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Effect Of The Zr^{4+} -Oxide Additives On Raman Spectra And Superconducting Properties Of 2212-BPSCCO



Corresponding Author

Khaled M.Elsabawy
Chemistry Department, Faculty Of
Science, Tanta University, 31725
Tanta, (EGYPT)
E-Mail : ksabawy@yahoo.com

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Co-Authors

M.Jansen², Hosny A.El-Dally¹, Morsy M.A.Sekkina¹
¹Chemistry Department, Faculty Of Science, Tanta University, 31725
Tanta, (EGYPT)
²Max Planck Institute for Solid State Research, Stuttgart-(GERMANY)

ABSTRACT

The undoped BPSCCO(Bi/Pb)₂Sr₂Ca₁Cu₂O₈ and the family of the general formula (Bi_{1-x}Zr_xPb)₂Sr₂Ca₂Cu₃O₈, (where 0.1 ≤ x ≤ 0.3) were prepared by both route the high temperature solid state reaction and freeze dry (solution) routes at sintering temperature 865°C under O₂ stream. The superconducting measurements proved that, best T_c = 74.33 K is for undoped PBSCCO, while the lowest T_c = 65.5 K is for the doped sample with x = 0.3 mole% indicating that superconductive transition temperatures T_c decrease regularly with increasing Zr⁴⁺-dopant concentration from x = 0.1 to 0.3 respectively. Also SEM analysis for micro-morphological properties was performed as preliminary tool for proving molar ratios and nature of micro-morphological structure of the prepared samples. ZrO₂ additives exhibit strong interactions on different Raman spectral modes of 2212-superconducting phase.

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KEYWORDS

Raman spectra;
oxides;
X-ray diffraction;
Superconductivity;
SE-microscopy.

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)₂Sr₂CaCu₂O_{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^[5,6]

and^{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 $\text{YBa}_2\text{Cu}_3\text{O}_z$ ^[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, 11, 12 and 13] and is dependent on the cationic substitutions^[14, 15 and 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 $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$, 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 $\text{BiSrCaCu}_2\text{O}_x$ ^[32], $\text{Bi}_2\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{O}_x$, $\text{Bi}_2\text{Sr}_2\text{Ca}_4\text{Cu}_5\text{O}_x$ ^[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 stoichiometry^[35-41].

Many previous authors^[27-31] investigated the doping effect of 3d-elements ($M = \text{Sc, Ti, V, ..., Fe, Co, Ni}$ 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 various phases present in BPSCCO regime including alkaline earth cuprate, CuO, Bi-2212, Bi-2223 and Pb-containing phases specially $(\text{Sr/Ca})_2\text{PbO}_4$.

Lu et al.^[48] have investigated the effect of MgO and Ag₂O 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_{cs} -offsets for 2212-BPSCCO varied in between 60 and 72K according to the amount of HgO added.

Orlova et al.^[50] have investigated the effect of ZrO₂ 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 ZrO₂ (5Wt%).

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The aim of the present work is to investigate the influence of high valency cations Zr^{4+} inclusion additives on the hole-superconducting and physical properties PBSCCO regime trying to:

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).

EXPERIMENTAL

Samples preparation

1. Solid state route

The pure BPSCCO ($Bi_{0.5}Pb_{0.5}$) $_2$ Sr $_2$ Ca $_1$ Cu $_2$ O $_8$ and its variant zirconium/cerium 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 by the conventional solid state reaction method and sintering procedure using the appropriate amounts of ZrO $_2$, Ce $_2$ O $_3$, Bi $_2$ O $_3$, PbO, SrCO $_3$, CaCO $_3$ and CuO each of highly pure chemical grade purity. The mixtures were calcined at 800°C under a compressed O $_2$ atmosphere for 20 hrs then reground and pressed into pellets (thickness 0.2 cm and diameter 1.2 cm) under 6 Ton/cm 2 . Sintering was carried out under oxygen stream at 835°C for 200 hrs. The samples were slowly cooled down (20°C/hr) till 500°C and annealed there for 20 hrs under oxygen stream. The furnace is shut off and cooled slowly down to room temperature. Finally the materials are kept in vacuum desiccator over silica gel dryer. A levitation preliminary superconductivity test was thoroughly applied for the achievement of superconductive phase and hence superconductivity.

2. Solution route

The pure ($Bi_{0.5}Pb_{0.5}$) $_2$ Sr $_2$ Ca $_1$ Cu $_2$ O $_8$ 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 at the Max Planck Institute for Solid State Research (Stuttgart-Germany).

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) at max planck institute (Stuttgart-Germany).

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 30K using liquid helium refrigerator at the max planck Institute for solid state research (Stuttgart-Germany).

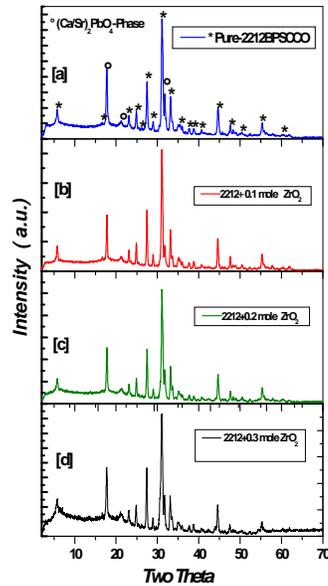
Raman spectroscopy measurements

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 = 0.4mW with microscope objective = x20 at Max Planck institute (Stuttgart-Germany).

RESULTS AND DISCUSSION

Phase Identification

Figure(1a-d) and figure(1e-h): display the X-ray powder diffraction patterns of the pure ($Bi_{0.5}Pb_{0.5}$) $_2$ Sr $_2$ Ca $_1$ Cu $_2$ O $_8$ 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 solid state route and freeze drying technique respectively. Analysis of the corresponding 2θ values and the interplanar spacings $d(A^\circ)$ were carried out, and indicated that, the X-ray crystalline structure mainly belongs to a single tetragonal phase 2212 in major besides Ca $_2$ PbO $_4$ secondary phase in minor. The unit cell dimensions were calculated using the most intense X-ray reflection peaks (see TABLE 1) to be $a=b=3.8136A^\circ$ and $c=30.7632A^\circ$ for the pure



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

Figure (1a-d): X-ray diffraction patterns for pure and vari-ant ZrO_2 added 2212-BPSCCO superconductors

2212-BPSCCO phase which is in full agreement with those mentioned in literature.

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

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 ($Zr^{4+} = 0.72 \text{ \AA}$ while Bi^{3+} is 1.17 \AA) 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:

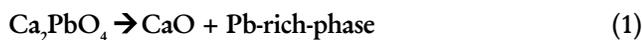
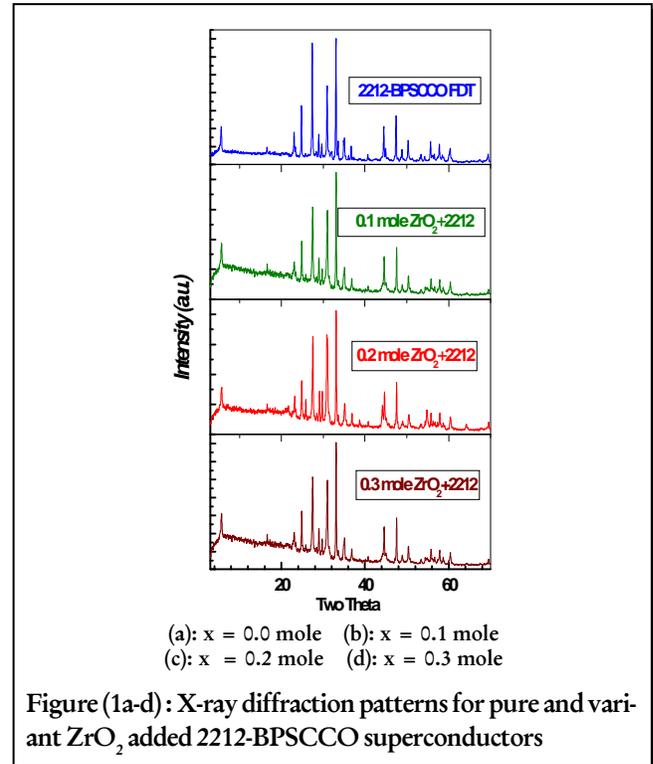


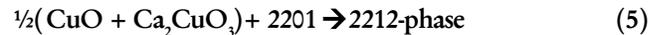
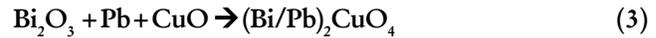
TABLE 1 : The calculated lattice parameters for the prepared samples.

Material	a=b(\AA)	c(\AA)
$(Bi_{0.5}Pb_{0.5})_2Sr_2Ca_1Cu_2O_8$	3.8136	30.7632
$BiZr_{0.1}PbSr_2Ca_1Cu_2O_z$	3.8254	30.5320
$BiZr_{0.2}PbSr_2Ca_1Cu_2O_z$	3.8312	30.1927
$(BiZr_{0.3}PbSr_2Ca_1Cu_2O_z)$	3.8234	30.1831



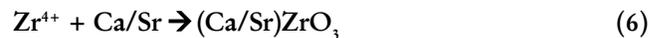
(a): $x = 0.0$ mole (b): $x = 0.1$ mole
(c): $x = 0.2$ mole (d): $x = 0.3$ mole

Figure (1a-d): X-ray diffraction patterns for pure and vari-ant ZrO_2 added 2212-BPSCCO superconductors



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 :



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 Figure 1d), 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

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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	2212	x=0.1	x=0.2	x=0.3
Ref.[51]Ref.[54]	x = 0			
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)₂PbO₄

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

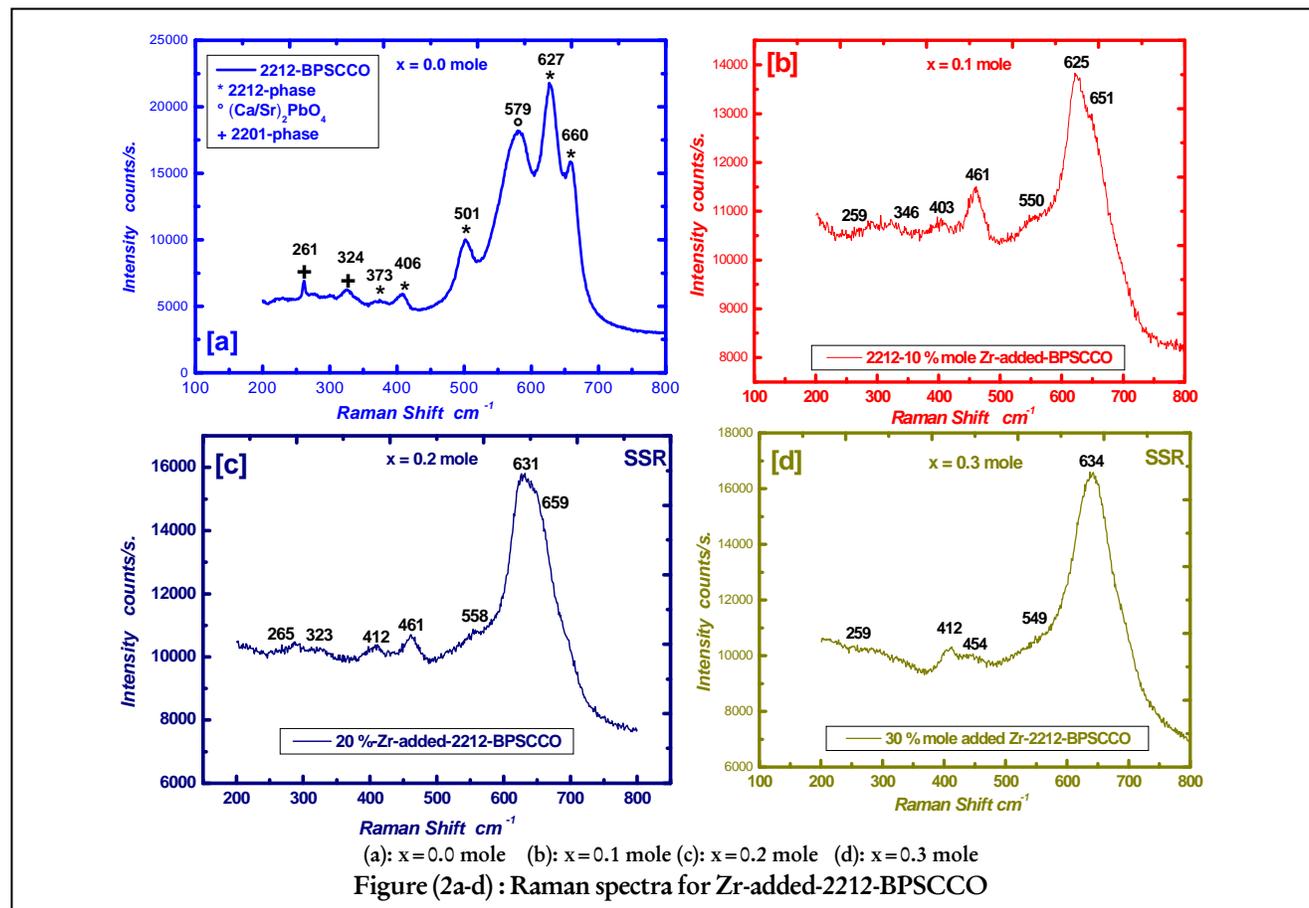
Figures (2a-d): shows the Raman spectrograms for pure and Zr(IV)-added 2212-BPSCCO system.

From the modes frequencies which are listed and

compared with some references see TABLE (2), one can indicate that 2212-BPSCCO phase is the dominating phase present in our polycrystalline BPSCCO beside small traces of strontium calcium plumbates and 2201-impurity phases.

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 $\sim 630 \text{ cm}^{-1}$ 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 $\sim 324 \text{ cm}^{-1}$ which is ascribed to the 2201 phase as reported in^[54] and the band appears $\sim 500 \text{ cm}^{-1}$ 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 $\sim 497 \text{ cm}^{-1}$ which is fully supporting our results. The band appears $\sim 560 \text{ G}10 \text{ cm}^{-1}$ is indicated by existence of lead-rich phase $(\text{Sr}/\text{Ca})_2\text{PbO}_4$ 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 SEM-micrograph for pure and Zr-doped PBSCCO with $x=0.1 \rightarrow 0.3$ mole % applied on the ground powders that prepared by (SSR). The average particle size was calculated to be in between 0.2 and $0.7 \mu\text{m}$.

TABLE 3-6, the EDX examinations for random spots in the same sample confirmed and are consistent with our XRD analysis for polycrystalline-shouldered-PBSCCO, such that the differences in the molar ratios EDX estimated for the same sample is emphasized and an evidence for the existence of 2212 superconductive phase with good approximate molar ratios.

From Figure (3a-d), it is so difficult to observe inhomogeneity within the micrograph due to that the powders used are very fine and the particle size estimated is too small.

The grain size for 2212-phase was calculated according to; Scherrer's formula^[56],

TABLE 3: EDX elemental data for pure 2212-BPSCCO(SSR)

Element	Wt %	2212-BiPb 2212-BiPb				
		Average At %	K-Ratio	Z	A	F
O K	15.88	55.25	0.029	1.194	0.1531	1.0004
CaK	5.29	7.13	0.0379	1.1433	0.6253	1.0021
CuK	18.22	13.48	0.1831	1.0246	0.9507	1.0313
PbL	18.96	5.65	0.1513	0.8181	1.0118	1.0178
BiL	19.68	5.98	0.1664	0.8175	1.0131	1.0211
SrK	21.32	12.51	0.1923	0.9674	0.9783	1
Total						

TABLE 4: EDX elemental data for 0.1 mole added-ZrO₂-2212-BPSCCO(SSR)

Element	Wt %	0.1Zr-BiPb 2212-BiPb				
		Average At %	K-Ratio	Z	A	F
OK	15.88	53.56	0.029	1.194	0.1531	1.0004
CaK	5.29	7.13	0.0379	1.1433	0.6253	1.0021
CuK	18.22	15.48	0.1831	1.0246	0.9507	1.0313
PbL	17.96	6.08	0.1513	0.8181	1.0118	1.0178
BiL	19.68	5.28	0.1664	0.8175	1.0131	1.0211
SrK	20.32	12.51	0.1923	0.9674	0.9783	1
ZrK	2.65	1.57	0.0253	0.9735	0.9825	1
Total						

TABLE 5: EDX elemental data for 0.2mole added-ZrO₂-2212-BPSCCO(SSR)

Element	Wt %	0.2Zr-BiPb 2212-BiPb				
		Average At %	K-Ratio	Z	A	F
OK	18.02	57.36	0.0321	1.1852	0.1504	1.0003
CaK	7.41	9.42	0.0528	1.1347	0.6264	1.0017
CuK	14.67	11.76	0.1464	1.017	0.9491	1.0339
PbL	24.23	5.96	0.2027	0.8121	1.0143	1.0156
BiL	15.21	3.71	0.1276	0.8115	1.0153	1.0185
SrK	16.39	9.52	0.154	0.9602	0.9787	1
ZrK	4.07	2.27	0.0386	0.9662	0.9821	1
Total						

$$B = 0.87\lambda / D \cos\theta \quad (5)$$

where D is the crystalline grain size in nm, θ , half of the diffraction angle in degree, λ is the wavelength of X-ray source (Cu-K α) in nm and B, degree of widening of diffraction peak which is equal to the difference of full width at half maximum (FWHM) of the peak at the same diffraction angle between the mea-

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TABLE 6 : EDX elemental data for 0.3 mole added-ZrO₂-2212-BPSCCO(SSR)

Element	Wt %	0.3-ZrBiPb 2212-BiPb				
		Average At %	K-Ratio	Z	A	F
OK	13.75	51.42	0.0247	1.1987	0.1496	1.0005
CaK	4.62	6.49	0.0333	1.1471	0.6278	1.0023
CuK	20.04	17.77	0.2016	1.0275	0.9533	1.0275
PbL	16.16	4.39	0.1369	0.8192	1.0113	1.0225
BiL	16.52	4.45	0.1406	0.8186	1.0127	1.0266
SrK	23.81	15.31	0.2259	0.9681	0.9798	1
ZrK	5.11	3.16	0.0489	0.9738	0.9837	1
Total						

sured sample and standard one.

From SEM-mapping the estimated average grain size was found to be (1.2-1.85 μm) which is relatively large in comparison with that calculated applying scherrer's formula for pure 2212-phase (D ~ 0.06 μm).

This indicates that, the actual grain size in the material bulk is smaller than that detected on the surface morphology. Furthermore, in our EDX analysis, zirconium was detected in the elemental analysis qualitatively with good approximate to the actual molar ratio but not observed at 2212 grain boundaries which confirm that, zirconate has diffused regu-

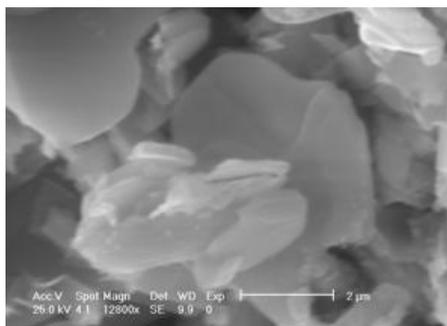
larly into material bulk of superconducting 2212-phase and Zr-ion might induce in the crystalline structure through solid state diffusion reaction by some extent. The inclusion of Zr-ion is confirmed also by the depression in T_c of Zr-added PBSCCO.

These results are in agreement with^[51]. But they detected zirconate in the grain boundaries which is not observed in our SEM-micrographs indicating its bulk locality as in our view.

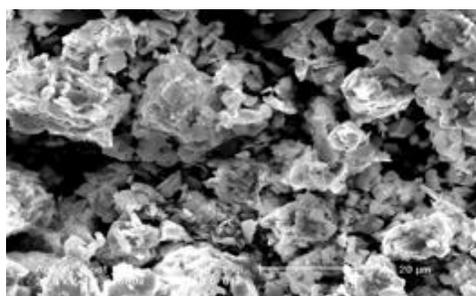
Figure (4a-d), show the SEM-micrograph for pure and Zr-doped PBSCCO with x=0.1→0.3 mole prepared by freeze drying Tchnique. The samples were measured as fine ground powders, the average particle size estimated to be in between 0.3 and 1.4 μm which is considered high to that estimated from solid state route. The micrographs taken are more homogeneous than those for samples prepared via solid state route which reflect the priority to freeze drying technique than solid state route (SSR).

TABLE (7-10), 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.

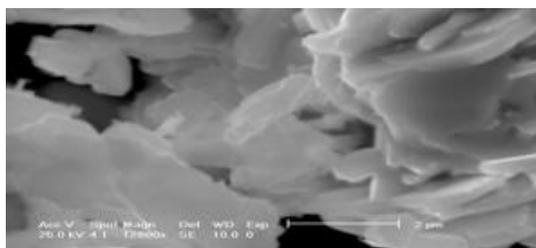
The analysis of EDX data obtained from TABLE (3) for pure 2212BPSCCO prepared by solid state route (SSR) give us the following, stoichoimetric



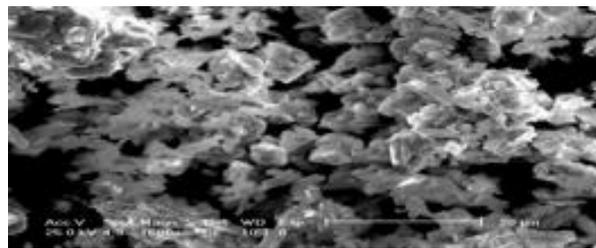
[a]: Pure-2212-BPSCCO(SSR).



[b]: 0.1mole -ZrO₂added-BiPb-2212(SSR).

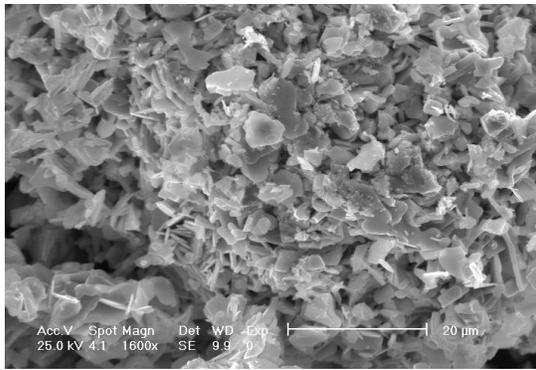


[c]: 0.2mole -ZrO₂added BiPb2212(SSR).



[d] 0.3 mole -ZrO₂added BiPb-2212(SSR).

Figure (3a-d) : SE-micrographs for pure and Zr-added 2212-BPSCCO with different amplification factors prepared via solid state route (SSR)



[a]: Pure BiPb-2212 (FDT)

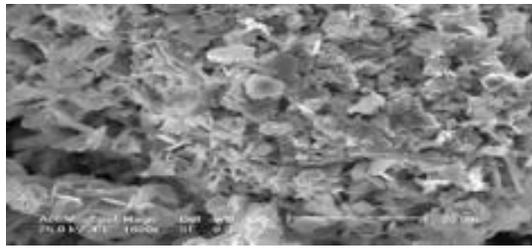
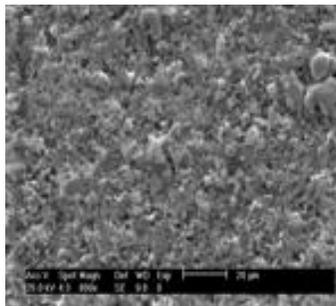
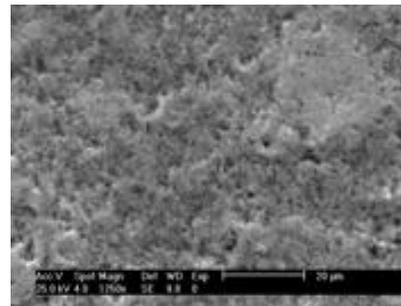
[b]: 0.1 mole -ZrO₂-added BiPb-2212 (FDT)[c]: 0.2 mole -ZrO₂-added BiPb-2212 (FDT)[d] 0.3 mole -ZrO₂-added BiPb-2212 (FDT)

Figure (4a-d): SE-micrographs for pure 2212-BPSCCO prepared by freeze drying technique(FDT) and variant added-ZrO₂ samples

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 freeze dry technique see TABLE 7 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 7 : EDX elemental data for pure -2212-BPSCCO (FDT)

Element	Wt %	2212-BiPb 2212-BiPb				
		Average At %	K-Ratio	Z	A	F
OK	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
Total						

Superconductivity measurements

Figure(5a-e): 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 solid state route(SSR).

It is clear that, only 2212-undoped PBSCCO sample exhibits $HT_c \sim 74.33$ K corresponding to 2212-phase which is annealed in oxygen and is noticeable clearly in our XRD as major phase. This confirmed magnetically the existence of 2212 in highly pure phase, while the samples with Zr-dopant x = 0.1– 0.3 mole exhibit slight decreasing in their T_c 's 68.7, 67.5

TABLE 8 : EDX elemental data for 0.1 mole

Element	Average At %	K-Ratio	Z	A	F
OK	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
Total	-	-	-	-	-

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TABLE 9: 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
Total	-	-	-	-	-

TABLE 10: 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
Total	-	-	-	-	-

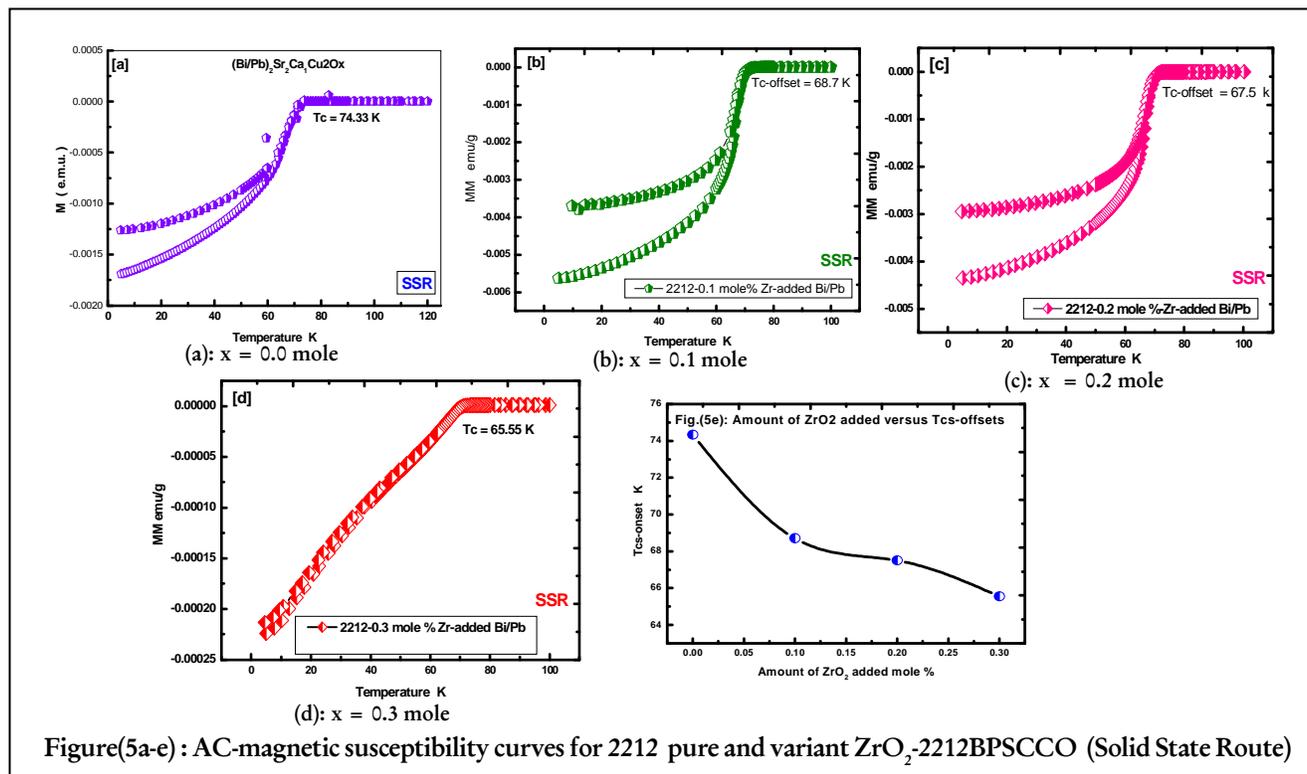
and 65.55K respectively due to zirconate intermediate inclusions decreasing the fraction of superconductive 2212-phase ratio as show in Figure 5e.

From Figure 5d it is clear that, the minimum $T_c \sim 65.55K$ corresponds to the maximum addition ratio $x=0.3$ mole due to the existence of both non-superconducting zirconate and Ca_2PbO_4 -phase which are maximum at $x=0.3$ mole. Bradea et al.^[57] reported a similar behaviour of suppressing in the T_c 's of 123-YBCO with addition of non-superconducting $BaZrO_3$ from zero till 30Wt% without degradation of the bulk superconductivity of YBCO.

Figure 6a-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 BPSCCO sample exhibits $HT_c \sim 74.95K$ corresponding to 2212-phase which is annealed in oxygen and noticeable clearly in our XRD as major phase and this t_c for 2212-phase is relatively better than that prepared by freeze dry technique $\Delta T_c=0.65K$. 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 T_c 's 70.7, 69.34 and 68.3K respectively, which reflects the promotion of the homogeneity degree in freeze drying (FDT) technique than that prepared by normal SSR (see figure7).



Figure(5a-e) : AC-magnetic susceptibility curves for 2212 pure and variant ZrO_2 -2212BPSCCO (Solid State Route)

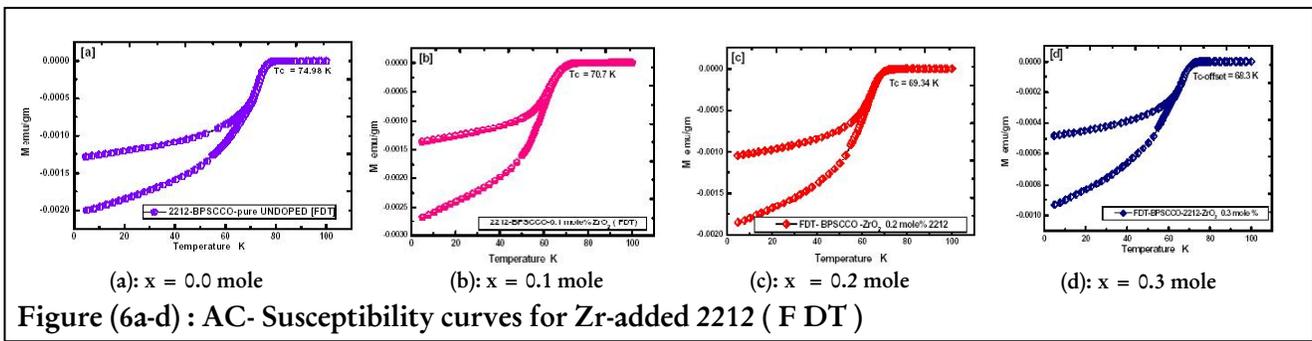


Figure (6a-d) : AC- Susceptibility curves for Zr-added 2212 (F DT)

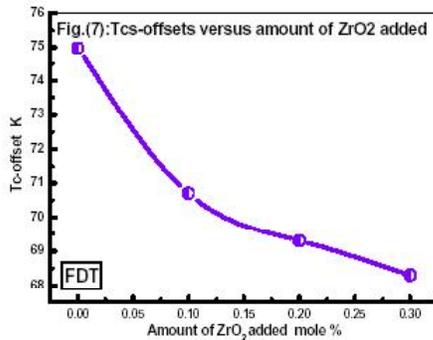


Figure 7: Tcs-offsets versus amount of ZrO2 added

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 $T_c=2.75$ K emphasize that, impurity phases such as zirconate inclusions or lead-rich plumbates dispersed regularly through out the sample mixture with minimum ratios of formation achieving maximum degree of homogeneity as confirmed in SEM and EDX analyses.

CONCLUSION

The pure BPSCCO ($\text{Bi}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$) and its variant zirconium containing composites with general formula: $\text{Bi}_{1+x}\text{Zr}_x\text{PbSr}_2\text{Ca}_1\text{Cu}_2\text{O}_z$ and where $x=0.1, 0.2$ and 0.3 mole% respectively were prepared by the conventional solid state reaction method. Additionally, Zr-added BPSCCO series was reprepared also via solution route (freeze drying technique). ZrO_2 has a limited effect on the main crystalline superconductive 2212-phase as x amount added increases. Only lead-rich-plumbates appears as secondary phase in minor. SE-microscopy accompanied with EDX proved that, solution route was the best in the degree of homogeneity 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.

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