NANO-SYNTHESIS OF PROMISING FAMILIES OF HT_C-SUPERCONDUCTORS TO SAVE ELECTRICAL LOSS IN THE ELECTRICAL POWER IN SAUDI ARABIA NET

(FREEZE DRY SYNTHESIS OF NANO-Zr-ADDED-2212-BPSCCO-SUPERCONDUCTOR)

Khaled M. Elsabawy[a,b]* and **Waheed F. El-Hawary[a,c]**

Saving energy loss through the conduction is the major objective of several advanced countries so superconductors are the essential material to achieve such these demands. The present investigations were concerned by synthesis of pure BPSCCO ($Bi_{0.5}Pb_{0.5})_2Sr_2Ca_1Cu_2O_8$ and its variant zirconium containing composites with general formula : $Bi_{1+x}Zr_xPbSr_2Ca_1Cu_2O_z$, where x=0.1, 0.2 and 0.3 mole % respectively, were prepared via solution 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 along 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 T_c'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 .

*Corresponding Authors
    *E-mail: ksabawy@yahoo.com and
    ksabawy@hotmail.com
[a]   Department of Chemistry, Faculty of Science, Taif
       University, 888- Taif, Kingdom of Saudi Arabia
[b]   Materials Unit , Chemistry Department ,Faculty of Science,
       Tanta University, 31725-Tanta –Egypt
[c]   Department of Chemistry, Faculty of Science, Cairo
       University, Egypt

Introduction

The cuprates offer a wide field of possibilities in terms of chemical composition, leading to required 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.[1416]

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 following layers sequences Cu-O, Sr-O and Bi-O and 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] $Bi_2Sr_2Ca_3Cu_4O_x$, $Bi_2Sr_2Ca_4Cu_5O_x$[33,34] 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 stoichiometry.[35-41]

Many previous workers[27-31] have 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 HT_c-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 determined 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, T_c's-offsets for 2212-BPSCCO variated in between 60 and 72 K according to the amount of HgO added.

Orlova et al.[50] have determined the effect of ZrO_2 addition (1 wt.% to 5 wt.%) 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 stabilizing oxygen content by using high charge cation (Zr^{4+}) partially in place of lower one (Bi^{3+}/Pb^{2+}) site to avoid toxicity of heavy metal (lead) and enhancing the super-conduction 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 program for sensitive samples ~ 90 h).

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_α 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:

Fig. 1a-d 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(Å) 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 Å and c=30.7732 Å for the pure 2212-BPSCCO phase which is in full agreement with those mentioned in literature.

Table 1. The calculated lattice parameters for the prepared samples

Material	a = b (Å)	c (Å)
$(Bi_{0.5}Pb_{0.5})_2Sr_2CaCu_2O_8$	3.8141	30.7832
$BiZr_{0.1}PbSr_2CaCu_2O_z$	3.8254	30.5720
$BiZr_{0.2}PbSr_2CaCu_2O_z$	3.8332	30.1827
$(BiZr_{0.3}PbSr_2CaCu_2O_z$	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→ 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 Å while Bi^{3+} is 1.17 Å) and alteration of Ca/Sr ratios which for c-axis is dependent.[2]
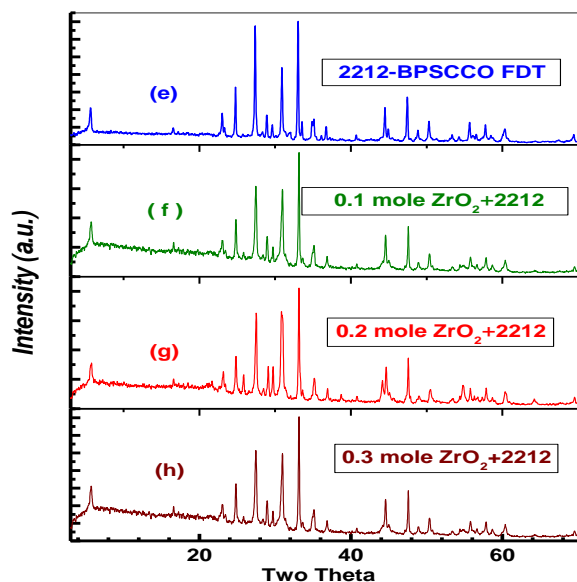
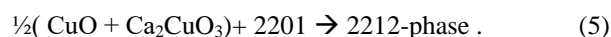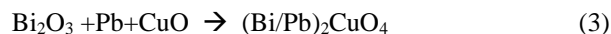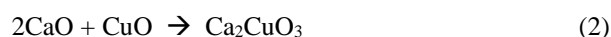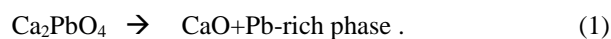Figure 1.a-d. X-ray diffraction patterns for the pure and variant ZrO_2 2212-BPSCCO superconductors prepared by freeze drying technique. (e): x=0.0 mole; (f): x = 0.1 mole; (g): x=0.2 mole; (h): x=0.3 mole

Some authors such as Lu et al.[48] reported that the formation of 2212-phase comes from the step sequence reaction:

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

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

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

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

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

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 :

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

$$(Ca/Sr)ZrO_3 + CuO + 2201 - Bi_2Sr_2CuO_4 +$$

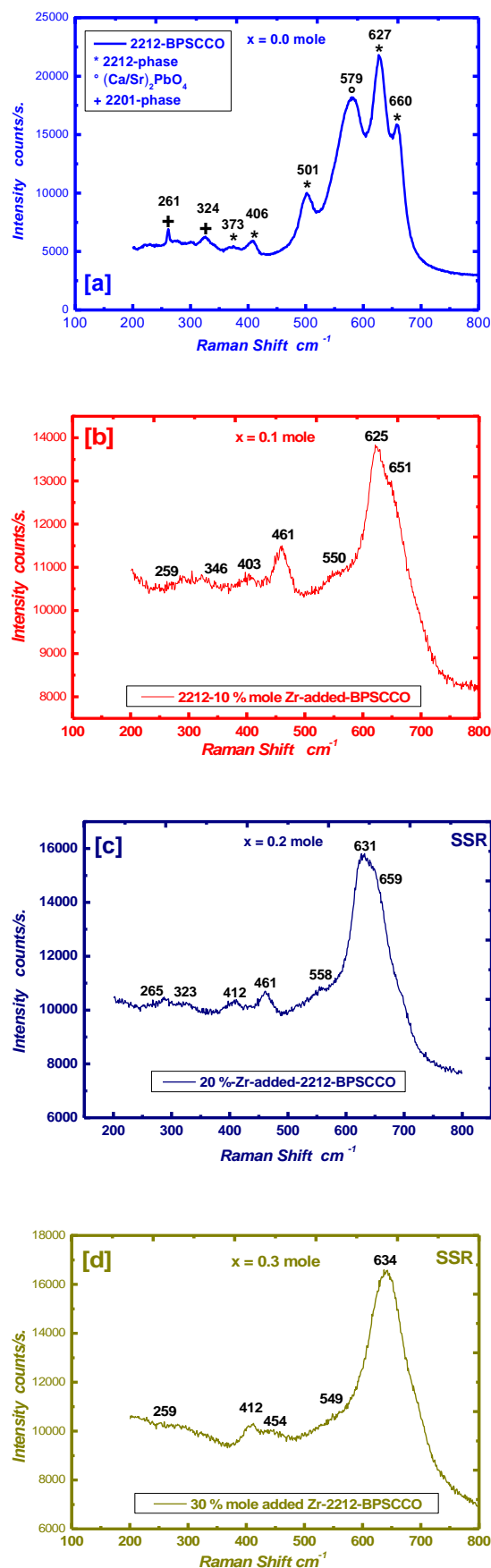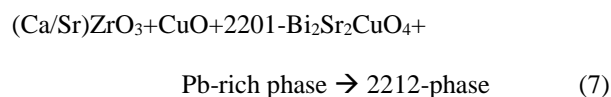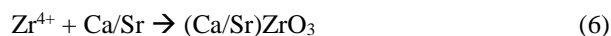$$Pb\text{-rich phase} \rightarrow 2212\text{-phase} \qquad (7)$$

Figure 2.a-d. Raman Spectra for Zr-added-2212-BPSCCO; (a): *x*=0.0 mole; (b): *x*=0.1 mole; (c): *x*=0.2 mole; (d): *x*=0.3 mole

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 Fig.1d), these results are in partial agreement with Kazin et al.[51]

Liu et al.[52] support 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

Figs. 2a-d show the Raman spectra 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 .

It can be concluded from references[47,53,54] 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]

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

References		2212			
51	**54**	**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 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 Fig. 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 ±10 cm^{-1} is indicated by existence of lead-rich phase $(Sr/Ca)_2PbO_4$ as reported in[47] that also confirmed in our XRD.
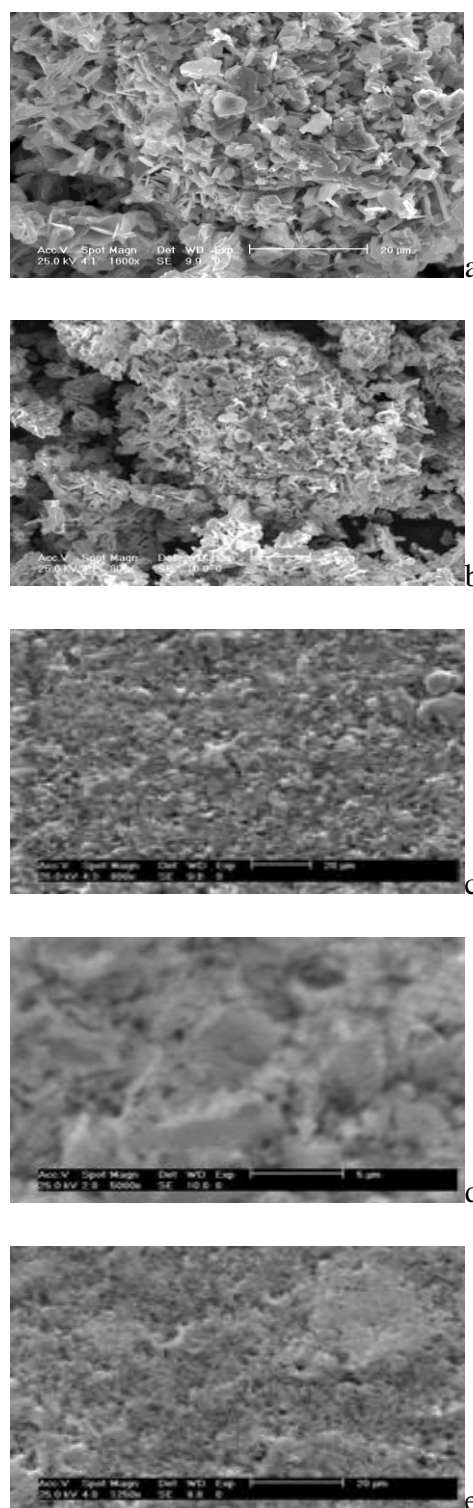

Figure 3.a-e. SE-micrographs for pure 2212-BPSCCO prepared by Freeze Drying Technique (FDT) and variant added-ZrO2 samples. [a]: Pure BiPb-2212 (FDT); [b]: 0.1 mole -ZrO_2-added BiPb-2212 (FDT); [c]: 0.2 mole -ZrO_2-added BiPb-2212 (FDT) [d] and [e] 0.3 mole -ZrO_2-added BiPb-2212 (FDT).

Table 3. EDX elemental data for pure -2212-BPSCCO (FDT).

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

From Fig.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

Fig.3a-d, show the *SE*-micrographs for pure and Zr-doped PBSCCO with x = 0.1 → 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) .

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 .

Superconductivity measurements

Fig. 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).

One can indicate that, 2212-undoped PBSCCO sample exhibits HT_c ~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 ΔT_c=0.65 K .This confirmed magnetically the existence of 2212 in highly homogeneous pure phase[56,57], while the samples with Zr-dopant *x*=0.1–0.3 mole exhibit slight surpress in their T_c'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 T_c's between the minimum T_c's samples with x=0.3 mole is ΔT_c = 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 .
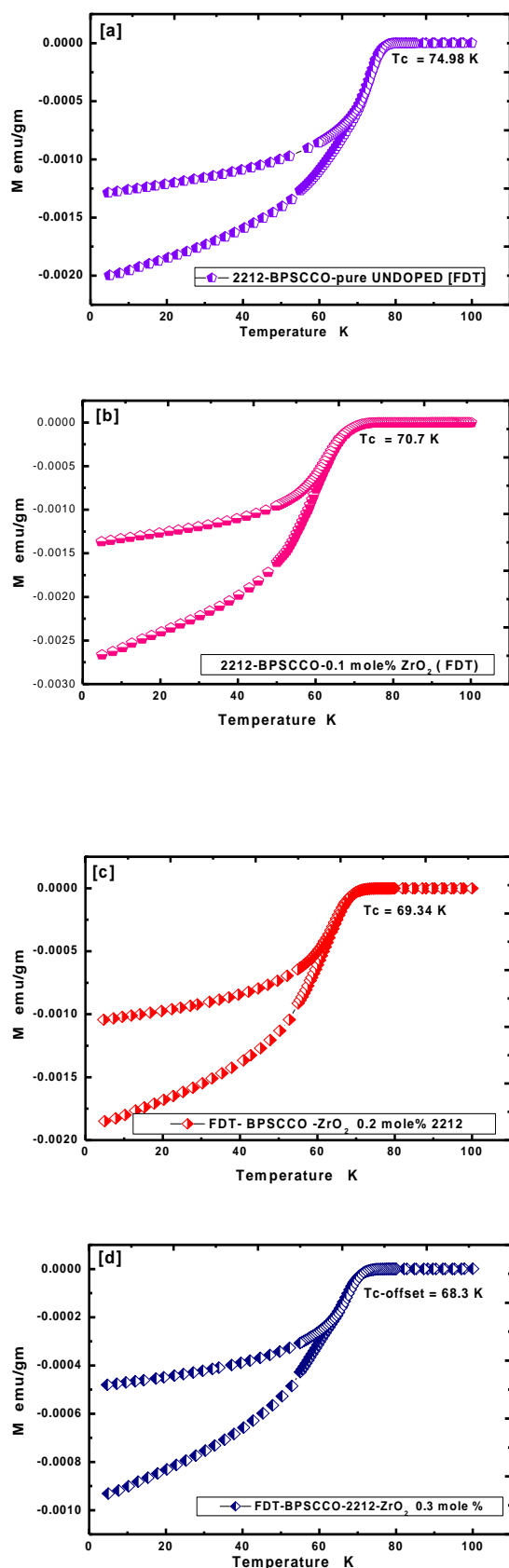
Fig.(4a-d): AC- Susceptibility curves for Zr-added 2212 (F DT).(a): x=0.0 mole, (b): x=0.1 mole, (c): x=0.2 mole and (d): x=0.3 mole

Conclusions

Conclusive remarks can be summarized as

1-Solution 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 homogeneities 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 T_c'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 .

Aknowlegements

References

[1]Chen C. H., Werder D. J., Espinosa G. P. and Cooper A. S., *Phys. Rev. B* , **1989**, *39*,4686**.**

[2]Schneck J., Pierre L., Tolédano J. C. and Daguet, C. ,*Phys. Rev. B* , **1989**, *39*, 9624.

[3]Maeda A., Hase M., Tsukada I., Noda, K., Takebayashi S. and Ushinokura K., *Phys. Rev. B*, **1990**, *41*, 6418.

[4]Weber M., Amato A., Gygax F. N., Schenk A., Maletta H., Duginov V. N., Grebinnik V.G., Lazarev A. B., Olshevsky V. G., Pomjakushin V. Y., Shilov S. N., Zhukov V. A., Kirillov, B. F., Pirogov A. V., Ponomarev A. N., Storchak V. G., Kapusta S. and Bock J., *Phys. Rev. B,* **1993**, *48*, 13022.

[5] Régi F. X., Schneck J., Savary H., Daguet C. and Huet F., *IEEE Trans. Appl. Supercond.*, **1993**, *3*, 1190.

[6]Ma J., Alméras P., Kelley R. J., Berger H., Margaritondo G., Cai X. Y., Feng Y.and Onellion M. ,*Phys. Rev. B*, **1995**, *51*, 9271.

[7]Winkeler L., Sadewasser S., Beschoten B., Frank H., Nouvertné F.and Güntherodt G., *Physica C*, **1996**, *265*, 194.

[8]Manifacier L., Collin G. and Blanchard N., *Int. J. Modern Phys. B,* **1998**, *12*, 3306.

[9] Lindemer T. B., Hunley J. F., Gates J. E., Sutton A. L., Brynestad J. and Hubbard C., *J. Am. Ceram. Soc.*, **1989**, *72*, 1775.

[10]Allgeier C. and Schilling J. S., *Physica C*, **1990**, *168*, 499.

[11]O'Bryan H. M., Rhodes W. W. and Gallagher P.K. *Chem. Mater.,* **1990**, *2*, 421.

[12]Presland M. R., Tallon J. L., Buckley R. G. and Flower N. E., *Physica C*, **1991**, *176*, 95.

[13]Sieburger R., Müller P. and Schilling J. S., *Physica C*, **1991**, *181***, 335.

[14]Manthiram A. and Goodenough J. B., ,*Appl. Phys. Lett.* **1988***, 53*, 420.

[15]Groen W. A., Leeuw D. M. and Feiner L. F., *Physica C,* **1990,** *165*, 55.

[16]Mitzi D. B., Lombardo L. W., Kapitulnik A., Laderman S. S. and Jacowitz R. D. ,*Phys. Rev. B,* **1990,** *41*, 6564.

[17]Tallon J. L., Buckley R. G., Gilberd P. W. and Presland M. R., *Physica C*, **1989,** *158,* 247.

[18]Williams G. V. M., Pooke D. M., Pringle D. J., Trodahl H. J., Tallon J. L., , Crossley A. and Cohen L. F., *Phys. Rev. B,* **2001,** *63*, 589.

[19] Niu H., Fukushima N. and Ando K.; *Jap. J. Appl. Phys*., **1988,** *27*, 1442.

[20]Morris D. E., Hultgren C. T., Markelz A. M., Wei J. Y. T., Asmar N. G. and Nickel J. H. ,*Phys. Rev. B* , **1989**, *39*, 6612.

[21]Zhao J. and Seehra M. S., *Physica C*, **1989,** *159*, 639.

[22]Presland M. R., Tallon J. L. ,Buckely R. G., Liu R. S. and Flower N., *Physica C*, **1990,** *176*, 95.

[23]Kao H. C. I., Chen W. L., Wei T. P., Lui J. C. and Wang C. M., *Physica C,* **1993,** *177*, 376.

[24]Tarascon J. M., McKinnon W. R., Barboux P., Hwang D. M., Bagley B. G., Greene L. H., Hull G. W., Lepage Y., Stoffel N. and Giround M., *Phys. Rev. B***, 1988**, *38*, 885.

[25]Chudnovsky E. M., *Phys. Rev. Lett*., **1990***, 65*, 3060 .

[26]Hazen R. M., Prewitt C: T., Angel R. G., Ross N. L., Finger, L. W., Hadidiacos C.G., Veblen D. R., Hor P. H., Meng R. L. and Chu C. W., *Phys. Rev. Lett*.,**1988**, *60*, 1174.

[27]Sunshine S. A., Siegrist, T., Schneemeyer L. F., Murphy D.W., Cava R.J., Batlogg B., Van Dover R.B. , Nakahara S. , Farrow R. , Marsh P., Rupp L.W. and Peck W.P., *Phys. Rev. B*, **1988**, *38*, 898.

[28]Statt B. W., Wang Z., Lee M. G., Yakhmi J. V., De P.C., Major J. F. ,and Rutter J. W., *Physica C,* **1988***, 15*, 156 .

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

[30]Ueyama M., Hikata T., Kato T. and Sato K., *Jap. J. Appl. Phys*., **1991**, *30*, 1384.

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

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

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

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

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

[36]Sastry P. V., Yakhmi J. V. and Iyer R. M., *Physica C,* **1989**, *161*, 665.

[37]Dorris D. E., Prorok B. C.,Lanagan M. T., Sinha S. and Poepppel R. B. ,*Physica C,* 1993, *212*, 66.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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