

Influence of lithium-holmium co-doped on structural and electrical properties of BSCCO superconductor

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$\text{Bi}_2\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_4\text{Cu}_6\text{Li}_x\text{Ho}_x\text{O}_y$ ($0.0 \leq x \leq 0.5$) samples were prepared by doping with Li and Ho at changing ratios and using melt-quenching method. Thus, the influences of different doping levels of Li and Ho on the structural and electrical properties of the BPSCCO compound have been investigated by electrical resistivity, Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and Energy Dispersive X-Ray Spectroscopy (EDX) techniques. It has been observed that, with increasing Li and Ho doping, the high- T_c Bi-(2223) phase gradually transforms into the low- T_c Bi-(2212) and Bi-(2201) phases. However, It should be pointed out that these low- T_c superconducting phases are formed at all the doping levels, but increasing amount with increasing concentration of Li and Ho. Therefore, while the electrical resistivities in the normal states increase, the superconducting transition temperatures, T_c , hole concentrations, p , and the magnitudes of thermoelectric powers of all the samples decrease with increasing Li and Ho concentration x . As a result, the results suggest that with the increase in Li and Ho amount the superconductivities of all the samples are suppressed due to the destruction of the phase coherence by pair-breaking effects, or, to the hole filling mechanism with increasing x .

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1. Introduction

The effect of substitution, of some different ions other than the main matrix ions, on the transition temperature T_c of high temperature superconductors have been classified into several types by Eisaki et al. [1]. They showed that the substitution to the site location next to the apical oxygen, let us call A, especially has an influence on T_c . One of the systems where foreign element can be substituted to the A site is $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{RE}_x\text{Cu}_2\text{O}_y$. In this system, T_c depends strongly on the RE element even if the ratio of Sr^{2+} to RE^{3+} were kept constant [1, 2]. This suggest than the site A acts not simply as a carrier reservoir but also plays a more important role in the occurrence of superconductivity. Eisaki et al. argued that the suppression of T_c of $\text{Bi}_2\text{Sr}_{1.6}\text{RE}_{0.4}\text{CuO}_y$ when RE is replaced by an element with a smaller ionic radius is due to a local disorder introduced by the substitution [1, 3]. In that case, the whole phase diagram may be affected by the disorder [4]. As pointed out above an interesting research area of superconductivity receiving a great deal of attention is the substitutional studies. In this content, there have been several reports on microstructural, electrical and physical properties of BPSCCO superconducting systems too [5-11]. Many workers have observed that the substitution acts as a probe of the chemical and structural environment which determines whether or not the system exhibits superconductivity [12]. These studies explain the decrease in T_c for same doping materials with increasing substitutional concentration, and the subsequent metal-insulator cross over, due to the decrease in the average valance of the copper, brought about by the excess charges induced by doped ions, e.g. rare earth ions. It is known

that Pb substitution at the Bi site in Bi-(2212) significantly reduces the electromagnetic anisotropy [13]. Also, the Pb substituted (2212) has shown enhanced J_c in applied fields, compared to Pb free Bi-(2212) [14]. In a recent work, it is found that when RE ions are substituted in place of Sr in (Bi, Pb)-(2212), the flaky nature and the texture of the grains gradually deteriorate with an increase in RE concentration [15]. However, It is expected that there is a great scope for a further improvement of T_c if the deterioration of the microstructure of the RE and Pb substituted Bi-(2212) could be suppressed.

In order to explore the effects of the doping on the physical and electrical properties of the BPSCCO system extensive studies have been done by using different doping elements [9, 16-18]. The properties of BPSCCO can be governed by the doping or intercalation of the elements having a different ionic radii. Alkaline metals could be the candidate for the doping, since their ionic radii include those of Pb, Bi, Sr and Ca [19]. The effects of the alkaline metal doping in BPSCCO system were studied by Sykorova et al. and Kawai et al. [19, 20]. In their works, the T_c was found to increase by Li and Na doping, but to decrease by K and Rb doping. It was also found that the alkaline metals drastically decrease the formation temperature of the Bi-(2212) phase [11]. Thus, it might be interesting to investigate the effects of co-doping of the alkaline metals and RE elements on the properties of the BPSCCO system. The study is attractive especially from the viewpoint of changing carrier concentrations.

In this work, therefore, we synthesized the compounds, $\text{Bi}_2\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_4\text{Cu}_6\text{Li}_x\text{Ho}_x\text{O}_y$ ($0.0 \leq x \leq 0.5$), by using the well known melt-quenching method and studied the effects of co-doping of Li and Ho on the

superconducting, structural and electrical properties of the BPSCCO system.

2. Experimental procedure

The appropriate amounts of the starting materials; Bi_2O_3 , PbO , SrCO_3 , CaO , CuO , Li_2O and Ho_2O_3 in fine powders forms and in the stoichiometric ratios of ($0.0 \leq x \leq 0.5$) were first well mixed by milling and calcined at 750°C for 5 h in air in order to obtain the $\text{Bi}_2\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_4\text{Cu}_6\text{Li}_x\text{Ho}_x\text{O}_y$ compounds. The calcined powders were then placed in a platinum crucible and heated at 1150°C until the samples were completely melted. The melts were poured onto a pre-cooled cooper plate and pressed quickly by another cooper plate to obtain approximately 1.2 to 2 mm thick plates of amorphous materials. The glass materials were then crushed and grained to obtain fine glass powders. The mixture was re-grained for about one hour and the resulting powder was then pressed into pellets of 10 mm diameter by applying a pressure of 22 bars. Finally, the precursor materials were annealed at 850°C for 100 h in air in order to achieve better crystallized material with better superconducting properties. Hereafter the samples with x values of 0.00, 0.10, 0.20, 0.30, 0.40 and 0.50 are labeled as A, B, C, D, E and F, respectively. Resistivity measurements were carried out on our samples using a standard four probe method with silver paint contact. The SEM investigations were performed using a JEOL SEM 7700F, equipped with an EDX system. The XRD was performed by employing a Bruker D8 Advance X-ray diffractometer with a $\text{CuK}\alpha_1$ radiation.

3. Results and discussions

To decide the proper sintering temperatures of the samples, first their thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out in air. For example, TGA and DTA results for the samples A, B and F during the heat process are presented in Figs. 1a and 1b, respectively. TGA data in Fig. 1a indicate that while the samples have almost constant weight losses below 850°C , above 850°C a gradual decrease in then are observed until $\approx 1100^\circ\text{C}$. Thus, for all the samples, the calcinations and sintering temperatures were set at about 850°C . It is believed that the weight losses are related to the oxidation of the samples. From the Fig. 1b, it is obvious that the DTA analysis of the samples A, B and F with increasing temperature in air demonstrate wide glass transition or crystallization peaks around 450°C , and endothermic peaks at about 850°C . It is known that the crystallization of the Bi-(2201) phase begins at 430°C and completes below 750°C , and some impurity phases precipitate above 485°C .

On the other hand, above 640°C the reaction proceeds and the major part of the reaction produces the Bi-(2212) phase. Hence, the endothermic peaks of the samples around 850°C are related to a transition to the Bi-(2212) phase [11]. However, it is believed that with increasing temperature the Bi-(2212) phase is converted to the Bi-(2223) phase. The resistivity (ρ) versus temperature (T) curves for the samples A, B, C, D, E and F are shown in Fig. 2. It is obvious that all of the samples show a metallic behavior in their resistivity above their respective superconducting transition temperatures, $T_{c.onset}$. For the sample A (undoped) the $T_{c.onset}$ of superconductivity is 86 K, and $T_{c.offset}$ of superconductivity is 81 K, namely the resistivity goes to zero at $T_{c.offset}=81$ K. Hence, there is a superconducting transition interval ΔT of about 5 K, and the Bi-(2223) phase is the dominant phase in the sample A. The values of $T_{c.onset}$ of the samples B, C, D, E and F are 84, 76, 75, 61 and 55 K, respectively, while $T_{c.offset}$ of those samples are 74, 60, 55, 43 and 36 K (see Table 1). Those data indicate that the superconducting properties of the samples decrease with increasing x . Consequently, the samples with higher doping (Li, Ho) concentrations exhibit lower $T_{c.onset}$ and $T_{c.offset}$ temperature due to the decreasing rate of formation of the Bi-(2223) phase [22, 23], as indicated by the XRD patterns of the samples (See Fig. 5). It is known that the superconducting properties of the BPSCCO systems depend on their oxygen content. Therefore, according to the Table 1 the decreasing superconducting transition temperatures indicate a decrease in oxygen contents of the compounds with increasing (Li, Ho) doping. As a result, also suppressed electrical properties are obtained for the (Li, Ho) doped BPSCCO system. Furthermore, the intergrowth of the impurity phases in the BPSCCO grains, the weak coupling between them and the BPSCCO grains, and some structural distortions may also cause a decrease in the T_c values and an increase in the normal state resistance values.

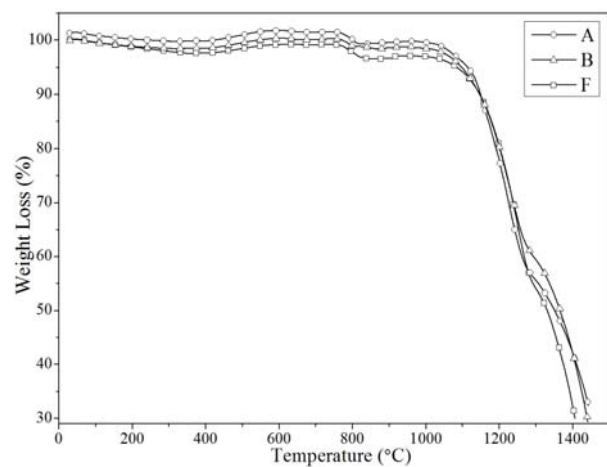


Fig. 1a. TGA curves of the sample A, B and F

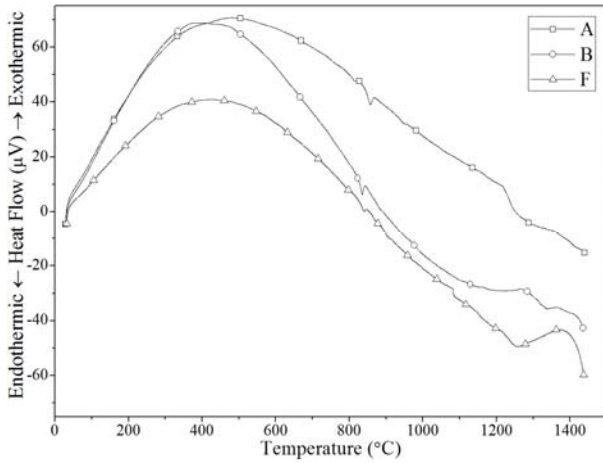


Fig. 1b. DTA curves of the sample A, B and F

It is generally believed that one of the key parameters for controlling T_c is the charge carrier concentration, p , in the CuO_2 planes. Presland et al. [24] found an empirical relation;

$$T_c/T_c^{\max} = 1 - 82.6(p - 0.16)^2 \quad (1)$$

Table 1. Structural and electrical properties of the $\text{Bi}_2\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_4\text{Cu}_6\text{Li}_x\text{Ho}_y\text{O}_z$ samples.

Samp.	(Li, Ho) content, x	$a(=b)$ (Å)	c (Å)	Unit cell volume, (Å^3)	$T_{c.onset}$ ($^{\circ}\text{K}$)	$T_{c.offset}$ ($^{\circ}\text{K}$)	ΔT ($^{\circ}\text{K}$)	p , Hole number	TEP, S (10^{-4}V/K)
A	0.00	5.380	30.57	884.830	86	81	6	0.133	-1,7635
B	0.10	5.385	30.52	885.026	84	74	15	0.126	-1,5646
C	0.20	5.395	30.46	886.570	76	60	26	0.109	-1,2051
D	0.30	5.400	30.30	883.548	75	55	60	0.103	-1,1070
E	0.40	5.405	30.27	884.309	61	43	63	0.100	-1,0621
F	0.50	5.410	30.20	883.897	55	36	63	0.095	-9,9257

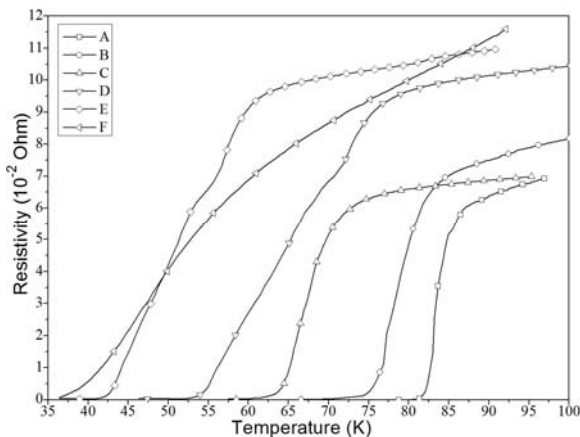


Fig. 2. The resistivity versus temperature curves of the samples A, B, C, D, E and F

between T_c and Sr- hole doping in $\text{La}_{1-x}\text{Sr}_x\text{CuO}_4$, where T_c^{\max} is the maximum attainable T_c and p is the hole concentration per Cu atom in the CuO_2 planes. According to Eq. 1 T_c appears to be maximized at the hole concentration $p \sim 0.16$ and to fall to zero at $p \sim 0.05$ on the underdoped side and at $p \sim 0.27$ on the overdoped side. The above relation has been found to be remarkably general for an analysis of T_c versus doping concentration in oxygen [23, 24]. Therefore, the relation has often been used as a convenient representation of the relation between T_c and the hole concentration for all the hole doped cuprates too. The p -values for the materials of the present investigation are obtained by using the Presland formula (Eq. 1) and are given in the Table 1. The results are plotted against concentration x in Fig. 3 and show that the p -values of our samples decrease with increasing (Li, Ho) doping and however, are not much lower than the undoped Bi-(2223) system, which points out that the amount of (Li, Ho) dopant is far from the overdoping limit, in agreement with the results of Satyavathi et al. [25]. Therefore, the increase in the normal state resistance values of the samples and the decrease in the superconducting transition temperatures, T_c can be attributed to the hole filling mechanism, which was previously described by other groups [26, 27].

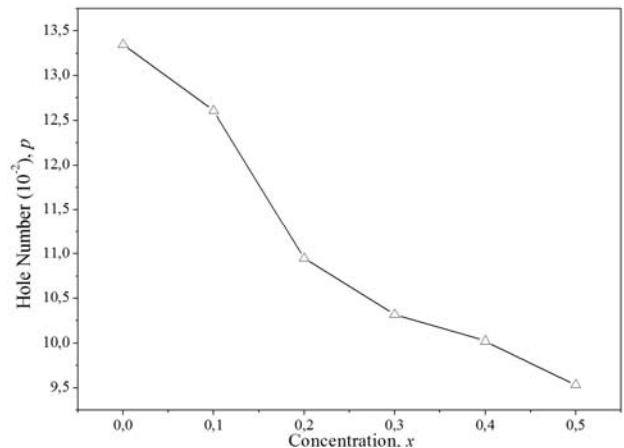


Fig. 3. Hole number versus concentration for $\text{Bi}_2\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_4\text{Cu}_6\text{Li}_x\text{Ho}_y\text{O}_z$

The studies of the thermoelectric power, (S), are complementary to the resistivity measurements. Since, S is highly sensitive to the details of the charge transport mechanisms, and hence some informations can be obtained about the nature of the charge carriers, the charge concentration and the band structure. The studies of S as a function of the carrier concentration and temperature have been done on Bi-based systems [28]. It is more or less established that the high- T_c superconducting oxides are strongly correlated systems. The expression for S , at high temperatures was derived by different groups [29, 30] and was modified by Cooper et al [31]; according to them, the thermoelectric power of HTSC materials at high temperatures can be described by the formula,

$$S = \frac{k_B}{e} \left[\ln\left(\frac{1-p}{2p}\right) - \ln 2 \right] \quad (2)$$

where p is the hole concentration. Using the p -values of the samples given Table 1, the S values of our samples have been calculated and are given in Table 1, and are plotted against concentration x in Fig. 4. As can be seen from the Fig. 4 the magnitude of S decreases almost linearly with increasing (Li-Ho) concentration. There is a hole like conduction in the (Li-Ho) doped samples as well as in the underdoped sample A, since, the S -values of are negative and the plot have positive slope. In other words, the major charge carriers in the samples are holes. We believe that the negative S -values of the samples are caused by the contributions of both Bi-(2223) and Bi-(2212) phases.

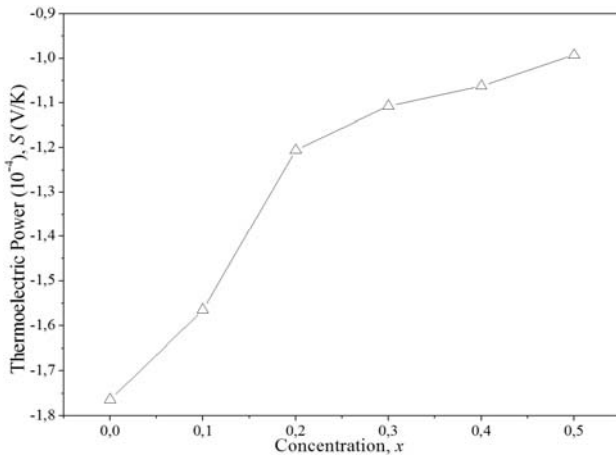


Fig. 4. Concentration dependencies of TEP for $\text{Bi}_2\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_4\text{Cu}_6\text{Li}_x\text{Ho}_x\text{O}_y$

Fig. 5 displays XRD patterns of the samples A, B, C, D, E and F samples. The sample A (with $x=0.00$) has both the high T_c -((2223) and the low T_c -((2212) phases. On the other hand, the X-ray diffraction patterns for the samples B, C, D, E and F, indicate that increasing the amount of Li and Ho ions (x) in the samples slightly worsens the superconducting phases and properties. Namely, the high T_c phase (2223) gradually disappears with increasing x and even the main phases of the samples

D, E and F appear to be only the Bi-(2212) and Bi-(2201) phases. As a result for $x > 0.2$ the structure of the compounds changes. Hence, the XRD studies have revealed that with the increasing amount of (Li-Ho) ions in the samples, high T_c -((2223) phase has gradually transformed into the Bi-(2212) and Bi-(2201) phases, but some non-superconducting impurity phases have also appeared. Therefore, It can be concluded that the volume fraction of the high T_c -((2223) phase decreases with increasing amount of Li and Ho which can explain why the hole concentration and the magnitude of S decreases with increasing x . It is obvious that when (Li-Ho) are doped into the Bi-system, the phase coordination is destroyed and multiphase, complex and deformed structure are formed. The crystal symmetry of all the samples is found to be tetragonal. The unit cell parameters of the samples are presented in Table 1. As can be seen from the Table 1, with increasing doping of (Li-Ho) a monotonic decrease in the c -parameter with a simultaneous elongation of the a -parameter have been observed, and thus these behaviors are obviously correlated with the decreasing hole concentration in the CuO_2 plane with increasing x . The compression in the c -parameter increasing x from 0.1 to 0.5 may be attributable to the fact that ionic radius of both Li^{1+} ($=0.76 \text{ \AA}$) and Ho^{3+} ($=0.90 \text{ \AA}$) are lower than that of $\text{Bi}^{3+}=1.17 \text{ \AA}$. Since, it is believed that Li and Ho ions go into the bismuth oxide layers in the main matrix and increase the oxygen content. This situation produces a distortion on the lattice structure; while slightly increasing the a -parameter at the same time decreases the c - parameter. As a result a slight increase in the cell volume was observed. On the whole one can conclude that, the addition of (Li-Ho), causes a change in a and c -parameters, decreases the hole concentration, leading to a decrease in the magnitude of S and an increase in the normal state resistivity, as expected.

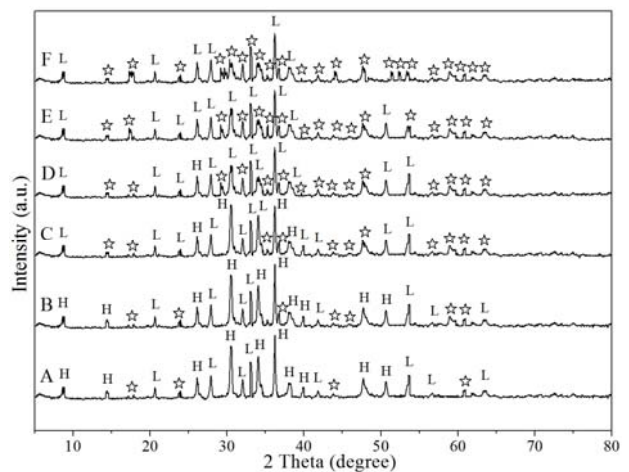


Fig. 5. XRD patterns of the $\text{Bi}_2\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_4\text{Cu}_6\text{Li}_x\text{Ho}_x\text{O}_y$ samples. A, B, C, D, E and F

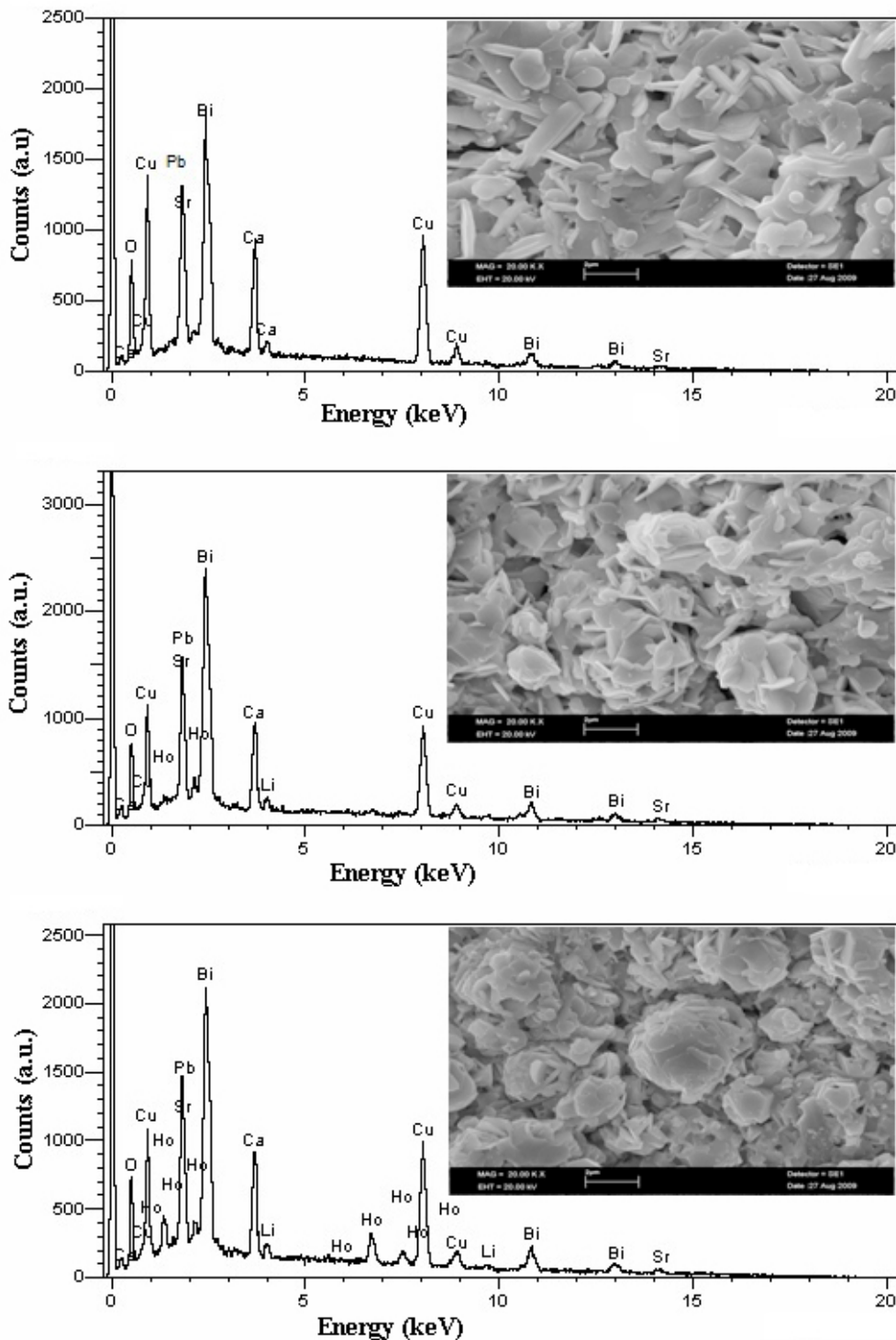


Fig. 6 a, b and c. SEM images, and EDX spectra of $\text{Bi}_2\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_4\text{Cu}_6\text{Li}_x\text{Ho}_y\text{O}_y$, indicating the elemental distribution in the samples A, B, and F, respectively

As an example, SEM images and EDX spectra of the samples A, B and F are also given in Figs. 6a, b and c. From the SEM images it is seen that the microstructure consist of large chaotically distributed crystals of plate-like grain forms with porous regions between them. With increasing amount of (Li-Ho), a decrease takes place in the grain sizes, and whereas, an increase is observed in the

number of porosities. It is also clear from the figures that the grain boundaries are in touch as to form weak bonds between each other. The decrease in the grain size and the distribution of grains on the surface of the samples indicate the influence of different ratio of (Li-Ho) on the morphology of the samples. The samples contain some impurities which are not diffused into the structure. This is

most probably either due to the thermal process duration or to the improper setting of the sintering temperature to obtain good crystallized superconducting samples. This conclusion is confirmed with the obtained low T_c values. Thus, incompatible with XRD results, it is observed that the doping of the BPSCCO with (Li-Ho) ions cause a change in the structure and as a result forces the samples to have lower T_c phases. Quantitative analyses of a chosen part of the samples A, B and F were also performed by an EDX analyses (see Figs.6a, b and c). In other words, EDX analyses were performed on some chosen grains of the samples. It is clear that the materials have mainly the expected compositions. The presences of (Li-Ho) are detected in the doped samples (B and F) with a corresponding reduction in Cu. This supports the fact that the (Li-Ho) atoms are successfully doped into the Bi-system, and form a structure with an almost identical initial stoichiometry.

4. Conclusion

The $\text{Bi}_2\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_4\text{Cu}_6\text{Li}_x\text{Ho}_x\text{O}_y$ ($0.0 \leq x \leq 0.5$) compounds have been successfully prepared by using the melt-quench method. From the electrical resistivity measurements, we conclude that the transition temperatures, hole concentrations and the magnitude of the thermoelectric power of the samples decrease with increasing doping of (Li-Ho). The XRD, SEM and EDX analyses, and lattice parameter results support the conclusions. The above results indicate that the doping of Li and Ho into the BPSCCO degrade the superconducting properties of the pure Bi-(2223) phase and confirm that the hole carrier concentration is at an optimum value in the pure phase of the Bi-system. All these observations lead us to conclude that the increasing (Li-Ho) doping concentration negatively affects the superconducting properties of the BPSCCO superconducting system.

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