YBa_2Cu_3O_{7-\delta}$, YBCO is so drawn such that it is shifted by (half diagonal of one of its cubes). That the Y and the Ba atoms are drowning on the edge of the crystal (Baetzold, 1988). The unit cell is orthorhombic with $N = 13$ atoms. The corresponding crystal structure, with the a and b axes differing by less than 2% generally c axis is parallel to the long cell dimension. The size of the unit cell has been found considering the lattice constants are $a = 3.822 \text{ \AA}$, $b = 3.891 \text{ \AA}$ and $c = 11.677 \text{ \AA}$, respectively.



Figs. (1a-1b): schematic diagram of two different model of crystal structure of YBCO compound (Baetzold, 1988), (Khosroabadi *et al.*, 2002).

The Cu(2), O(2), and O(3) atoms make up the superconducting CuO_2 planes, which are important features of Y_{123} compounds. The CuO chains are believed to act as charge reservoirs. Between the CuO chains and CuO_2 planes are the O(4) atoms commonly referred to as apical oxygen atoms.

Starting from the above model the sum of electrostatic potential energy EP of the Y^{3+} ion with charge $(+3e)$ with all other ions of the crystal of charge (q_i) depending on valence of the ions at distances r_{ij} can be calculated easily from reference (Wright and Butler.,1990).

$$EP = \frac{1}{4\pi\epsilon_0} (N_{Ca} N_j) \sum_i^j \left[\frac{q_i q_j}{r_{ij}} \right] Z \quad \dots\dots\dots(1)$$

where N_{Ca} is the valence of the Ca ion, N_j is the valence of the other element in the $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ compound, q_i and q_j are electric charges of i and j ions and equal to 1.6×10^{-19} Coulomb and ϵ_0 is electric permittivity in free space and Z oxygen content in the $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ compound.

Since Ca content changed we must consider the total change in the positions of atoms and also the change in charge. The oxygen content was taken from the relation between Ca content and oxygen content that obtained from figures in the references (Nazarova *et al.*, 2004).

$$Z = 7 - \frac{n_{Ca}}{2} \quad \dots\dots\dots(2)$$

where n_{Ca} is Ca content and Z oxygen content in the $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ compound. Also by using the relation from equation 2 reference (Nazarova *et al.*, 2004). Y substitution by Ca was

considered from equation 3 which combined the effect of change of valance (N_{Ca}), by addition of Ca content.

$$N_{Ca} = 3(1 - n_{Ca}) + 2n_{Ca} \quad \dots\dots\dots (3)$$

N_{Ca} is the valence of the Ca ion, also the ratio of oxygen content R_0 in the compound is calculated by using the equation:

$$R_0 = 1 - \left[\frac{7-Z}{4} \right] \quad \dots\dots\dots (4)$$

The hole concentraton p_h can be calculated in the CuO_2 plane of the $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ compound by using the equation 5 taking from references (Schleicher *et al.*, 1999), when the critical temperature (T_c) and maximum critical temperature are known.

$$p_h = 0.16 \mp 0.11 \sqrt{1 - \frac{T_c}{T_{c \max}}} \quad \dots\dots\dots (5)$$

p_h is hole concentration, (T_c) is the critical temperature and ($T_{c \max}$) is the maximum critical temperature. By applying fitting method to figures (2, 3, 4, 5) we can determine the relation between electrostatic potential energy in the Y123 compound and (T_c), Ca content, oxygen content, Volume parameter, and hole concentration.

Furthermore, the value of hole concentration obtained from the above equation is agreement with the plot of relation between the hole concentration and critical temperature as in reference (Naqib *et al.*, 2009).

RESULTS

This research has investigated the effect of Ca content on crystal structure of superconductor, electrostatic potential energy, hole concentration and critical temperature in the YBCO compound. The result, will be shown in the following curves (2, 3, 4, 5, 6, 7, 8).

Fig. (2-a): shows the EP and (T_c) as a function of Ca content in $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ compound the increase of Ca leads to decrease of (T_c) (Giriet *et al.*, 2005). The calculated values of EP with the increasing of Ca content in $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ show corresponding changes are indicating a relation between change of charge content in the crystal.

Fig. (2-b): shows EP and (T_c) as a function of the lattice parameter (a_{Ca}), with increase of calcium content in $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ compound there is a good agreement in changes of both EP and (T_c) with the lattice parameter (a_{Ca}).

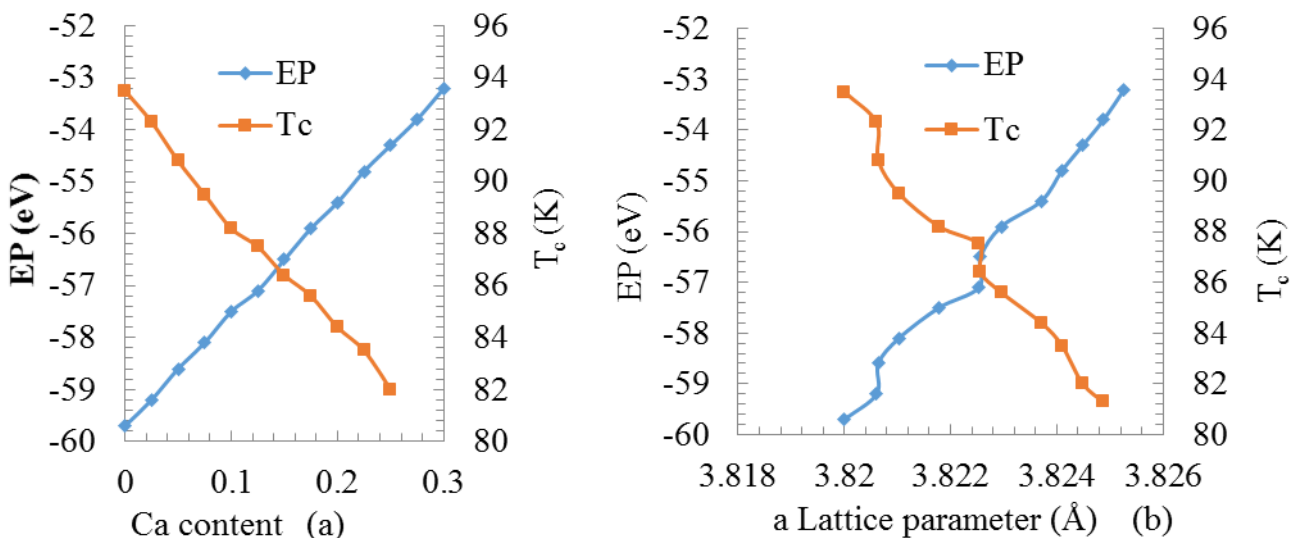


Fig. (2-a): The variation of EP and (T_c) as a function of Ca content and Fig.(2-b): the variation of EP and (T_c) as a function of lattice parameter (a_{pa}) .

The Fig.(3-a): shows EP and lattice parameter (a_{pa}) as a function of Ca content in the $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ compound it is evident that there is an increase in EP and lattice parameter (a_{pa}) with increasing of Ca content it is evident that there is a systematic relation between them.

Fig. (3-b): shows EP and the volume lattice parameter as a function of calcium content in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ compound it is evident that there is an increase in EP with the increasing of Ca content where there is a corresponding increase in the volume parameter it is evident that there is a systematic relation between them.

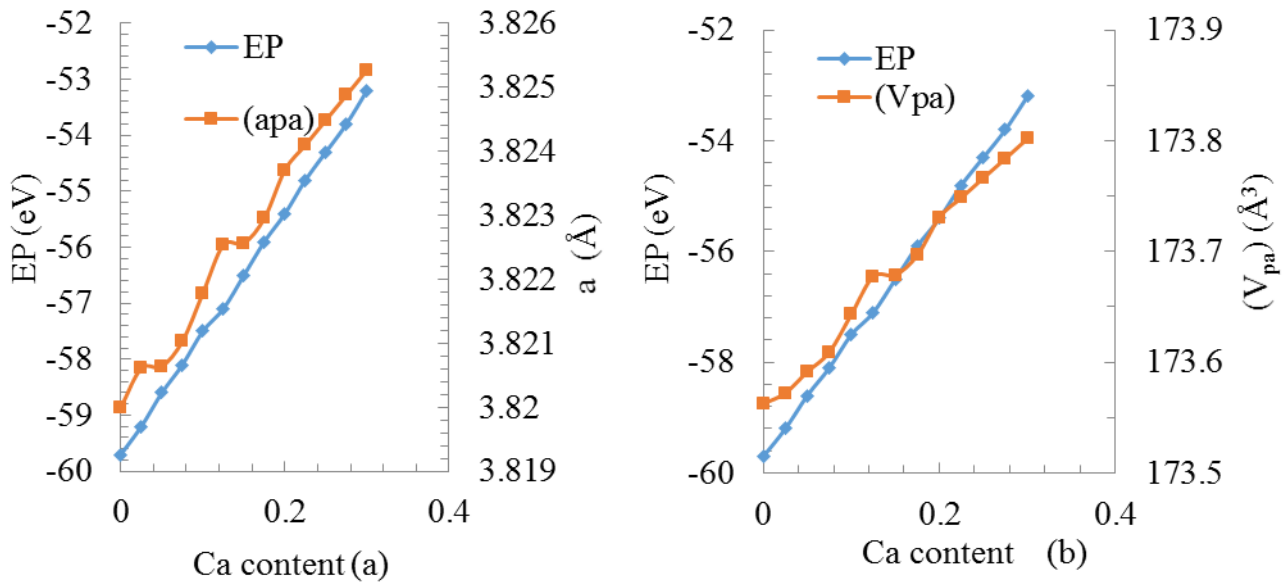


Fig. (3-a): The variation of EP and lattice parameter (a_{pa}) and Fig.(3-b): the variation of EP and volume lattice parameter as a function of Ca content.

In Fig. (4): the EP and orthorhombicity of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ compound as a function of calcium content in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ compound there is increasing of EP and decreasing of orthorhombicity with increases of Ca content in the compound. The sharp decrease of orthorhombicity in the beginning is due to the sharp change in lattice parameter (a_{pa}) , after 0.05 concentration there is a linear decrease with EP.

From Figs. (2, 3 and 4) many important relations between electrostatic potential and superconducting parameters can be found and we can derive a fitting relations between them

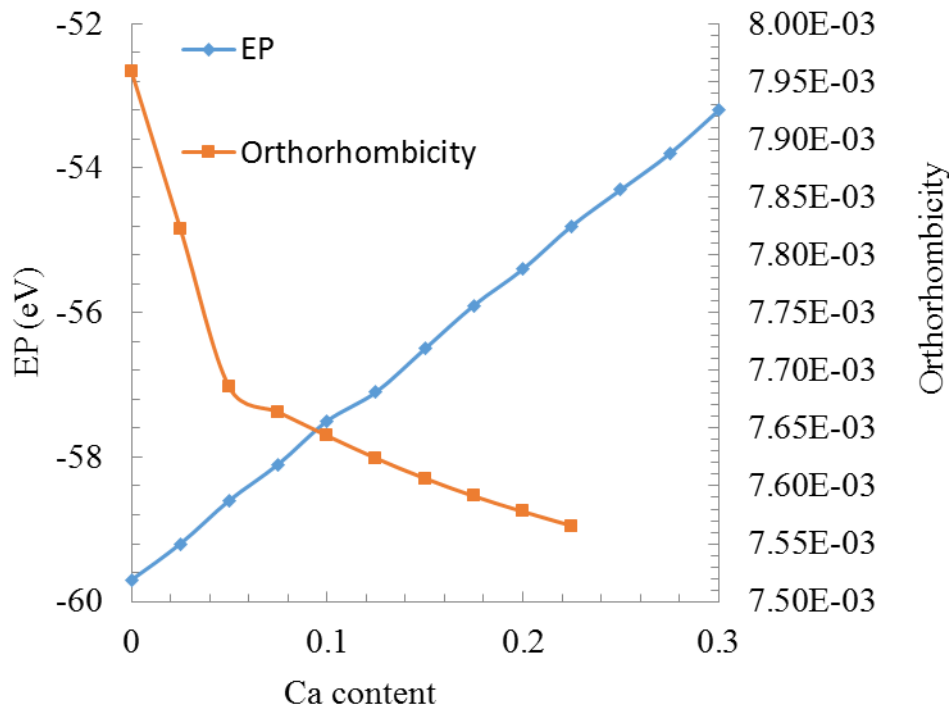


Fig. (4): The variation of EP and orthorhombicity as a function of Ca content

From Figs. (2, 3 and 4) many important relations between electrostatic potential and superconducting parameters can be found and we can derive a fitting relations between them.

Fig. (5-a): shows a good relation between Ca content and the electrostatic potential energy with correlation factor $R = 0.990$ the fitted relation is:

$$EP = -12.64n_{Ca} + 59.71 \quad \text{.....(6)}$$

Fig. (5-b): shows a good relation between lattice parameter (a_{pa}) and electrostatic potential energy with $R = 0.988$ and with fitting relation:

$$EP = -1191a_{Ca} + 4610 \quad \text{.....(7)}$$

Fig. (6-a): is the relation between volume lattice parameter and electrostatic potential energy and correlation factor $R = 0.99$ with fitting relation:

$$EP = -25.65V_{pa} + 4511 \quad \text{.....(8)}$$

V_{pa} is volume lattice parameter.

Fig. (6-b): shows the relation between orthorhombicity and electrostatic potential energy in polynomial form with $R = 0.96$ and relation:

$$EP = 6 \times 10^7 \theta^2 + 87957\theta + 3396 \quad \text{.....(9)}$$

θ is orthorhombicity of compound.

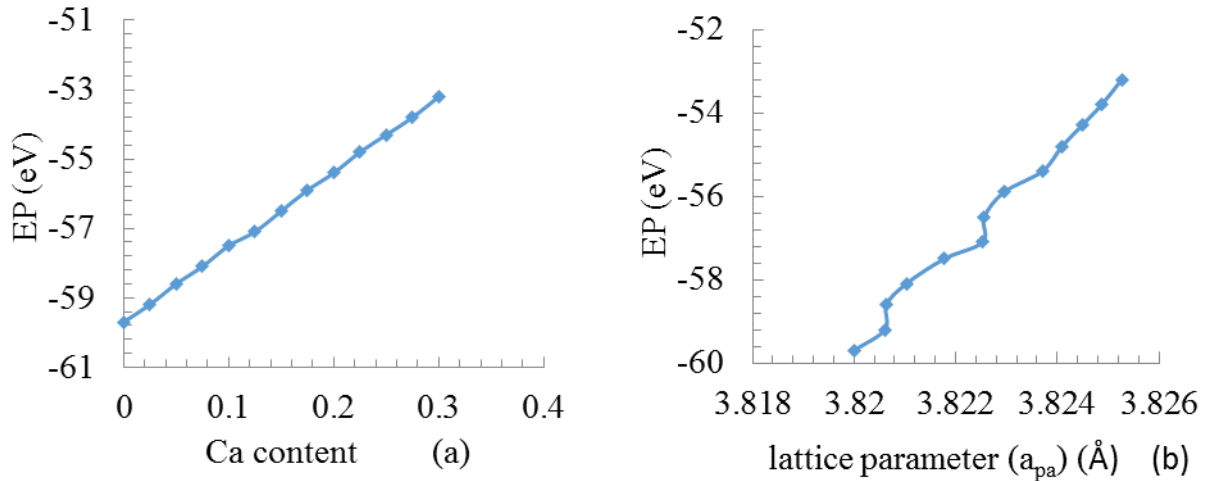


Fig. (5-a): The variation of EP as a function of Ca content and Fig. (5-b): the variation of EP as a function lattice parameter (a_{pa}) in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$.

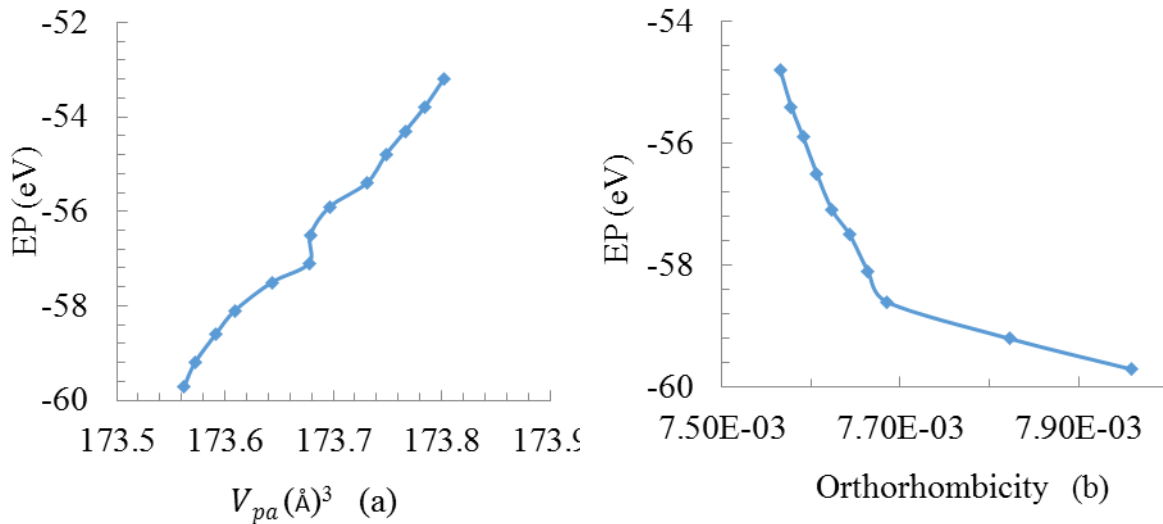


Fig. (6-a): The variation of EP as a function of volume lattice parameter (V_{pa}) and Fig.(6-b): the variation of EP as a function of orthorhombicity.

Fig.(7-a): shows the relation between Ca content and hole concentration, the dependence is logarithmic with $R=0.98$ and the relation is:

$$p_h = 0.011 \ln(n_{Ca}) + 0.212 \quad \dots\dots\dots(10)$$

p_h is hole concentration in CuO_2 plane.

Fig. (7-b): shows the relation between the hole concentration and electrostatic potential energy in polynomials with $R=0.996$ and relation

$$EP = 4393 p_h^2 - 1433 p_h + 57.135 \quad \dots\dots\dots(11)$$

In Fig.(8-a): shows that as critical temperature is increasing the electrostatic potential energy decrease and we can determine the relation between EP and (T_c) from data fitting obtained from figure (8-a) that as in the equation (12)

$$EP = -0.4877T_c - 14.28 \quad \dots\dots\dots(12)$$

Shown the dependence of both the electrostatic potential energy and hole concentration on Ca content.

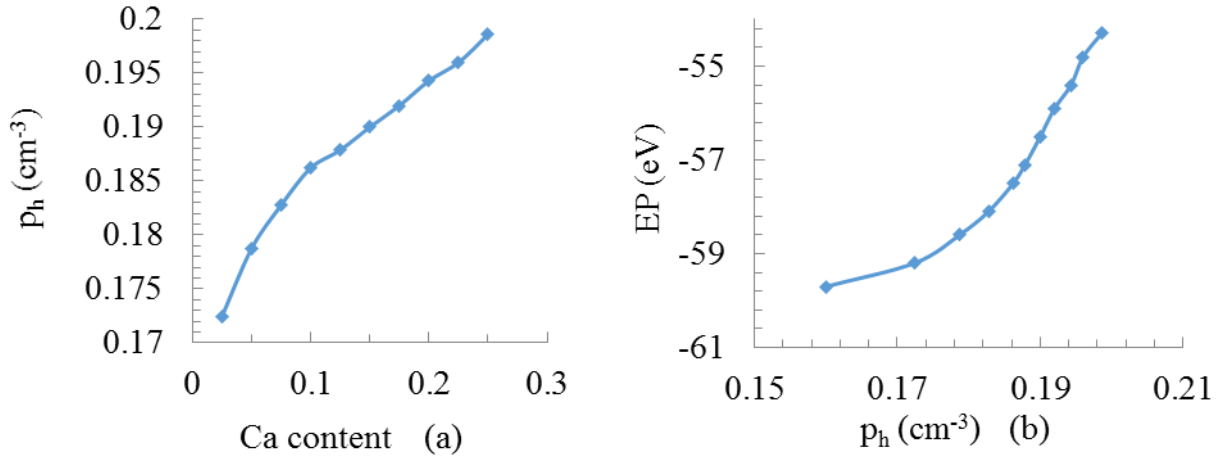


Fig. (7-a): The variation of hole concentration as a function of Ca content and Fig. (7-b): the variation of EP as a function of hole concentration.

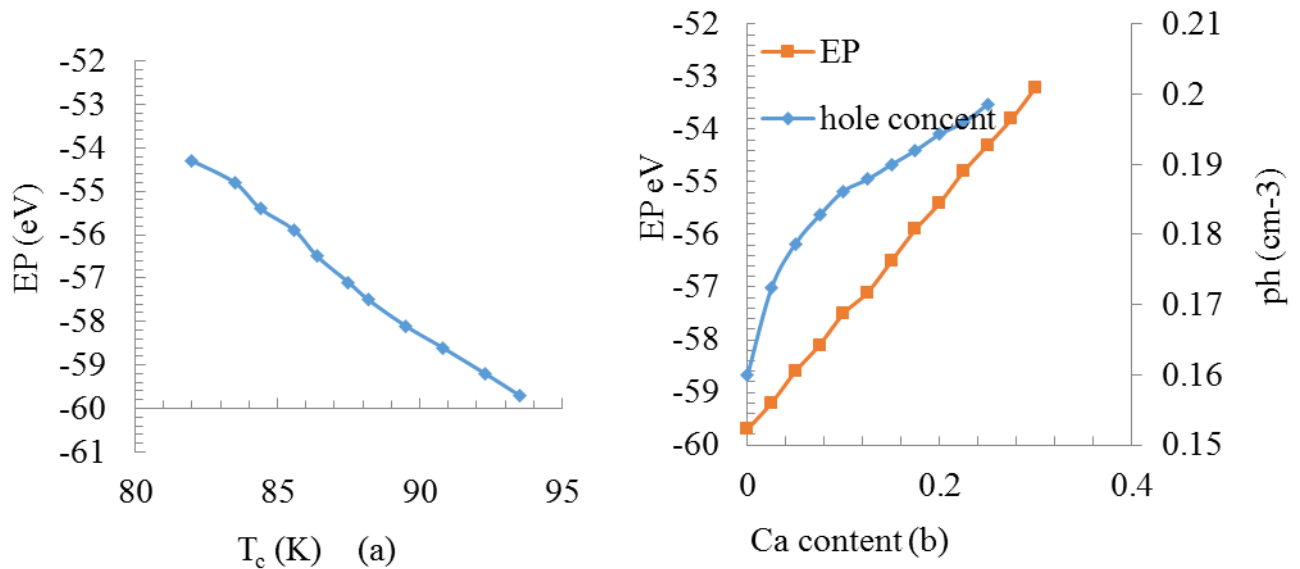


Fig. (8-a): The variation of EP as a function of T_c and Fig. (8-b): the variation of EP and hole concentration as a function Ca content.

DISCUSSION

With Y substitution by the calcium, the critical temperature and other superconducting parameters such as lattice parameter (a_{pa}), volume lattice parameter (V_{pa}) and orthorhombicity will be changing. In this work we proved that there is a very good correlation $R=0.990$ between Ca content in compound and the electrostatic potential energy with linear relation (equation 6). Furthermore good relation between EP and lattice parameter (a_{pa}) in relation (equation 7) and also (V_{pa}) and EP from (equation 8). And finally orthorhombicity and EP (equation 9). According to the crystal model of Fig.(1), replacement of Y^{+3} by Ca^{2+} would increase the PE due to two factors, one is decreasing of charge from +3 to +2 and increasing the ionic radius from the small ionic radii Y^{+3} (1.019) Å by the large ionic radii of Ca^{2+} (1.12) Å. The big ionic radius of Ca^{2+} and weak

coulomb attraction will increase the lattice constant (a_{pa}). Substitution by Ca^{2+} increases number of holes in the CuO_2 plane. At the same time oxygen content in CuO chain decreases (Giri *et al.*, 2005), (Han *et al.*, 2001), because Ba ions become nearer to the Ca^{2+} and thus nearer to the CuO_2 plane this is due to the increase of EP. Also the decrease of the (T_c) can be explained as due to decrease of oxygen because increase of the EP means loosening of the ionic bonds between central ion and other ions of the crystal. All above effects lead to increase the holes in the CuO_2 plane due to replacement of the Y^{3+} by Ca^{2+} and transfer of holes from CuO_2 plane to CuO chain (Giri *et al.*, 2005), (Singh *et al.*, 2012).

From Fig. (7-b) shows direct dependence of hole concentration ions and EP this may explain the experimental facts that current increases with increasing Ca in YBCO.

CONCLUSIONS

Ca^{2+} substitution for Y^{3+} (0 - 0.3) leads to increase EP which caused by increasing ions volume and decreasing of charge, this explains change of superconducting structure parameters such as: lattice parameter (a_{pa}), volume parameter (V_{pa}) and orthorhombicity.

(T_c) decreases, with increasing Ca content due to the disorder in the superconducting CuO_2 planes with Ca doping due to increase of EP which leads to flattening of the CuO_2 . Increases of EP lead to change of the crystal structure and thus decreasing oxygen content and as a result decreasing of (T_c).

Ca^{2+} substitution for Y^{3+} increases the overall hole concentration, this substitution effect, first takes place in CuO_2 planes and also because oxygen removing from $\text{CuO}_{1-\delta}$ chains. to compensate the additional effect of Ca current. These results will increase the superconducting current although the (T_c) was decreasing.

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