

EFFECT OF Mo-DOPING ON THE STRUCTURE AND TRANSPORT PROPERTIES OF THE Y-123 SYSTEM

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Abstract

Superconducting samples of the system $\text{YBa}_2\text{Cu}_{3-x}\text{Mo}_x\text{O}_y$ ($0 \leq x \leq 0.3$) were prepared using the solid state reaction method. The transport of all air sintered samples were found to be enhanced by sintering in oxygen atmosphere. On the other hand, the superconducting transition temperature was found to decrease with increasing Mo-content in both air and oxygen sintered samples which was attributed to a decrease in hole concentration on Cu-O planes by Mo-doping. X-ray diffraction patterns and calculated lattice parameters indicated an orthorhombic structure for the oxygenated samples with a tendency for a tetragonal one with increasing Mo-content. It was suggested that Mo substituted copper at Cu(1) sites where added oxygen atoms can partially occupy O(5) sites in the a-direction which was also supported from the obtained results of IR spectra.

Introduction

Since the discovery of high temperature superconductivity [1], a great amount of research has been conducted to understand the mechanism primarily responsible for the increased T_C . One superconducting phase has been determined to be $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ which possess an orthorhombic structure with two different copper sites conventionally referred to as Cu(1) and Cu(2) with population of

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1 to 2. Cu(1) has a square planar coordination due to the presence of two oxygen vacancies in the a-axis and forms Cu(1)-O chains along the b-axis. On the other hand Cu(2) has a tetragonal pyramidal coordination due to an oxygen vacancy in the c-axis and forms Cu(2)-O planes. It is well known [2] that the Cu(1)-O chains are believed to be the charge reservoir in YBCO while Cu(2)-O sheets are the conducting layers.

In ceramic oxide superconductors, the dopant ions substitution at host lattice sites play an important role in modifying the transition temperature in these materials [3]. At the Cu-sites, it was shown that the trivalent non-magnetic ions such as Al and Ga depress T_C moderately [4,5] while the depression of T_C in case of trivalent magnetic Co and Fe [6] is rather rapid and include an O-T phase transition at $x = 0.1 - 0.15$. On the other hand, substituting the divalent non-magnetic Zn [7] introduces deleterious depression of T_C while the magnetic Ni [7,8] shows a smallest depression and the crystal structure remain an orthorhombic one in both cases. Similar results to that of Ni doping has been reported [9] for V substitution in Y-123 compound.

In the present work resistivity, magnetic susceptibility, x-ray diffraction, and IR measurements have been carried out in order to elucidate the effect of Mo doping with different concentrations on the transport properties and structure of YBCO compound.

Experimental

The raw materials Y_2O_3 , $BaCO_3$, CuO and MoO_3 with purity 99.98% were dried for 10 hr in an oven at $120^\circ C$. Appropriate amounts of the dried raw materials were weighed according to the stoichiometric composition $Y_1Ba_2Cu_{3-x}Mo_x$ where $x = 0, 0.02, 0.05, 0.08, 0.10, 0.15$ and 0.3 . The powder was ground using agate mortar for $\frac{1}{2}$ hr followed by mechanical grinding for 10hr. Then, it was slowly stirred in 100ml acetone for 24 hr to ensure homogeneity, dried in an oven at $80^\circ C$ for 24hr and reground for 10hr. The solid state reaction technique was used where the powder was sintered at $950^\circ C$ for 15hr in air flow, then slowly annealed to room temperature. After it was twice reground and sintered it was pressed into pellets and sintered again before measurements (run1). Same tablets of run(1)

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were subjected to another sintering and annealing process (run2) in oxygen flow (2.5l/min). The resistance of the samples was measured using a standard four-probe method down to 14K. Magnetic susceptibility was employed using the mutual inductance technique. The x-ray diffraction data were obtained using Co K α radiation with $\lambda = 1.791\text{\AA}$. IR spectra were recorded using Perkin-Elmer spectrophotometer at room temperature.

Results and Discussion

Fig. (1) displays the temperature dependence of reduced resistance R_T/R_{298} for the undoped and Mo-doped samples sintered and annealed in air (run 1). All samples exhibit a semiconducting behaviour above T_C , which indicate the passage directly from a superconducting to a semiconducting behaviour without going through a nonsuperconducting metallic state. Moreover, the normal state resistivity is found to decrease in the doping range $0 \leq x \leq 0.05$ and increase in the doping range $0.05 \leq x \leq 0.3$.

The carriers of superconductivity in the Y-123 system are likely to be pairs of holes, the concentration of which could be changed by varying the cation and /or oxygen content [10], Taking into consideration that these samples were sintered and annealed in air, it is expected that the oxygen content is low and oxygen site occupancies at O(1) and O(5) are the same i.e. oxygen disordering so that the crystal structure is expected to be of a tetragonal phase. For $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, the tetragonal phase is semiconductive and T_C is maximized by reducing x to ≤ 0.1 and obtaining a fully oxygenated phase. In addition, it may be suggested that the optimal of Cu^{3+} content which must be achieved for optimal hole doping of the CuO_2 planes (hole concentration of 0.16 per CuO_2 plane [11]) has not been reached in this medium of lower oxidizing potential. This could explain the slightly lower T_C^{onset} of 88 K for the pure sample compared to reported corresponding value of 92 K [12].

For Mo-doped samples, both of T_C onset and zero resistance temperature T_C offset are found to decrease with increasing Mo-content. Molybdenum is known to have two different coordination states i.e. 4- and 6- coordination. Therefore, substitution of Mo for copper in Cu(1) sites even as Mo^{4+} reduces the $\text{Cu}^{3+}/\text{Cu}^{2+}$ ratio

which is related to the average valence sum (AVS) of copper [9]. Also, hole concentration on the CuO planes decreases as O(4) atoms in the Ba-O planes move towards the Cu(1) layer while the barium atom move opposite to it. Such a process is typically opposite to that of charge transfer mechanism, Where charge is transferred via the O(4) ion movement toward Cu(2) layer and Ba towards Cu(1) atoms. Increasing the Mo-content is associated with an increase in Mo^{6+} which could also occupy the Cu(1) site and attract more oxygen atoms that can partially occupy the unoccupied O(5) site along the a-axis to form a pyramidal octahedral configuration. Therefore, the prepared samples are expected to become more hole underdoped with increasing Mo-content which explains the reduction of T_C offset values from 72 K for $x = 0$ to 36 K for $x = 0.3$.

Again, referring to Fig. (1) the observed increase in normal state resistance for samples with high Mo-content is mainly due to the effect of grain boundaries which strengthens with Mo-doping. However, its observed initial decrease for $x \leq 0.05$ can be attributed to an induced conductivity by electron hopping between different valence states of Mo, the value of which depends on the relative concentration of each valence state.

The obtained results of magnetic susceptibility of these samples as a function of temperature are illustrated in Fig. (2). The samples exhibit a diamagnetic shift indicating a superconducting state at temperatures which are lower than their corresponding values of bulk conductivity. This can be attributed to the formation of partial zero resistivity pathes across the sample causing the normalized resistance to drop faster initially than its susceptibility counterpart (Fig.3). The magnetically T_C offset values reported here are the temperature at which χ starts to level out. Again, inspection of Fig. (2) it is to be noticed that the sample with $x = 0.15$ exhibits two steps transition indicating the presence of two superconducting phases with different transition temperatures. Such a behavior is not clearly demonstrated in Fig. (1).

The temperature dependence of reduced resistance for the samples of run (2) which were sintered and annealed in oxygen for 5 hr is represented in Fig. (4). It is evident that the $R(T)$ trends for these oxygen rich samples are very different from those of oxygen deficient

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samples (Fig.1) especially for low Mo-content. Both of the pure and Mo-doped samples up to $x = 0.05$ exhibit a metallic behaviour down to T_C^{offset} after which a sharp transition takes place with a transition width of 2-5 K depending on the Mo-content. These different trends {Figs (1)&(4)} could be explained as follows. It is known that bulk superconductors are array of weak links which behave like Josephson junction. The possible reasons for the formation of these weak links are misorientation of grain boundaries and compositional variations at grain boundaries. SEM/EDS studies on the effect of sintering atmosphere on the weak-link behaviour [13] reveal that S-I-N-S type of weak-link samples sintered in air could be modified to S-N-S type when sintered in oxygen. On the other hand, the transition temperature T_C^{offset} of the pure sample is found to increase from 73.5 to 87.5 by oxygen treatment (run 2) which could be attributed to an increase in oxygen content so that oxygen ordering forms and the crystal structure is an orthorhombic as will be discussed in the next paragraph. For Mo-doped samples, the same enhanced superconducting properties have been achieved relative to these of run (1). However, as for samples of run (1) Mo-doping retain its underdoping effects so that a depression in T_C values is observed with increasing Mo-Content.

The structure of the oxygenated samples were characterized by powder x-ray diffraction where the diffraction data were analyzed in the orthorhombic structure with Pmmm symmetry. The obtained structure parameters were refined so that the calculated pattern fits the observed one. The obtained lattice parameters a, b and c are plotted versus Mo-content (Fig.5). With increasing x-value, the lattice parameter in the b-direction decreases whereas along the a-axis increases indicating a tendency towards a tetragonal structure which can be attributed to the oxygen filling of the unoccupied O(5) site. This tendency is confirmed by the gradual decrease in the degree of the splitting of the diffraction peaks located at $2\theta = 55^\circ$ and 69° where the corresponding reflections indexed as 200 and 123 respectively have almost disappeared with $x = 0.1$ (Fig.6).

The relative change of the lattice parameters a and b can be recognized from the normalized orthorhombic strain [12] defined as

$$\eta = \{2(b-a)/(b+a)\} \times 100\%$$

The normalized orthorhombic strain was found to decrease with increasing Mo-content up to $x = 0.15$ and almost kept constant for $x = 0.3$ in the same manner as T_C does (Fig.3). This suggests a strong correlation to exist between T_C and η (Fig.7) in such way that increasing normalized orthorhombic strain leads to higher T_C values. Again, referring to Fig.(5), the lattice constant c is found to be reduced with Mo-doping which can be explained by a strong attraction between the apical O(4) and the substituted Mo ions at Cu(1) sites. A displacement of about 0.5- 0.6 Å has been reported for iron substituted in YBCO [14].

The IR spectra of the oxygenated samples with different Mo-content are shown in Fig. (8). The main IR features of the obtained spectra of the pure sample ($x = 0$) is the appearance of five absorption peaks labeled as P_1 and P_4 to P_7 . Starting from the high frequency side, the absorption peak P_1 located at $\sim 630 \text{ cm}^{-1}$ can be assigned to asymmetric stretching vibration of Cu(1) – O(1) bond along the b-axis [15-17]. The remaining four absorption IR peaks located at frequencies of about 400, 360, 312 and 270 cm^{-1} could be assigned to vibration of Cu-O bond bending in Cu(1) – O(1), asymmetric vibration of Cu-O bond bending of CuO_2 network [15], O(2)/O(3) bond bending modes with the containing planes and Y vibration parallel to the CuO_2 planes[18] respectively. It is to be mentioned that the two IR peaks (P_2 , 590 cm^{-1} and P_3 , 580 cm^{-1}) are related to the pure sample and are associated with asymmetric stretching vibration of the two dimensionally CuO_2 planes and asymmetric stretching vibration of O(4) – Cu(1) – O(4) along c axis respectively. These two peaks are obscured by the adjacent P_1 peak ($x = 0$) and become apparent at $x \geq 0.05$.

Introducing Mo for copper with $x = 0.02$, no detectable spectral changes are observed other than a shoulder indicating the appearance of a peak at $\sim 340 \text{ cm}^{-1}$ (M_1), a marked increase in the intensity of absorption at $\sim 470 \text{ cm}^{-1}$ reflecting the appearance of a broad peak (M_2) and associated with another one (M_4) at about 960 cm^{-1} . M_1 could be assigned to MoO_4 while both of M_2 and M_4 could be assigned to MoO_6 . These assignment are in agreement with other reported

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values for ν_4 of MoO_4 tetrahedra and ν_5 & ν_3 of MoO_6 octahedron respectively [19-21].

Upon increasing the Mo-content to 0.05, a considerable spectral changes have been found. The P_1 peak which is related to Cu-O bonds introduced by oxygen vacancies in the one-dimensional Cu-O chain of the pure sample has been disappeared and replaced by another peak located at $\sim 670 \text{ cm}^{-1}$ (M_3). It is suggested that the M_3 peak could be assigned to Mo-O-Mo stretching vibration modes where the added oxygen atoms occupy O(5) sites to form Mo-O(5)-Mo or Mo-O(5)-Cu molecular complex along the a-axis. Two atoms of Mo may preferentially form a pair with a bridge of one oxygen atom on the a-axis in the Mo-doped samples as x exceeds 0.05. Similar observations have been found for Fe substitution for copper [16]. On the other hand, the frequency shift of optical phonons of M_3 towards lower values for $x = 0.15$ is an indication of a tendency for a phase transition [22] which supports the above obtained results.

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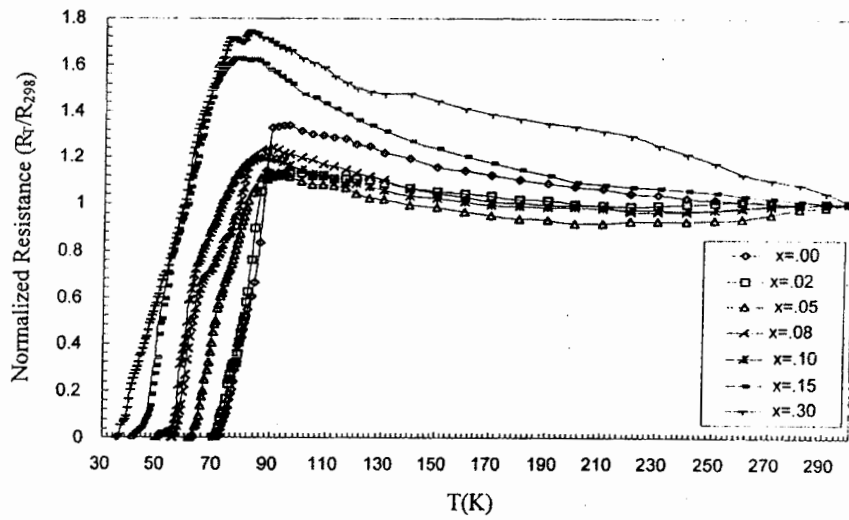
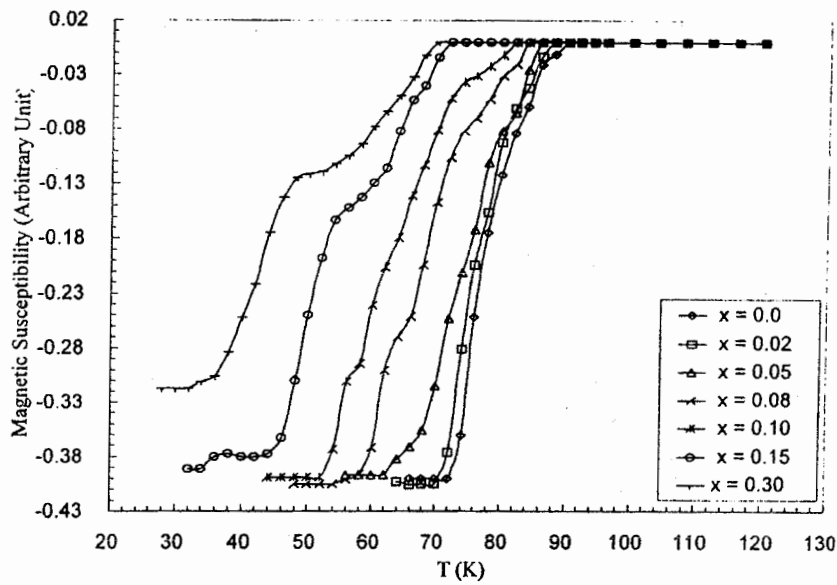


Fig.(1) :Temperature dependence of reduced resistance for samples of run (1)



.Fig.(2) :Temperature dependence of magnetic susceptibility for samples of run (1)

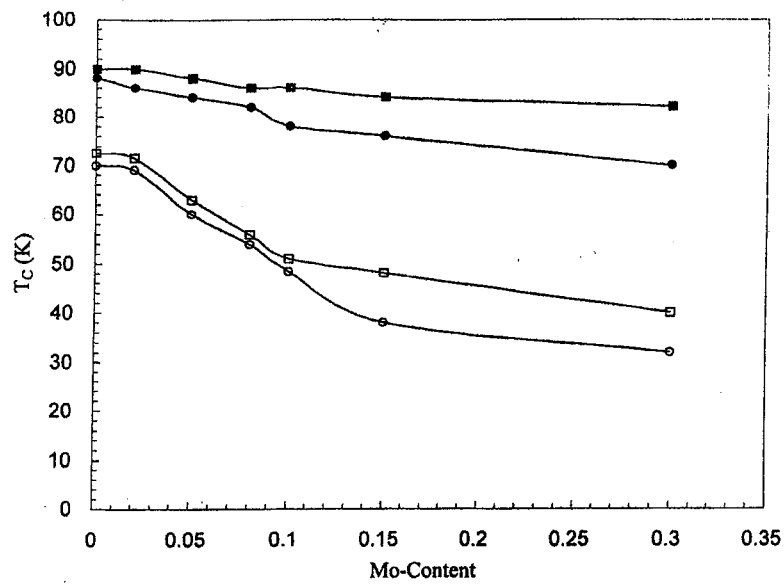


Fig.(3) : Mo-Content dependence of T_c^{onset} and T_c^{offset} , as determined from electrical (■, □) and magnetic (●, ○) measurements respectively

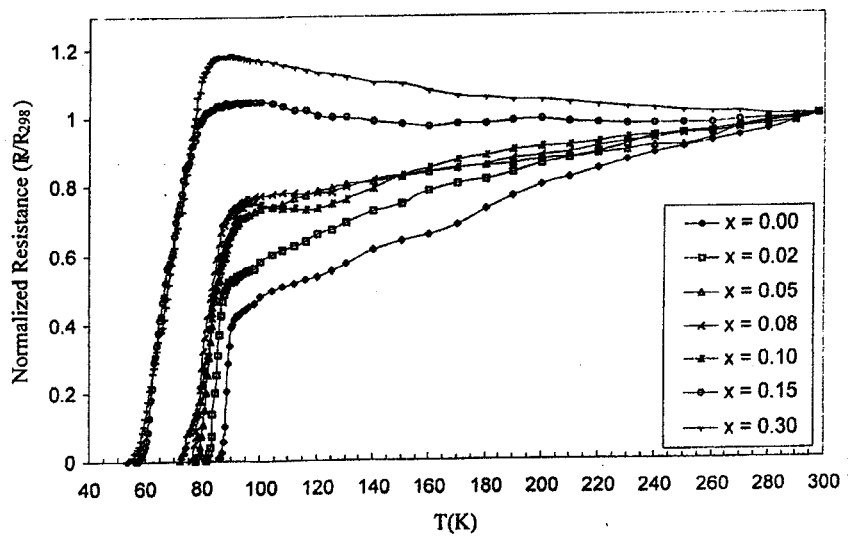


Fig.(4) :Temperature dependence of reduced resistance for samples of run (2)

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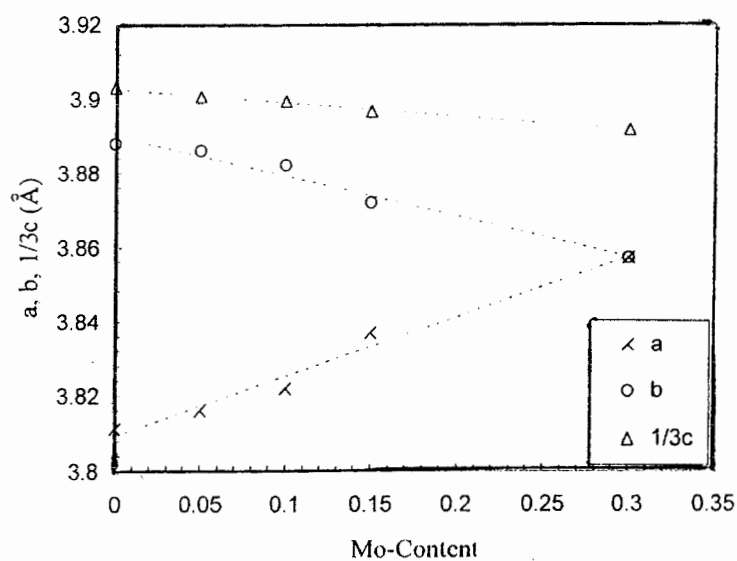


Fig.(5) : variation of lattice parameters of oxygenated samples (run2) with Mo-content

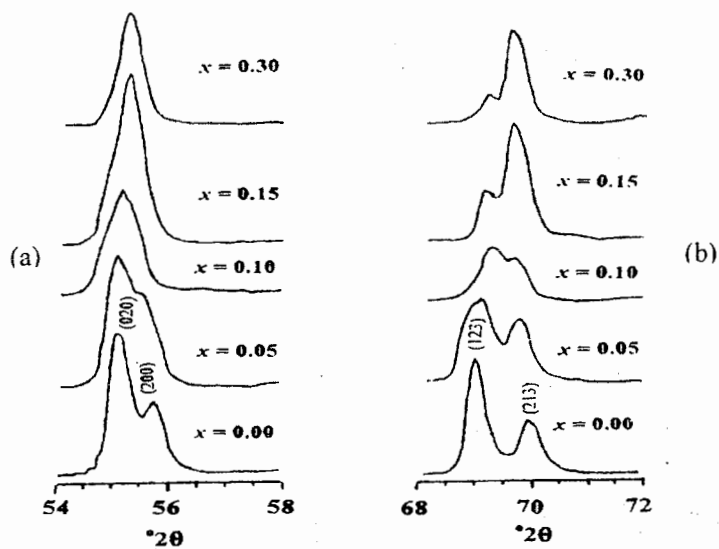


Fig.(6): XRD patterns of oxygen sintered samples in the region $2\theta = 55^\circ$ (a) and 69° (b).

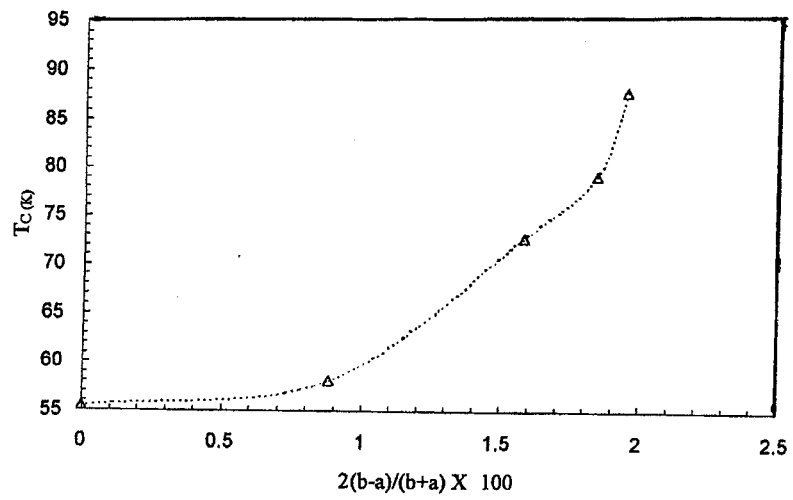


Fig. (7): T_c dependence of the normalized orthorhombic strain

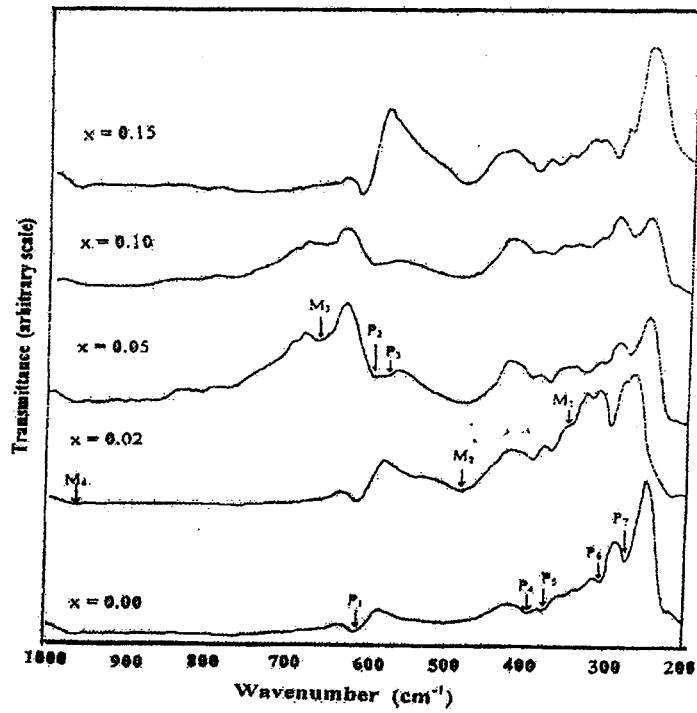


Fig.(8): IR spectra of undoped and Mo-doped samples

تأثير التطعيم بعنصر المولبدنيوم على الخصائص التركيبية والتوصيل الكهربى للنظام Y-123

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ملخص البحث :

تم تحضير عينات فائقة التوصيل الكهربى للنظام $Y_1Ba_2Cu_{3-x}Mo_xO_y$ ($0 \leq x \leq 0.3$) وذلك بطريقة تفاعل الحالة الصلبة ، أظهرت القياسات حدوث تحسن فى التوصيل الكهربى للعينات المحضرة بالحرق فى الهواء وذلك عند إعادة حرقتها فى جو من الأكسجين .

على الناحية الأخرى فقد تناقصت قيم درجة الحرارة الحرجة لجميع العينات بزيادة عنصر المولبدنيوم المضاف والذى تم تفسيره بتناقص كثافة الفجوات المتواجدة على مستويات Cu-O مع زيادة نسبة التطعيم .

أكدت قيم أبعاد الشبكة البللورية ، المحسوبة من قياسات حيود الأشعة السينية ، التركيب البللور (Orthorhombic) مع حدوث تحول للتركيب (Terragonal) بزيادة نسبة عنصر المولبدنيوم المضاف .

اقترحت هذه النتائج إحلال أيون المولبدنيوم مواقع Cu (1) فى الشبكة البللورية مع حدوث إضافة لذرات أكسجين لتحتل مواقع O (5) وقد أيدت ذلك قياسات طيف الأشعة تحت الحمراء .