Study of Substitution Mechanism in the Superconductor La_2CuO_4

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ABSTRACT

The aim of the research is to understand the mechanism of process of substitution of the ion Sr^{+2} instead of La^{+3} in the superconductor La_2CuO_4. Calculations of electrostatic potential(E. P.) for two probable positions is done to determine the site of minimum energy, the site of La around Cu ion is the minimum in energy on all the range of concentrations of the Sr ion. The changes in E. P. by substitution helps in understanding some aspects of the complex synthesis procedure of La_2CuO_4 compound and especially the high and the long period preparation temperature which gives full action of electrostatic forces.

Key words : ionic substitution , superconductor La$_2$CuO$_4$,HTSC.

La_2CuO_4

. La_2CuO_4 La^{+3} Sr^{+2}

La .

La_2CuO_4

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INTRODUCTION

High Temperature Superconductors (HTSC) was discovered by (Bednorz and Muller, 1986), since that time great experimental efforts. Especially when the transition temperature reaches 95 K which is above the boiling point of liquid nitrogen (Wu *et al*, 1987) in the superconductor YBa$_2$Cu$_3$O$_7$ (YBCO). The HTSC are CuO based ceramics that

reveal superconductivity near and above 100 K. Soon   after this discovery many other superconducting compounds with higher critical temperature was synthesized, by great experimental efforts on substituting other rare earth and other near ions. Representative of such high temperature superconducting compounds are Bi-Sr-Ca-Cu-O (BSCCO), and Ba-Sr-Ca-Cu-O (BSCCO) (Sharp, 1990). Since the discovery of the compound Hg-Ba-Ca-Cu-O (HBCCO) with the critical temperature 135 K there is no such great advances in elevating the critical temperature (Chu, 2002).

Basic unit of the formation of the HTSC are the Pervoskite structure which is an insulator. By substituting for certain atoms in the unit cell, it become superconductors. A tremendous quantity of substitution have been tried to improve mechanical, magnetic and transport properties of these materials (Lynn, 1990).

Superconductivity observed in La_2CuO_4 system which is shown Figure 1. When La is partially substituted by Ba   then forming the compound $La_{2-x} Ba_x CuO_4$ the value of T_C reaches maximum value when x = 0.15. Substitution by divalent ions $M = Ba^{2+}, Sr^{2+}, Cu^{2+}$ Leads to appearance of superconductivity in a group of compounds $La_{2-x}M_xCuO_{4-y}$ for (0.05 < x < 0.3) by the variations in x and M (Takagi et al , 1989) .

The aim of this research is to study the of substitution mechanism of Sr^{2+} ion instead La^{3+} in the compound La_2CuO_4 by Calculation of E . P. to find the sit of minimum energy change for the Sr Ion in all range of concentration of Sr^{2+} .
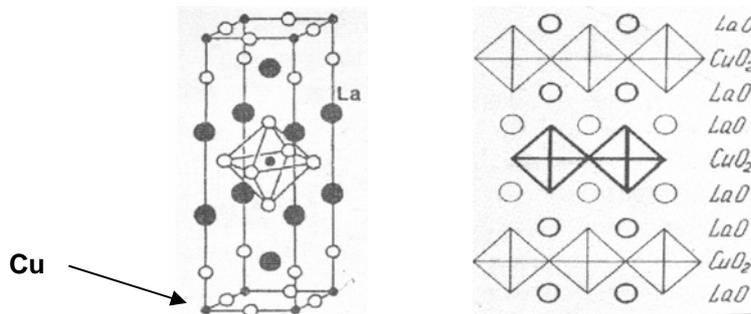

Fig.1:   Left drawing   the crystal structure of La_2CuO_4, on which shown the octahedral structure surrounding the Cu ion, right drawing is a two dimensional representation of the same compound   (Illushin and Zoobov, 1991)

Theory

The structure   of the Superconducting phase was identified as a derivative of the layered pervoskite and shown in figures 1and 2. Fig.2 shows CuO_2 Octahedral which consist of central Cu ion an 6 O ions, with Cu-O length of 1.9 Å in the a-b plane and 2.4 Å in c direction. Also the Cu atom occur at (000) and (½, ½ , ½) lattice sites in the unit cell, similar to the body centered structure. The difference in valance by substitution bring about increase in the number of holes (Sharp, 1990). Superconductors with hole conduction are called P-type similar to that found in semiconductors .

Since La^{3+}, Sr^{2+} are large ions the compound formed have the formula A_2BO_4, a tetragonal structure with c = 3a. Where a is the length of the cell edge of the pervoskite building bricks (Sharp, 1990).
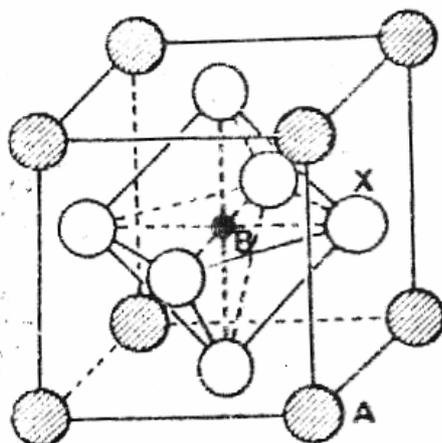

Fig.2: Central cube in the La_2CuO_4 crystal ,with pervoskite structure, where A , B and x representing (La or Sr) , Cu and O respectively (Santoro, 1990) .

The CuO compounds are insulators (Sharp, 1990) by substituting a certain atoms in the unit cell, these materials are made to behave as metals and may become superconductors (Wright and Butler, 1990). The process of substitution was done experimentally, little is done to understand theoretically what happens during substitution. one of the reasons as we think is the good gained results of ever higher temperature superconductor, but soon this good results was stopped, and more than one decade was elapsed and record transition temperature is not changed. Here we try to read the main features for a better theoretical understanding of the experimental procedure.

Great number of studies (Santoro, 1990) by X-ray, electron and neutron diffraction of HTSC during substitution by different percentages of substituent's show after a thermal treatments in certain atmospheres that these substituent's are taken certain positions in the crystal unit cell with the substituted ions also distributed approximately in a uniform manner in the whole superconducting specimen (Shelton ,1990).

For the compound La_2CuO_4 as shown in figures 1and 3, there are two positions for the Sr atom to be substituted one position is that the substituted atom takes the position of one of the eight La atoms around the Cu-O octahedral and the position is denoted as La(1), the other probable position is in one of the positions of the other La two atoms above and below the Cu-O octahedral as seen also in figure 3 where position is denoted as La(2) .
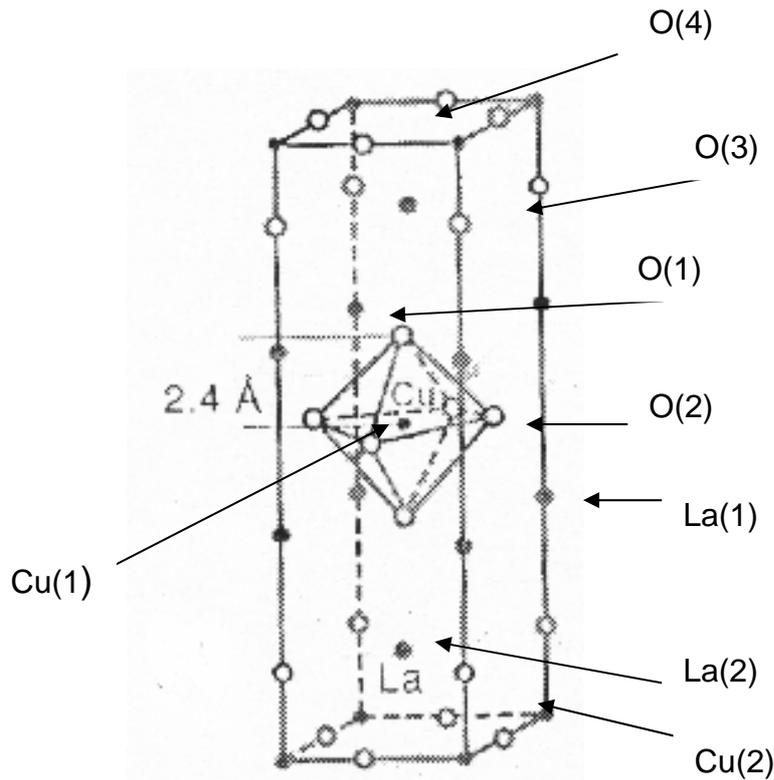
Fig. 3: Crystal structure of the compound La_2CuO_4 , here nomination the sites of the atoms
is done to understand the process of substitution (Sharp, 1990) the arrows on the
figure and their nominations is drawn by the author.

Many researches concluded that the substituted atom takes the position La(1) but there is
no proof for such assumption. Here we try to analyze this contradiction and to do this the
following facts must be considered :

1 – The HTSC are ionic compounds (Wright and Butler, 1990) .
2 – Accordingly electrostatic forces play a major role in formation of the compound .
3 – The valance of the substituted ions.
4 – The difference in energy between the two position of settlements of the substituted
      ion.
5 – The size of the original and the substituted ion.
6 – Atom will prefer the position of the least change in the energy of the crystal.
Therefore a need to calculate the electrostatic energy is necessary which includes
many of the factors which we have already stated.

The size of the substituted ion
      Size of the substituted ion plays a role in determining the position of the substituted
ion, since there is a difference in radii of the ions this accordingly affect the E. P, especially
if their is a big difference in radii of the ions. But here the substituted ion Sr (1.13 Å) has
approximately the same radius as that of La (1.15 Å) the difference is very small and in

calculating the E. P. very little difference appear when putting the size factor under consideration .

The electrostatic energy

Great number of literature concluded that one of the important properties of the HTSC are their ionic bonds (Wright and Butler, 1990). This is one of the main properties of the pervoskite structures. Since all the HTSC are derived from materials with pervoskite structures (Sharp, 1990).

If we try to compute the electrostatic energy (E.P.), which as we think: is an important parameter, because it determine to a big extent the energy that combine the system of atoms in the crystal, and any change in it (substitution of a new atom) affect the combining energy of the whole system this will affects also charge distribution inside the crystal, because it affect the charge balance by the introduction of the new ion, with different valances .

To calculate the electrostatic energy E for the crystal we use the following relation (Kittle, 2005).

$$E = \frac{1}{4\pi\varepsilon_o} \sum_{1}^{i} \frac{Qq_i}{r} \quad \text{…………………………………………………} \quad (1)$$

Q, q_i, r are the charge of the reference ion, the charge of the ion i and the distance between them respectively. Madelung method (Kittel, 2005) was not followed strictly because of the anisotropy and the distortion of this crystal as shown in the figures 1,2 and 3. So we have to modify (equation 1) to account for the three type of ions present in the crystal (i.e. Cu ,O , Ba), thus
Calculation of EE for the crystal depend on the site of the reference atom ,

$$E = \frac{1}{4\pi\varepsilon_o} \left(\sum_{1}^{m} \frac{Qq_{Cu}}{r_{Y-Cu}} + \sum_{1}^{n} \frac{Qq_O}{r_{Y-O}} + \sum_{1}^{l} \frac{Q_{Ba}}{r_{Y-Ba}} \right) \quad \text{………………………} \quad (2)$$

and the distance of the other atoms relative to it .therefore we need to identify the positions and distances of the atom in the crystal .

positions and distances of the atom in the crystal

For our crystal La_2CuO_4 , and as shown in figures 1 and 2. The crystal have tetragonal structure as shown in figure 3. with c = 3a (Sharp, 1990). Where a is the length of the cell edge of the pervoskite building bricks.

The c and a dimensions as measured by X-ray and neutron diffraction and for the compound La_2CuO_4 are (Santoro, 1990) :
   c = 13.288 Å
   a = 3.787   Å

In figure 3 the crystal structure for La_2CuO_4 is shown and the main atomic sites for this crystal is nominated. In the table 3 positions for the above atoms are tabulated, for the equal atomic sites like (La(1) ,O(2) ..etc) we refer to site near the reference point

Table 1: Atomic positions of the main atomic sites in the crystal of the superconductor
La$_2$CuO$_4$

Atomic site	x	Y	Z	Reference
Cu(1)	0.5 a	0.5 a	0.5 c	Santoro, 1990
Cu(2)	0	0	0	Santoro, 1990
La(1)	0	0	0.362 c	Santoro, 1990
La(2)	0.5 a	0.5 a	0.138 c	Picket, 1989
O(1)	0.5 a	0.5 a	0.681 c	Sharp, 1990
O(2)	0.5 a	0	0.5 c	Sharp, 1990
O(3)	0	0	0.182 c	Picket, 1989
O(4)	0.5	0	0	Santoro, 1990

We have two probable situations where the Sr ion can be settled the first situation is the site of one from the eight La (1) ions surrounding the Cu (1) ion. The other probable site is the site of one of the two La (2) ion in the upper and lower parts of the crystal. In order to determine the most probable situation the following must be considered. The site that Sr Ion will choose must not lead to breaking the crystal, and as a result changing its nature, but we want this substitution to improve superconducting properties of the crystal unit cell. This condition lead us to go to the fact that the system is still stable if the change of its total energy is minimum by the substitution depend. So the site of stability of the Sr ion is the one that will produce minimum energy change in crystal energy.

So since the HTSC compounds are ionic compounds as its already mentioned above we must calculate the change in the electrostatic potential (E.P.)   due to the substitution.

Calculation of Electrostatic potential in Cu(1) site

In this site the Cu ion is surrounded by two O(1), and four O (2) ions and eight La (1) ions so :

The E.P. between Cu (1) and O (1) ions

$$E_{r_{Cu(1)-O(1)}} = \frac{1}{4\pi\varepsilon_o}(\sum_{1}^{2} \frac{Q_{O(1)}q_{Cu(1)}}{r_{Cu(1)-O(1)}}) \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (3)$$

and The E.P. between Cu (1) and O (2) ions

$$E_{r_{Cu(1)-O(2)}} = \frac{1}{4\pi\varepsilon_o} \sum_{1}^{4} \frac{Q_{(2)}q_{Cu(1)}}{r_{Cu(1)-O(2)}} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (4)$$

and   The E.P. between Cu (1) and La (1) ions

$$E_{Cu(1)-La(1)} = \frac{1}{4\pi\varepsilon_o} \sum_1^8 \frac{Q_{La(1)}q_{Cu(1)}}{r_{Cu(1)-La(1)}}) \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(5)$$

thus the total P. E. in the site Cu (1) before substitution of the ion Sr is :

$$E_{TCu(1)} = E_{r_{Cu(1)-O(1)}} + E_{r_{Cu(1)-O(2)}} + E_{Cu(1)-La(1)} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots (6)$$

and the total P. E. in the site Cu(1) after substitution of the ion Sr is :

$$E_{TCu(1)} = (E_{r_{Cu(1)-O(1)}} + E_{r_{Cu(1)-O(2)}} + E_{Cu(1)-La(1)})(1-x) - xE_{Cu(1)-Sr(1)} \quad \dots\dots\dots \quad (7)$$

where x is the concentration of Sr ions

Calculation of Electrostatic potential in La(2)site

In this site the La(2) ion is surrounded by one O(1) ,and four O(3) ions and four La (1) ions and so :
The E.P. between La(2) and O(1) ions

$$E_{r_{La(2)-O(1)}} = \frac{1}{4\pi\varepsilon_o} (\sum_1^1 \frac{Q_{O(1)}q_{La(2)}}{r_{La(2)-O(1)}}) \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (8)$$

The E.P. between La(2) and La(1) ions

$$E_{r_{La(1)-La(2)}} = \frac{1}{4\pi\varepsilon_o} \sum_1^3 \frac{Ql_{La(2)}q_{La(1)}}{r_{La(1)-La(2)}} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (9)$$

The E.P. between La(2) and O(3) ions

$$E_{r_{La(1)-O(3)}} = \frac{1}{4\pi\varepsilon_o} \sum_1^4 \frac{Q_{La(1)}q_{O(3)}}{r_{La(1)-O(3)}}) \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (10)$$

The E.P. between la(2) and O(4) ions

$$E_{r_{La(1)-O(4)}} = \frac{1}{4\pi\varepsilon_o} (\sum_1^4 \frac{Q_{La(1)}q_{O(4)}}{r_{La(1)-O(4)}}) \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (11)$$

The E.P. between la(2) and Sr(1) ions

$$E_{r_{La(2)-Sr(1)}} = \frac{1}{4\pi\varepsilon_o} \sum_1^1 \frac{Q_{Sr(1)}q_{La(2)}}{r_{La(2)-Sr(1)}}) \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots(12)$$

thus the total P. E. in the site La(2) before substitution of the ion Sr is :

$$E_{TLa(2)} = E_{r_{La(2)-O(1)}} + E_{r_{La(1)-La(2)}} + E_{r_{La(1)-O(3)}} + E_{r_{La(1)-O(4)}} + E_{r_{La(1)-Cu(2)}} \quad \dots\dots\dots.(13)$$

and the total P. E. in the site La(2) after substitution of the ion Sr is :

$$E_{TLa(2)} = (E_{r_{La(2)-O(1)}} + E_{r_{La(1)-La(2)}} + E_{r_{La(1)-O(3)}} + E_{r_{La(1)-O(4)}} + E_{r_{La(1)-Cu(2)}})(1-x) - xE_{r_{La(2)-Sr(1)}} \quad . (14)$$

where x is the concentration of Sr ions.

Calculations, Results and Discussion

The other parameters which are needed to calculate EE is distances between the atoms and the reference atom.

$r_{Cu-O(1)}$ =2.4 Å , (Sharp) distance for apex O atom from central Cu atom .
$r_{Cu-O(1)}$ = 1.9 Å (Sharp) distance for O atom in CuO plane from central Cu atom .

From the positions of the ions in table 1 , and using the above dimensions we can find :

$$r_{La(1)-La(1)} = \frac{13.288 - 3.620 \times 2}{13.288} c = 0.455\,c$$

the length of half diagonal is $D_{1/2} = \frac{a}{2}\sqrt{2} = 2.678$ Å

Substituting for a and c then $r_{Cu-La(1)}$ =3.570 Å
Mid point of the crystal = c/2 = 6.644 Å

$c_{O(1)}$ = 9.044 Å
$c_{La(2)}$ = 10.803 Å
$c_{La(1)}$ = 8.478 Å
$c_{O(3)}$ = 11.468 Å
$r_{La(2)-O(1)}$ = 1.759 Å
$r_{La(2)-La(1)}$ = 2.325 Å
$r_{La(2)-O(3)}$ = 2.759 Å
$r_{La(2)-O(3)}$ = 2.759 Å
$r_{La(2)-Cu(2)}$ = 3.653 Å
$r_{La(2)-O(4)}$ = 3.124 Å

Valance of the ions are La = +3 , Cu = +3 , Sr = +2 , O = -2 (Sharp, 1990) using the above values for the distances from the reference atom in the sites Cu(1), and by substituting in equations 7 we see the change in the electrostatic potential by substitution of Sr instead of one of the La(1) ions as in figure 4.
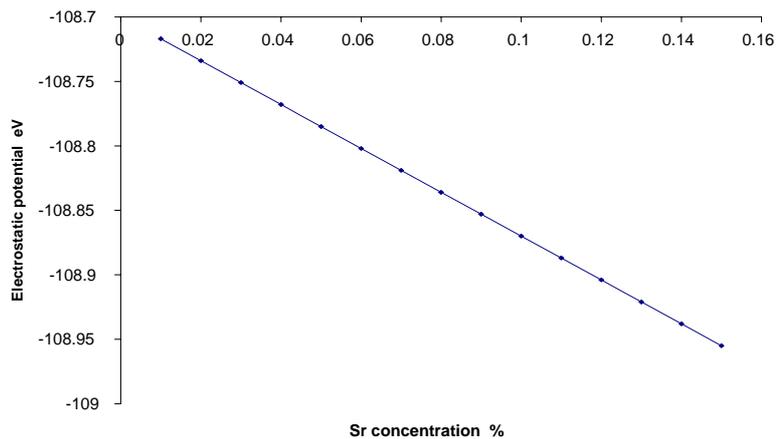

Fig. 4: Change in the electrostatic potential by substitution of Sr instead of one of the La(1)
        ions.

Using the above values for the distances from the reference atom in the sites La(2), and by substituting in equations 14 we see the change in the electrostatic potential by substitution of Sr instead of one of the La(2) ions as in figure 5.
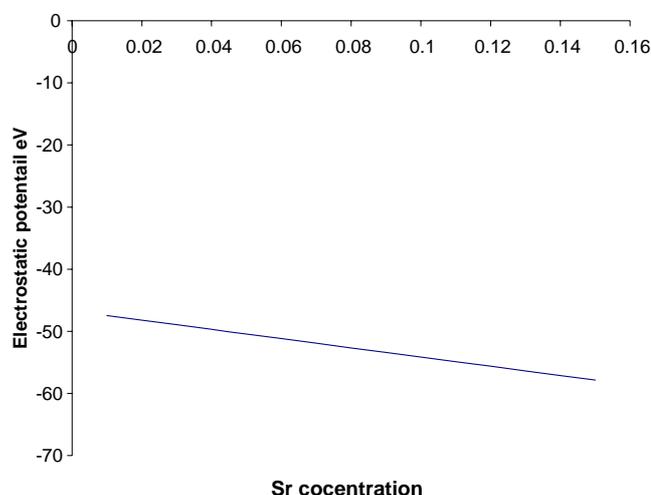

Fig. 5 : Change in the electrostatic potential by substitution of Sr instead La(2) ion .

By comparing the change in the P. E. by the substitution of the ion Sr in the sites Cu(1) and La(2) we find a great difference in the values of P.E. between the two sites, this is very evident in figure 6 where the P.E. is drawn as a function of Sr concentration for the two sites
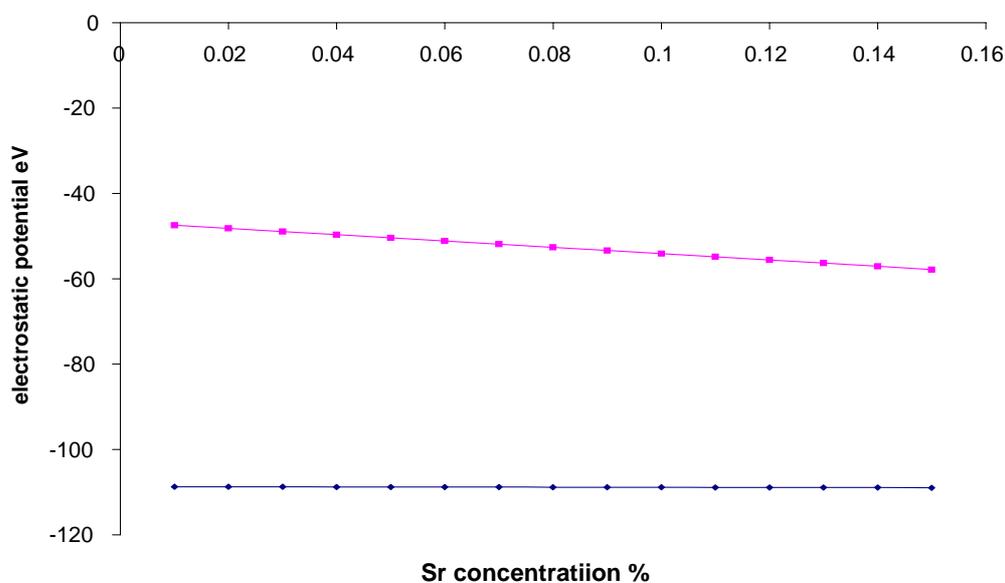

Fig. 6: Comparison of the drawing of P.E . as a function of Sr concentration for the sites La(2) (upper curve) and La(1) (lower curve) .

As shown from figure 6 substitution of Sr in the site La(2) lead to a greater change in (P. E.) than the substitution in the site Cu(1). This give indication that substitution instead of La(1) ion bring very small change in the P .E . so such substitution is the most probable Thus we have given the proof for settlement of Sr ion in the site. Our above result can explain the work of (Shelton, 1990) about the uniform distribution of the substituted atoms in the superconducting specimen, this happens because atoms takes certain sites in the crystal structure according to the (P. E.) for the crystal structure of that compound. This potential energy is the same for all crystals of the specimen so uniform substitution atoms occur.

As an ionic compound and as have been proved in this research that electrostatic potential play a major role in determining the site that the substituted atom will settled. This lead to think about the complex synthesis procedure (which will give a brief bellow) for the HTSC and one of them is the compound under study it is clear that electrostatic potential supply the stabilization of the superconducting compounds.

Complete synthesis procedure involve a sequence with individual steps. The starting materials are Cu and La oxides. The constituents powders must be mixed thoroughly the powders absorbed moister from air. This moister can be driven out by heat treatment. The mixed powder are pressed into pellet and in suitable crucible is subjected to a series of heat treatments to produce the solid state reaction that forms the K_2NiF_4-type phase   at temperature about 1000 C for 24 to 48 h, then if X-ray shows existence of secondary phase then heat   treatment repeated, then   another heat treatment at a lower temperature in Oxygen atmosphere then done, then slow cooling at a very slow rate is done .

The first step of synthesis is   mixing the oxides that forming the crystals approximately uniformly such that it is ready to the solid state reaction i.e. in any small volume of about volume of the crystal all constituents are exist. But in order that the above constituents will form the superconducting compounds, dissociation of this oxides must occur, and constituents must go into total or partial ionization, this lead to the action of the electrostatic forces to act between the ions and then forming the compound . In order that such dissociation of this oxides to occur, and constituents go into total or partial ionization high preparation temperature about 1100 K and its long duration, this long period give the sufficient time for the electrostatic forces to play its role so the that the compound is formed.

CONCLUSION

1 – Calculation of the electrostatic potential shows that change in the crystal energy is minimum if Sr is settled in one of the sites of the La ions around the central octahedral in the superconducting compound La_2CuO_4 in comparison with the sites of La ions above and below the central octahedral.

2 – Electrostatic potential of the crystal explains mechanism of substitution of Sr in the superconducting compound La_2CuO_4 this explains also some of the aspects of the complex procedure of synthesis of HTSC .

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