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# Nano-synthesis of promising families of HTc-superconductors to save electrical loss in the electrical Saudi Arabia net: Freeze dry synthesis of nano-Zr-added-2212-BPSCCO-superconductor

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## ABSTRACT

Saving energy loss through the conduction is the major goal for many advanced countries so superconductors are the essential material to achieve such these dreams. The present investigations were concerned by synthesis of pure BPSCCO $(Bi_{0.5}Pb_{0.5})_2\,Sr_2Ca_1Cu_2O_8$ and its variant zirconium containing composites with general formula : $Bi_{1+x}Zr_xPbSr_2Ca_1Cu_2O_z$ and, where x = 0.1, 0.2 and 0.3 mole % respectively, were prepared via soultion route (Freeze Drying Technique) to obtain nano-product. $ZrO_2$ has a limited effect on the main crystalline superconductive 2212-phase as x amount added increase as indicated in XRD measurements. SE-microscopy accompanied with EDX proved that, solution route was the best in the degree of homogneties and exact molar ratios. $ZrO_2$ exhibits strong interactions on Raman spectral modes of 2212-phase. $ZrO_2$ has a slight effect on Tc's even with maximum addition x = 0.3 mole. Finally the application of $ZrO_2$-nano-additives to the 2212-BPSCCO superconductors enhance the super-conduction mechanism and consequently save too much the amount of electricity loss on the main nets of electricity.



## KEYWORDS

Nano-additives;
Superconductors;
SEM;
XRD;
Raman spectra;
$ZrO_{2.}$

## INTRODUCTION

The cuprates offer a wide field of possibilities in terms of chemical composition, leading to tunable physical properties. Consequently, cationic substitutions and thermal treatments are commonly used as tools to modify the characteristics of a reference-compound.

Partial replacement of bismuth by lead in $(Bi/Pb)_2Sr_2CaCu_2O_{8+x}$ (Bi-2212) is known to induce important structural changes, as it suppresses the *c*-axis component of the modulation[1,2]. From the hole-doping point of view however, several reports suggest that Pb-incorporation does not affect the carrier concentration significantly[3,4].

It was noticed from resistivity measurements[5-7] or diamagnetic shielding observations[8] that the interlayer coupling would be affected instead, resulting in a reduction of the material's anisotropy. On the other hand, oxygen non-stoichiometry in the Bi-based cuprates was not studied as extensively as it was for example in $YBa_2Cu_3O_z$[9] and this is particularly true for the cation-substituted compounds. Nevertheless, it has been shown that oxygen excess in Bi-2212 varies in a small range but with a great effect on $T_c$[10-13] and is dependent on the cationic substitutions[14-16].

In the case of Bi-2212. The decrease of the oxygen content has been mentioned to explain the absence of a Pb-induced doping effect[17,18], but only a few data are available in the literature. Superconducting properties of Bi-2212 depend on oxygen content[19-23]. The superconducting transition temperature $T_c$ decreases for x =8.18 and is dependent on annealing temperature and cooling rate[24].

Oxygen vacancies have also been suggested as a major source of flux pinning in BSCCO[25]. The kinetics of oxygen motion and the formation and migration of oxygen defects in BSCCO have been studied by measurement of the oxygen –tracer diffusion parameters. These parameters provide not only input to the theoretical point –defect models, but can also be useful in developing fabrication techniques.

The pseudo-tetragonal 85 K -BSCCO superconductor of $Bi_2Sr_2CaCu_2O_x$ or 2:2:1:2 consists of one Ca atom symmetrically located between the layer sequences Cu-O, Sr-O and Bi-O each layer is parallel to the ab plane[26]. Most of studies reported on the 2223-phase are on Pb-doped compositions[27-31]. There are a few studies reported on the preparation of 2223 – from Pb free compositions containing a large excess of Bi, Ca / or Cu, for example, the nominal compositions $BiSrCaCu_2O_x$[32], $Bi_2Sr_2Ca_3Cu_4O_x$, $Bi_2Sr_2Ca_4Cu_5O_x$[33] and[34] were reported to lead a high volume fraction of the 2223 phase with variable amounts of impurity phases such as 2212, $Ca_2CuO_3$ and CuO.

A large number of precursor methods for preparation of 2223 were found to be superior to the conventional solid-state routes. It is known that, among the three superconducting phases of the Bi-Sr-Ca-Cu-O system, only 2201 is stable under high-oxygen pressures above 500°C both of 2212 and 2223-phases transform to a new non-superconducting orthorhombic perovskite with the same cation stoichiometery[35-41].

Many previous authors[27-31] investigated the doping effect of 3d-elements (M = Sc,Ti,V,..,Fe,Co,Ni and Zn) on the Cu-site of BPSCCO system and they reported that, the doping with 3d-elements affecting on stabilization of structural phase (2223) is responsible for HTc-superconducting properties and there is a correlation between 2223-superconductive phase stability and the valency of 3d-metal cation dopant. Reaction kinetics and phase purity of the products were observed to be dependent upon the starting precursors during the formation of 2223, 2212 invariably forms as an intermediates have been incorporated to form 2223 plus some of impurity phases. The presence of transient liquid phase such as $Ca_2PbO_4$ is reported to be essential for diffusion of additional Ca and Cu ions into the 2212 framework[42-45]. A special method was used to introduce Pb which significantly influenced the phase development and superconducting properties of the 2223 product[46].

Wu et al.[47] have used Raman techniques to identify variuos phases present in BPSCCO regime including alkaline earth cuprate, CuO, Bi-2212,Bi-2223 and Pb-containing phases specially $(Sr/Ca)_2PbO_4$.

Lu et al.[48] have investigated the effect of MgO and $Ag_2O$ oxides additives on the microstructure and superconducting properties of BPSCCO system and reported that, MgO addition did not affect the formation rate of 2212-phase which yields to 2223-phase, and could suppress the growth of Bi-free non-superconducting secondary phases furthermore, Shelke et al.[49] have investigated also the effect of HgO addition on the superconducting properties and microstructural properties of BPSCCO superconductor system deducing that, Tcs-offsets for 2212-BPSCCO variated in between 60 and 72 K according to the amount of HgO added.

Orlova et al.[50] have investigated the effect of $ZrO_2$ addition (1Wt% to 5Wt%) on the superconducting properties of sintered 123- Dy-Ba-Cu-O system and deduced that the best flux pinning in a magnetic field was achieved with maximum amount of addition $ZrO_2$ (5 Wt%). The aim of the present work is to investigate the influence of high valency cations nano-$Zr^{4+}$ inclusion additives on the hole-superconducting and physical properties PBSCCO regime aiming for:

1. Stabilizing oxygen content by using high charge cation ($Zr^{4+}$) partially in place of lower one ($Bi^{3+}$ /$Pb^{2+}$) site
2. to avoid toxicity of heavy metal (lead).

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3. Enhancing the superconduction mechanism to save energy loss during conduction.

## EXPERIMENTS

### Samples preparation

### Solution route (Freeze dry Synthesis)

The pure $(Bi_{0.5}Pb_{0.5})_2Sr_2Ca_1Cu_2O_8$ and its variant zirconium containing composites with general formula : $Bi_{1+x}Zr_xPbSr_2CaCu_2O_z$, where $x = 0.1, 0.2$ and 0.3 mole % respectively, were prepared using freeze drying technique starting with estimated nitrate solutions (0.2M) for all cations except lead took as lead acetate followed by mixing the exact volumes in liquid nitrogen matrix then the resultant forwarded into freeze drying machine (slow Programm for sensitive samples ~ 90 hrs). The obtained powders were ground and introduced to the same cycle of thermal treatment mentioned above.

### Phase identification

The X-ray diffraction (XRD) measurements were carried out at room temperature on the fine ground samples using Cu-$K_\alpha$ radiation source,Ni-filter and a computerized STOE diffractometer / Germany with two theta step scan technique.

Scannig Electron Microscopy (SEM) measurements were carried out using a small pieces of the prepared samples by using a computerized SEM camera with elemental analyzer unit (PHILIPS-XL 30 ESEM / USA)

### Superconducting measurements :

The cryogenic AC-susceptibility of the prepared materials was undertaken as a function of temperature recorded in the cryogenic temperature zone down to 30 K using liquid helium refrigerator.

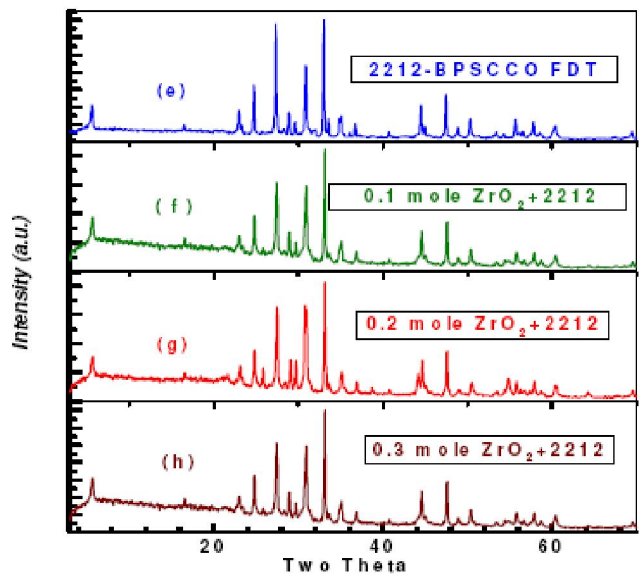
### Raman Spectroscopy measurements :

The measurements of raman spectra were carried out on the finally ground powders with Laser wavelength = 632.8 nm (He-Ne laser) and laser power applied to the site of the sample = 0.4 mW with microscope objective = x20.

## RESULTS AND DISCUSSION

### Phase identification:

Figure (1e-h) : displays the X-ray powder diffractometry patterns of the pure $(Bi_{0.5}Pb_{0.5})_2Sr_2Ca_1Cu_2O_8$ and variant Zr-additive content composites : $BiZr_{0.1}PbSr_2CaCu_2O_z$, $BiZr_{0.2}PbSr_2CaCu_2O_z$, and $BiZr_{0.3}PbSr_2CaCu_2O_z$ prepared via freeze drying technique respectively. Analysis of the corresponding 2θ values and the interplanar spacings d (A°) were carried out, and indicated that, the X-ray crystalline structure mainly belongs to a single tetragonal phase 2212 in major besides $Ca_2PbO_4$ secondary phase in minor. The unit cell dimensions were calculated using the most intense X-ray reflection peaks (see TABLE 1) to be $a = b = 3.8141$A° and $c = 30.7732$ A° for the pure 2212-BPSCCO phase which is in full agreement with those mentioned in literature.




**(e) x = 0.0 mole (f) x = 0.1 mole (g) x = 0.2 mole (h) x = 0.3 mole superconductors prepared by freeze drying technique.**

**Figure 1 (e-h) : X-ray diffraction patterns for the pure and variant $ZrO_2$ 2212-BPSCCO**

**TABLE 1 : The calculated lattice parameters for the prepared samples.**

| Material | a = b (A°) | c (A°) |
|---|---|---|
| $(Bi_{0.5}Pb_{0.5})_2Sr_2Ca_1Cu_2O_8$ | 3.8141 | 30.7832 |
| $BiZr_{0.1}PbSr_2Ca_1Cu_2O_z$ | 3.8254 | 30.5720 |
| $BiZr_{0.2}PbSr_2Ca_1Cu_2O_z$ | 3.8332 | 30.1827 |
| $(BiZr_{0.3}PbSr_2Ca_1Cu_2O_z$ | 3.8264 | 30.1731 |

It is obvious that the additions of $ZrO_2$ has a negligible effect on the main crystalline structure 2212-phase by increasing Zr-content ($x = 0.1 \rightarrow 0.3$ mole).

From TABLE (1) one can indicate that *c*-axis decreases as zirconium dopant concentration increase from 0.1 to 0.2 while no noticeable effect from 0.2 to 0.3. This is an indication for ($Zr^{4+}$) might substitute by some extent in the superconductive lattice and correlated with atomic radius of zirconium which is smaller than that of bismuth ($Zr^{4+}$ = 0.72 A° while $Bi^{3+}$ is 1.17 A°) and alteration of Ca/Sr ratios which for c-axis is dependent[2].

Some authors[48] reported that the formation of 2212-phase comes from the step sequence reaction:

$$Ca_2PbO_4 \rightarrow CaO + \text{Pb-rich-phase} \quad (1)$$

$$2CaO + CuO \rightarrow Ca_2CuO_3 \quad (2)$$

$$Bi_2O_3 + Pb + CuO \rightarrow (Bi/Pb)_2CuO_4 \quad (3)$$

$$(Bi/Pb)_2CuO_4 + 2SrO \rightarrow (Bi/Pb)_2Sr_2CuO_6 \text{ 2201-phase} \quad (4)$$

$$\tfrac{1}{2}(CuO + Ca_2CuO_3) + 2201 \rightarrow \text{2212-phase} \quad (5)$$

In this respect, one can expect that $ZrO_2$-additives to 2212 system produce some of Zr-based phases which is highly compatible with the superconductor phase specially the solubility of zirconium is enhanced via intermediate zirconate formation at the expense of the originally present Ca and Sr[51].

Thus, equilibrium between Bi-2201 and $Sr_{1-x}Ca_xZrO_3$ was achieved throughly the initial stage of synthesis :

$$Zr^{4+} + Ca/Sr \rightarrow (Ca/Sr)ZrO_3 \quad (6)$$

$$(Ca/Sr)ZrO_3 + CuO + 2201\text{-}Bi_2Sr_2CuO_4 + \text{Pb-rich} \rightarrow 2212 \quad (7)$$

Thus, the amount of zirconate might be amorphous and consequently too difficult to be detected by X-ray means even for maximum Zr-addition x = 0.3 mole. (see Figure1d),these results are in partial agreement with[51].

Liu et al.[52] supporte and reinforce our view in their studies on phase transformation and conversion for 2201->2212 deducing that the optimal annealing temperature to convert liquid phase of (Bi-Pb-Sr-Ca-Cu) mixture into 2212-phase is 795 °C and at annealing temperatures in the range (830-845 C°) 2223-phase decomposes to 2212 plus other phases and consequently 2212-becomes the major phase.

## Raman spectroscopy

Figures(2a-d) : shows the Raman spectrograms for pure and Zr(IV)-added 2212-BPSCCO system. From the modes frequencies which are listed and compared with some references see TABLE (2), one can indicate that 2212-BPSCCO phase is the domainating phase present in our polycrystalline BPSCCO beside small traces of strontium calcium plumbates and 2201-impurity phases.

**TABLE 2 : Mode Frequencies of Raman spectra recorded for Zr(IV) added-2212 BPSCCO in the present work in contrast with some references.**

| Present work | Mode frequencies $cm^{-1}$ | | Zr-added -2212 | |
|---|---|---|---|---|
| References Ref.51 Ref.54 | 2212 x= 0 | x = 0.1 | x = 0.2 | x = 0.3 |
| 282 285 | 261* | 259* | 265* | 259* |
| 296 295 | 324+ | 346+ | 323+ | 321+ |
| 313 355 | 373* | 403* | 412* | 412* |
| 391 400 | 406 | 461* | 461* | 454* |
| 469 465 | 501* | - | - | - |
| - 497 | 579° | 550° | 558° | 549° |
| 631 630 | 627* | 625* | 631* | 634* |
| 659 660 | 660* | 651* | 659* | - |

*** 2212-phase, + 2201-phase, ° $(Sr/Ca)_2PbO_4$**

It can be concluded from references[53,54,47] for the undoped 2212-phase the first order Raman mode frequencies are mainly located at the following ranges i.e., 290-330, 460-470, and 620-640 $cm^{-1}$ (the given ranges depend on samples compositions) and the most important modes frequencies are the $A_g$ mode of $O_{Bi}$ atoms vibration along the *c*-axis (290-330 $cm^{-1}$), the the $A_g$ mode of $O_{Sr}$ atoms vibration along the *c*-axis (460-470 $cm^{-1}$), and the the the $A_g$ mode of $O_{Bi}$ atoms vibration along the *a*-axis (620-640 $cm^{-1}$) which is induced by orthorhombic distortion. Furthermore, another shoulder peak (650-660 $cm^{-1}$) at the higher frequency side of the ~ 630 $cm^{-1}$ line which is fully typical with our results. This shoulder is ascribed to $A_g$ vibrational mode of extra oxygen atoms residing in the double layers[53,54].

It is important to notify that the mode frequency lying at ~ 630 $cm^{-1}$ is usually the most intense band for all three phases of BPSCCO superconductors (2201,2212 and 2223)when they are in a polycrystalline state[47].

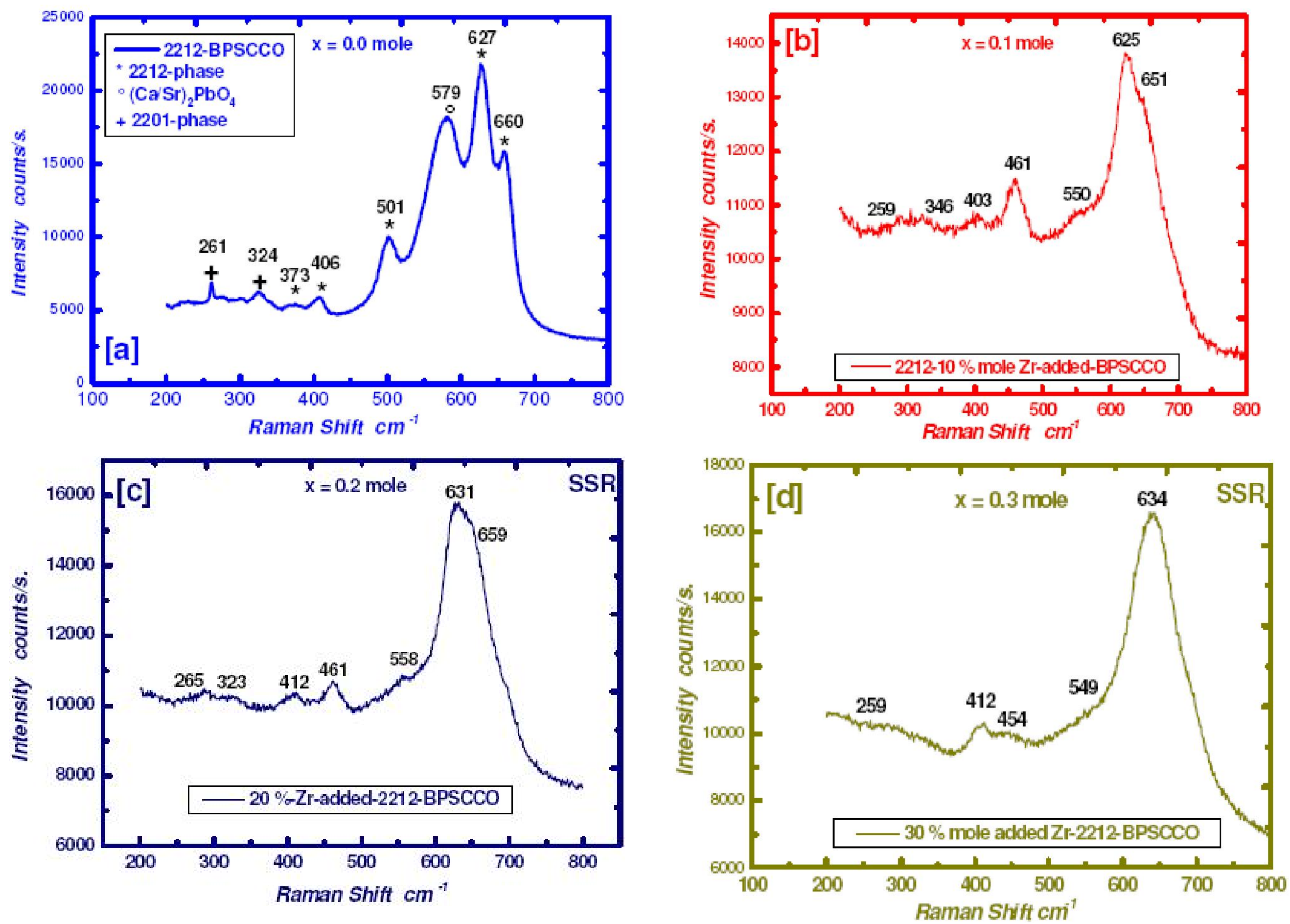
From Figure (2a-d), Raman spectrograph for 2212-BPSCCO and its added Zr-2212 samples, the only violation from references of single crystal Raman spectrum is the band lies ~324 $cm^{-1}$ which is ascribed to the 2201 phase as reported in[52] and the band appears ~ 500 $cm^{-1}$ which also belongs to our main phase 2212 as reported by Sapriel et al.[55] who appears in their Raman spectrogram for 2212 single crystal band lies ~

497 cm$^{-1}$ which is fully supporting our results. The band appears ~ 560 G10 cm$^{-1}$ is indicated by existence of lead-rich phase $(Sr/Ca)_2PbO_4$ as reported in[47] that also confirmed in our XRD.

From Figure (2a-d), it is clear that, as amount of Zr(IV)-added increases the bands lie ~ 579 corresponds to lead-rich phase plumbates) and the shoulder at 660 cm$^{-1}$ (corresponds to the vibrational modes of extra oxygen atoms inside the bi-layer BPSCCO[53,54]) begin to be broad till complete broadening with maximum addition x = 0.3 mole. In our opinion it might due to Zr(IV) added consumes some extent of Sr/Ca and extra oxygen to form zirconate impurity amorphous phase as described in eq.(6).

**SE-microscopy measurements**

Figure (3a-d), show the *SE*-micrographs for pure and Zr-doped PBSCCO with x = 0.1 $\rightarrow$ 0.3 mole prepared by *Freeze Drying Technique*. The samples were measured as fine ground powders, the average particle size estimated to be in between 0.3 and 1.4 μm which is considered high to that estimated from solid state route. The micrographs taken are more homogeneous than those for samples prapared via solid state route which reflect the priority to freeze drying technique than solid state route (SSR).




**(a) x = 0.0 mole (b) x = 0.1 mole (c) x = 0.2 mole (d) x = 0.3 mole**

**Figure 2a-d : Raman Spectra for Zr-added-2212-BPSCCO**

TABLE (3-6), is the EDX average data estimated from examinations of random spots inside the same sample for pure and Zr-added polycrystalline doped – PBSCCO prepared by freez dry technique.

The analysis of EDX data obtained from TABLE (3) for pure 2212BPSCCO prepared by solid state route (SSR) give us the following, stoichoimetric molar ratios Bi/Pb : Sr : Ca : Cu : O = 1.63 : 1.66 : 1 : 1.89 : 7.7 while the EDX analysis for the same parent pure-2212 BPSCCO prepared by freez dry technique see TABLE

(4) Bi/Pb : Sr : Ca : Cu : O = 1.84 : 1.98 : 1 : 1.98 : 8.13. These results proved that, the differences in the molar ratios EDX estimated for the same sample is totally better in FDT that emphasized also in their magnetic behaviour and good evidence for the existence of 2212 superconductive phase with good approximate molar ratios.

**TABLE 3 : EDX elemental data for pure-2212-BPSCCO (FDT).**

| 2212-BiPb | 2212-BiPb | | | | | |
|---|---|---|---|---|---|---|
| **Element** | **Wt %** | **Average At %** | **K-Ratio** | **Z** | **A** | **F** |
| O K | 15.63 | 51.25 | 0.029 | 1.1894 | 0.1531 | 1.0004 |
| CaK | 5.14 | 6.32 | 0.0379 | 1.1433 | 0.6253 | 1.0021 |
| CuK | 18.11 | 12.48 | 0.1831 | 1.0236 | 0.9507 | 1.0323 |
| PbL | 18.71 | 5.65 | 0.1513 | 0.8181 | 1.0218 | 1.0178 |
| BiL | 19.24 | 5.98 | 0.1664 | 0.8155 | 1.0121 | 1.0211 |
| SrK | 21.21 | 12.51 | 0.1923 | 0.9674 | 0.9783 | 1 |

**TABLE 4 : EDX elemental data for 0.1 mole added-$ZrO_2$-2212-BPSCCO (FDT).**

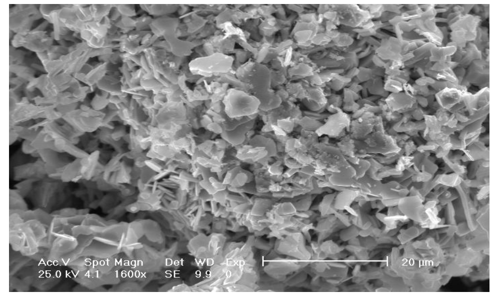
| Element | Average At% | K-Ratio | Z | A | F |
|---|---|---|---|---|---|
| O K | 53.26 | 0.029 | 1.194 | 0.1531 | 1.0004 |
| CaK | 7.53 | 0.0379 | 1.1433 | 0.6253 | 1.0021 |
| CuK | 15.13 | 0.1831 | 1.0246 | 0.9507 | 1.0313 |
| Bil | 14.18 | 0.1664 | 0.8175 | 1.0131 | 1.0211 |
| SrK | 13.31 | 0.1923 | 0.9674 | 0.9783 | 1 |
| ZrK | 1.657 | 0.0253 | 0.9735 | 0.9832 | 1 |

**TABLE 5 : EDX elemental data for 0.2 mole added-$ZrO_2$-2212-BPSCCO (FDT).**

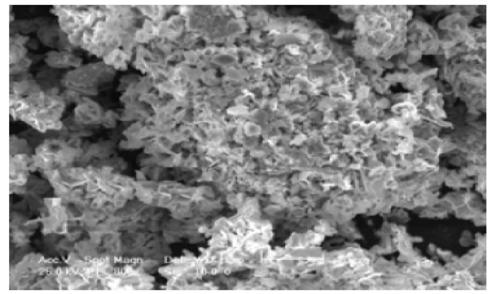
| Element | Average At % | K-Ratio | Z | A | F |
|---|---|---|---|---|---|
| O K | 53.56 | 0.029 | 1.194 | 0.1631 | 1.0004 |
| CaK | 7.63 | 0.0379 | 1.1433 | 0.6253 | 1.0021 |
| CuK | 15.18 | 0.1831 | 1.0246 | 0.9507 | 1.0313 |
| BiL | 14.28 | 0.1664 | 0.8175 | 1.0131 | 1.0211 |
| SrK | 13.31 | 0.1923 | 0.9674 | 0.9783 | 1 |
| ZrK | 3.157 | 0.0253 | 0.9735 | 0.9831 | 1 |

**TABLE 6: EDX elemental data for 0.3 mole added-$ZrO_2$-2212-BPSCCO (FDT).**

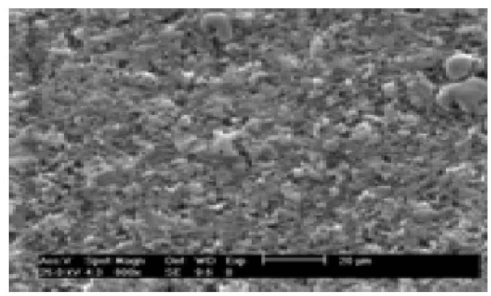
| Element | Average At % | K-Ratio | Z | A | F |
|---|---|---|---|---|---|
| O K | 52.53 | 0.029 | 1.194 | 0.1531 | 1.0004 |
| CaK | 7.63 | 0.0379 | 1.1433 | 0.6233 | 1.0023 |
| CuK | 15.32 | 0.1831 | 1.0246 | 0.9507 | 1.0313 |
| BiL | 14.61 | 0.1664 | 0.8175 | 1.0131 | 1.0221 |
| SrK | 13.56 | 0.1923 | 0.9674 | 0.9783 | 1 |
| ZrK | 4.61 | 0.0253 | 0.9735 | 0.9824 | 1 |



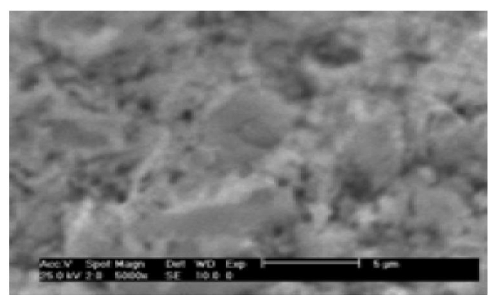
**(a) Pure BiPb-2212 (FDT).**

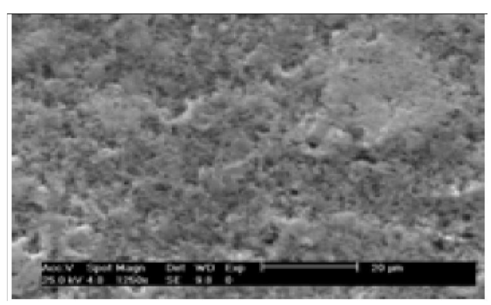


**(b) 0.1 mole -$ZrO_2$-added BiPb-2212 (FDT) .**



**(c) 0.2 mole -$ZrO_2$-added BiPb-2212 (FDT).**



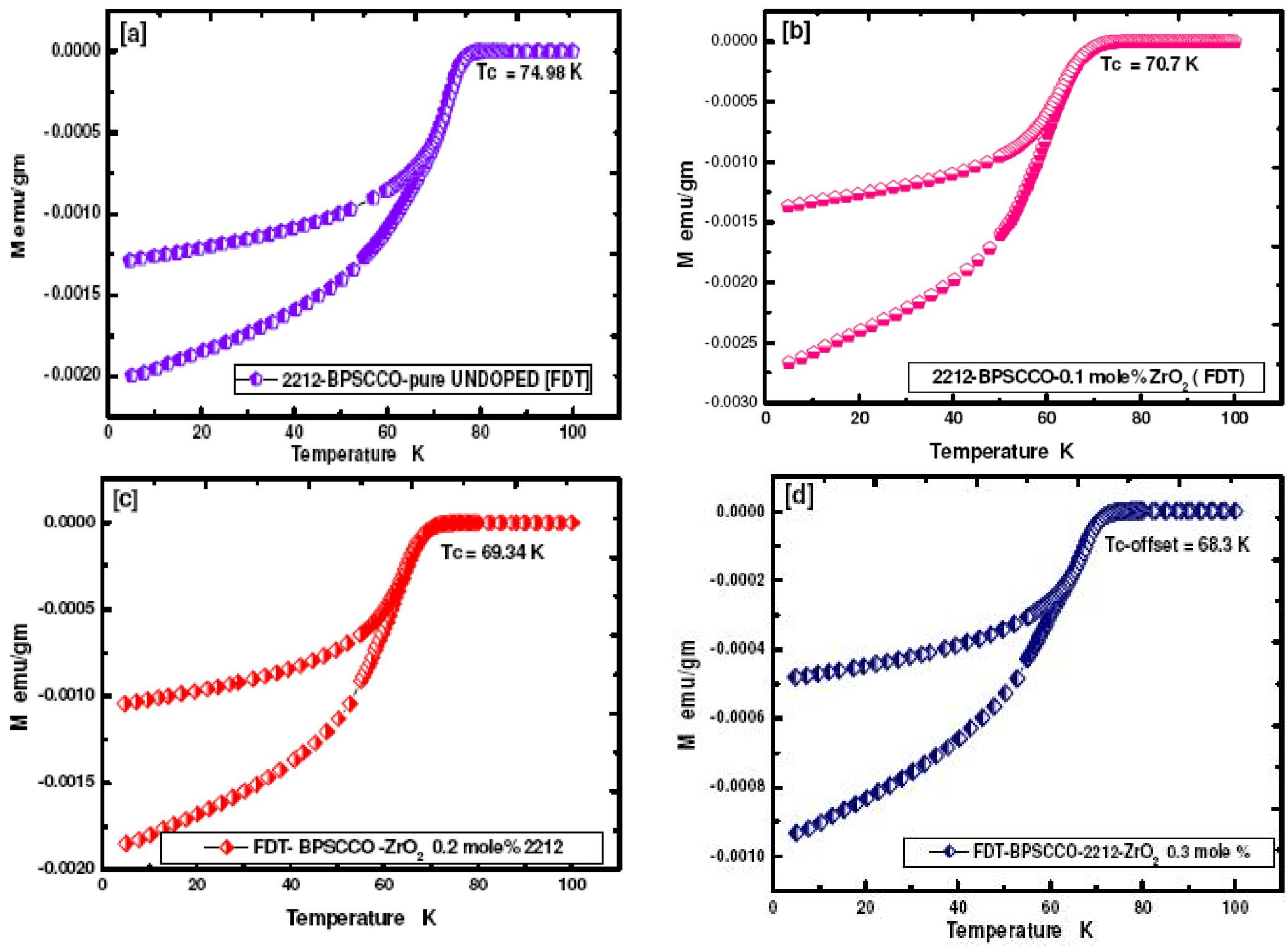


**(d) 0.3 mole -$ZrO_2$-added BiPb-2212 (FDT) .**

**Figure 3a-d : SE-micrographs for pure 2212-BPSCCO prepared by Freeze. Drying Technique (FDT) and variant added-ZrO2 samples.**

## Superconductivity measurements

Figure (4a-d): shows the AC-magnetic susceptibility curves (Meissner & Shielded lines) for pure and Zr-added samples with x = 0.1 – 0.3 mole respectively prepared through solution route *Freeze Drying Technique* (FDT).




**(a) x = 0.0 mole, (b) x = 0.1 mole, (c) x = 0.2 mole and (d) x = 0.3 mole**

**Figure 4a-d : AC- Susceptibility curves for Zr-added 2212 (F DT).**

One can indicate that, 2212-undoped PBSCCO sample exhibits HTc ~74.95 K corresponding to 2212-phase which is annealed in oxygen and noticeable clearly in our XRD as major phase and this tc for 2212-phase is relatively better than that prepared by freez dry technique $\Delta$Tc = 0.65 K. This confirmed magnetically the existence of 2212 in highly homogeneous pure phase, while the samples with Zr-dopant x = 0.1 – 0.3 mole exhibit slight surpress in their Tc's 70.7,69.34 and 68.3 K respectively, which reflects the promotion of the homogeneity degree in freeze drying (FDT) technique than that prepared by normal. One can compare between the two techniques of preparation SSR and FDT and conclude that, the differences in Tc's between the minimum Tc's samples with x = 0.3 mole is $\Delta$Tc = 2.75 K emphasize that, impurity phases such as zirconate inclusions or lead-rich plumbates dispersed regularly throughout the sample mixture with minimum ratios of formation achieving maximum degree of homogeneity as confirmed in SEM and EDX analyses.

## CONCLUSIONS

Conclusive remarks can be summarized as;

1. Soultion route (Freeze Drying Technique) yield to nano-product.
2. $ZrO_2$ has a limited effect on the main crystalline superconductive 2212-phase as Zr- amount added increases.

3. Only lead-rich-plumbates appears as secondary phase in minor.
4. SE-microscopy accompanied with EDX proved that, solution route was the best in the degree of homogneties and exact molar ratios.
5. $ZrO_2$ exhibits strong interactions on Raman spectral modes of 2212-phase.
6. $ZrO_2$ has a slight effect on Tc's even with maximum addition x = 0.3 mole.
7. Finally the application of $ZrO_2$-nano-additives to the 2212-BPSCCO superconductors enhance the super-conduction mechanism and consequently save too much the amount of electricity loss on the main nets of electricity.

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## REFERENCES

**[1]** C.H.Chen, D.J.Werder, G.P.Espinosa, A.S.Cooper; Phys.Rev.B, **39**, 4686 **(1989)**.
**[2]** J.Schneck, L.Pierre, J.C.Tolédano, C.Daguet; Phys.Rev.B, **39**, 9624 **(1989)**.
**[3]** A.Maeda, M.Hase, I.Tsukada, K.Noda, S.Takebayashi, K.Ushinokura; Phys.Rev.B, **41**, 6418 **(1990)**.
**[4]** M.Weber, A.Amato, F.N.Gygax, A.Schenk, H.Maletta, V.N.Duginov, V.G.Grebinnik, A.B.Lazarev, V.G.Olshevsky, V.Y.Pomjakushin, S.N.Shilov, V.A.Zhukov, B.F.Kirillov, A.V.Pirogov, A.N.Ponomarev, V.G.Storchak, S.Kapusta , J.Bock; Phys.Rev.B, **48**, 3022 **(1993)**.
**[5]** F.X.Régi, J.Schneck, H.Savary, C.Daguet, F.Huet; IEEE Trans.Appl.Supercond, **3**, 1190 **(1993).**
**[6]** J.Ma, P.Alméras, R.J.Kelley, H.Berger, G.Margaritondo, X.Y.Cai, Y.Feng, M.Onellion; Phys.Rev.B, **51**, 9271 **(1995)**.
**[7]** L.Winkeler, S.Sadewasser, B.Beschoten, H.Frank, F.Nouvertné, G.Güntherodt; Physica C, **265**, 194 **(1996)**.
**[8]** L.Manifacier, G.Collin, N.Blanchard; Int.J.Modern Phys.B, **12**, 3306 **(1998)**.
**[9]** T.B.Lindemer, J.F.Hunley, J.E.Gates, A.L.Sutton, Jr., J.Brynestad, C.Hubbard; J.Am.Ceram.Soc., **72**, 1775 **(1989)**.
**[10]** C.Allgeier, J.S.Schilling; Physica C, **168**, 499 **(1990)**.
**[11]** H.M.O'Bryan, W.W.Rhodes, P.K.Gallagher; Chem.Mater., **2**, 421**(1990)**.
**[12]** M.R.Presland, J.L.Tallon, R.G.Buckley, R.S.Liu, N.E.Flower; Physica C, **176**, 95 **(1991)**.
**[13]** R.Sieburger, P.Müller, J.S.Schilling; Physica C, **181**, 335 **(1991)**.
**[14]** A.Manthiram, J.B.Goodenough; Appl.Phys.Lett., **53**, 420 **(1988)**.
**[15]** W.A.Groen, D.M.de Leeuw, L.F.Feiner; Physica C, **165**, 55 **(1990)**.
**[16]** D.B.Mitzi, L.W.Lombardo, A.Kapitulnik, S.S.Laderman, R.D.Jacowitz; Phys.Rev.B, **41**, 6564 **(1990)**.
**[17]** J.L.Tallon, R.G.Buckley, P.W.Gilberd, M.R.Presland; Physica C, **158**, 247 **(1989)**.
**[18]** G.V.M.Williams, D.M.Pooke, D.J.Pringle, H.J.Trodahl, J.L.Tallon, J., A.Crossley, L.F.Cohen; Phys.Rev.B, **63**, 589 **(2001).**
**[19]** H.Niu, N.Fukushima, K.Ando; Jpn.,Appl.Phys., **27**, L1442 **(1988)**.
**[20]** D.E.Morris, C.T.Hultgren,A.M. Markelz, J.Y.T.Wei, N.G.Asmar, J.H.Nickel; Phys.Rev.B, **39**, 6612 **(1989)**.
**[21]** J.Zhao, M.S.Seehra; Physica C, **159**, 639 **(1989)**.
**[22]** M.R.Presland, J.L.Tallon, R.G.Buckely, R.S.Liu, N.Flower; Physica C, **176**, 95 **(1990).**
**[23]** H.C.I.Kao, W.L.Chen, T.P.Wei, J.C.Lui, C.M.Wang; Physica C, **177**, 376 **(1993)**.
**[24]** J.M.Tarascon, W.R.McKinnon, P.Barboux, D.M.Hwang, B.G.Bagley, L.H.Greene, G.W.Hull, Y.Lepage, N.Stoffel, M.Giround; Phys.Rev.B, **38**, 885 **(1988)**.
**[25]** E.M.Chudnovsky; Phys.Rev.Lett., **65**, 3060 **(1990)**.
**[26]** R.M.Hazen, C.T.Prewitt, R.G.Angel, N.L.Ross, L.W.Finger, C.G.Hadidiacos, D.R.Veblen, P.H.Hor, R.L.Meng, C.W.Chu; Phys.Rev.Lett., **60**, 1174 **(1988)**.
**[27]** S.A.Sunshine, T.Siegrist, L.F.Schneemeyer, D.W.Murphy, R.J.Cava, B.Batlogg, R.B.Van Dover, S.Nakahara, R.Farrow, P.Marsh, L.W.Rupp, W.P.Peck; Phys.Rev.B, **38**, 898 **(1988)**.
**[28]** B.W.Statt, Z.Wang, M.G.Lee, J.V.Yakhmi, P.C.De, J.F.Major, J.W.Rutter; Physica C, **15**, 156 **(1988)**.

[29] G.Calestani, C.Rezzoli, G.D.Andreetti, E.Buluggiu, D.C.Giori, A.Valenti, G.G.Ammoretti; Physica C, **158**, 217 **(1988)**.

[30] M.Ueyama, T.Hikata, T.Kato, K.Sato; Jpn., J.Appl.Phys., **30**, L1384 **(1991)**.

[31] Q.Li, K.Brodersen, H.A.Hjuler, T.Freltoft; Physica C, **217** 360 **(1993)**.

[32] D.C.Larbalesteir, X.Y.Cai, Y.Feng, H.Edelman, A.Umezawa, G.N.Riley, W.L.Carter; Physica C, , **221**, 299 **(1994)**.

[33] C.Namgung, E.E.Lachowski, J.T.S.Irvine, A.R.West; Powder Diff., **7**, 49 **(1992)**.

[34] D.Shi, M.Tang, M.S.Boley, M.Hash, K.Vandervoort, H.claus, Y.N.Lwin; Phys.Rev.B, **40**, 2247 **(1989)**.

[35] A.Sumiyama, T.Yoshitomi, H.Endo, J.Tsuchiya, W.Kijima, M.Mizuno, Y.Oguri; Jpn., J.Appl.Phys., **27**, 542 **(1988)**.

[36] P.V.S.Sastry, J.V.Yakhmi, R.M.Iyer; Physica C, **161**, 665 **(1989)**.

[37] D.E.Dorris, B.C.Prorok, M.T.Lanagan, S.sinha, R.B.Poepppel; Physica C, **212**, 66 **(1993)**.

[38] D.Pandey, R.Mahesh, A.K.Singh, V.S.Tiiwari, S.K.Singh; Solid State Commun., **67**, 655 **(1990)**.

[39] X.Zhengping, Z.Lian, J.Chunlin; Supercond.Sci. Technol., **5**, 240 **(1992)**.

[40] M.G.Smith, J.O.Wills, D.E.Poterson, J.F.Bingert, D.S.Phillips, J.Y.Coulter, K.V.Salazar, W.L.Hults; Physica C, **231**, 409 **(1994)**.

[41] R.Cloots, H.Bougrine, M.Houssa, S.Stassen, L.D.Urzo, A.Rulmont, M.ausloos; Physica C, **231**, 259 **(1994)**.

[42] P.V.S.Sastry, A.R.West; J.Mater.Chem., **4**, 647 **(1994)**.

[43] W.Wong-Ng, C.K.Chiang, S.W.Freiman L.P.Cook, M.D.Hiill; Am.Ceram.Soc.Bull., **71**, 1261 **(1992)**.

[44] Y.T.Huang, W.N.Wang, S.F.Wu, C.Y.Shei, W.M.Hurang, W.H.Lee, P.T.Wu; J.Am.Ceram. Soc., **73**, 3507 **(1990)**.

[45] Y.L.Chen, R.Stevens; J.Am.Ceram.Soc., **75**, 1150 **(1992)**.

[46] S.E.Dorris, B.C.Prorok, M.T.Lanagen, N.B.Browning, M.R.Hazen, J.A.Parell, Y.Feng A.Umezawa, D.C.Larbalester; Physica C, **223**, 163 **(1993)**.

[47] K.T.Wu, A.K.Fisher, V.A.Maroni; J.Mater.Res., **12**, 1195 **(1997)**.

[48] X.Y.Lu, A.Nagata, K.Sugawara, S.Kamada; Physica C, **335**, 51 **(2000)**.

[49] V.Shelke, H.Tewari, N.Gaur, R.Singh; Physica C, **300**, 217 **(1998)**.

[50] T.S.Orlova, J.Laval, C.N.Huong, A.Dubon; Supercond.Sci.Technol., **14**, 59 **(2001)**.

[51] P.E.Kazin, M.Makarova, M.Jansen, T.Adelsberger, Y.Tretyakov; Supercond.Sci.Technol., **10**, 616 **(1997)**.

[52] H.K.Liu, R.Zeng, X.Fu, S.X.Dou; Physica C, **325**, 70 **(1999)**.

[53] M.Cardona, C.Thomson, R.Liu, H.G.Von Schnering, M.Hartweg, Y.F.Yan, Z.X.Zhao; Solid State Commun., **66**, 1225 **(1988)**.

[54] L.A.Farrow, L.H.Greene, J.M.Tarascon, P.A.Morris, W.A.Bonner, G.W.Hull; Phys.Rev.B, **38**, 752 **(1988)**.

[55] J.Sapriel, L.Pierre, D.Morin, J.Toledano, J.Schneck, H.Savary, J.Chavignon, J.Primot, C.Daguet, J.Etrillard, Phys.Rev.B; **39**, 339 **(1989)**.

[56] L.D.Zang, J.M.Mu; ‘Nanomaterial Science, Liaoning Science& Technology Press, Shengyan, China’, **92**, **(1994)**.

[57] I.Bradea, S.Popa, G.Aldica, V.Mihalache, A.Crisan; J.Supercond., **15**, 237 **(2002)**.