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EPR investigations of Cu^{2+} ion in $Hg_{1-x}Tl_x\ Ba_2CuO_y$ ceramics at room temperature

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Abstract

A nearly single-phase $Hg_{1-x}\ Tl_x\ Ba_2\ Cu\ O_y$ samples with various Tl contents ($0 \leq x \leq 1$) have synthesized The dependence of the superconductivity transition temperature T_c and the behaviour of the room temperature EPR spectra of Cu^{2+} ions on the Tl content as well as the symmetry surrounding Cu^{2+} ions were investigated. The results suggest that the EPR signal can arise from Cu^{2+} defect in the (Hg/Tl)-O plane. The observed signals varied dynamically with the reduction of Tl^{3+} ion concentrations. The spectra shows rhombic g-tensor symmetry in the region $0.5<x\leq 1$, then shifted to an isotropic signal in the region$0\leq x\leq 0.4$ with Lorentzian lineshape. The increase of Tl content lowered the symmetry of the structure (rhombic g-tensor), reduced both T_c and the EPR signal intensity.

Introduction

Among the mercury based High Temperature Superconductors (HTSC) , general formula $Hg\ Ba_2\ Ca_{n-1}\ Cu_n\ O_y$ still the n=1 member $Hg\ Ba_2\ Cu\ O_y$ with $T_c = 94\ ^oK$ [1] is interesting because, the crystal symmetry is highly tetragonal, which enable us to ignore the in-plane anisotropy , (single CuO_2 layer in a unit cell). The doping levels of Hg-1201 can be controlled by changing oxygen content [2-4]. Accordingly, the preparation of single phase $Hg_{1-x}\ Tl_x\ Ba_2\ Cu\ O_y$ is considered. Experimentally, Hg-1201 system shows that T_c is decreased by Tl substitution in Hg site without change in both doping level and crystal structure [5,6]. This can be attributed to the differences in Hg and Tl oxidation states and the coordination chemistry (coordination between Cu^{2+} and the surrounding oxygen atoms). Superconductivity of such samples is believed to be originated from the presence of holes doping in the CuO_2 structural units. Hg and Tl atoms occupy the same sites in which extra oxygen atoms are introduced into the (Hg,Tl)-O layer [7], while both Cu and Tl atoms are considered to be a defect site in the Hg plane.

Electron Paramagnetic Resonance (EPR) studies of superconductors above T_c give information on the local environment and the symmetry of Cu^{2+} ions. The EPR of Cu^{2+} ions in most cuprate superconductors, such as YBCO , BSCO, and $LaCuO_4$ appears at splitting factor (g-values) in the region g=2→2.2 [8-12]. For single phase superconductors, no Cu^{2+} EPR spectrum exists. The absence of EPR signal of such single phase superconductor is assumed to be due to copper ion in diamagnetic valence states or in mixed valence states [13] , Cu^{2+} and Cu^{3+} valence states being not stable and fluctuating among these states and Cu^{2+} ions strongly antiferromagnetically coupled in pairs with diamagnetic ground state (S=0) and excited triplet state [14]. Also, the non observed broad EPR signals are due to the exceptional spin-spin dipolar coupling resulting from strong electron delocalization [15] . The observation of Cu^{2+} EPR signal is related to host Cu^{2+} ion and/or impurity phases containing Cu^{2+} ions [16] . The EPR Spectrum is characterized by the following parameters: (i) the intensity of signal and the linewidth (ii) The value of the g-tensor, which is given by the classical resonance condition for a free electron in a resonance magnetic field H_o , $h\upsilon = g\, \beta\, H_o$, where h is the Planck's constant , β is the Bohr magneton and υ is the frequency of the incident microwave radiation perpendicular to H_o .

In $Hg_{1-x}\,Tl_x\,Ba_2\,Cu\,O_y$ compounds , the average copper valence value is about +2 and two nonequivalent magnetically Cu sites exist in the unit cell . The first site Cu-O_1 has a planer coordination and the other site Cu(II) exists in (Hg/Cu) plane which lies in distorted oxygen environment. However, the oxidation states of both Cu and O ions at different lattice sites are uncertain, and the existence of Cu^{1+} , Cu^{2+} , and Cu^{3+} ions in the sample lattice is expected .

In the present work, a nearly single phases of $Hg_{1-x}\,Tl_x\,Ba_2\,Cu\,O_y$ with x varying from 0 to 1 could be synthesized to study the dependence of the EPR spectra of Cu^{2+} ions on Tl content at room temperature and the symmetry surrounding Cu^{2+} .

Experimental

Ceramic samples with nominal composition of $Hg_{1-x}\,Tl_x\,Ba_2\,Cu\,O_y$ (x = 0 → 1) were prepared by single step solid state reaction [17] using high purity powders of HgO , BaO , CuO and Tl_2O_3 . The mixture of oxides was pressed into pellets and inserted in an alumina crucible. The latter is sealed in quartz tube. The quartz tube was inserted inside a stainless steel tube. The sealed steel tube was heated to 810 ^oC by a rate of 150 $^oC/h$, held at this temperature for about 6h and then quenched into water . Phase characterization was examined by X-ray powder diffraction using CuKα radiation. The phase purity of the obtained samples was determined by fitting the main peak intinsities with those of tetragonal standards. The superconducting transition temperature T_c , was determined by dc electrical resistivity measurements using a conventional four-probe technique in the temperature range 300 K down to 20 K in closed cryogenic refrigeration system . The oxygen content "y" for all samples were determined by iodometric titration method [18]. For all samples containing Hg, the value of oxygen content is equal to y=4.11 , while for Tl Ba_2 Cu O_y sample y = 4.56 . The error between experiments in the presence of iodometric method was found to be ±0.01. Of course, the oxygen content is affected by annealing process specially in HTSC materials, because Oxygen in Cu(I) layer causes a broad superconducting temperature T_c . In our work all samples are quenched from 810°C, indicates a random oxygen content in the sample. It is expected that the disorder in the occupancy of oxygen sites in the basel plane is high in the quenched samples. Neutron diffraction experiment [7], shows that Cu-O bond length becomes longer when oxygen is removed from the sample, indicating that this bond length is sensitive to the effective charge in the Cu-O layer.

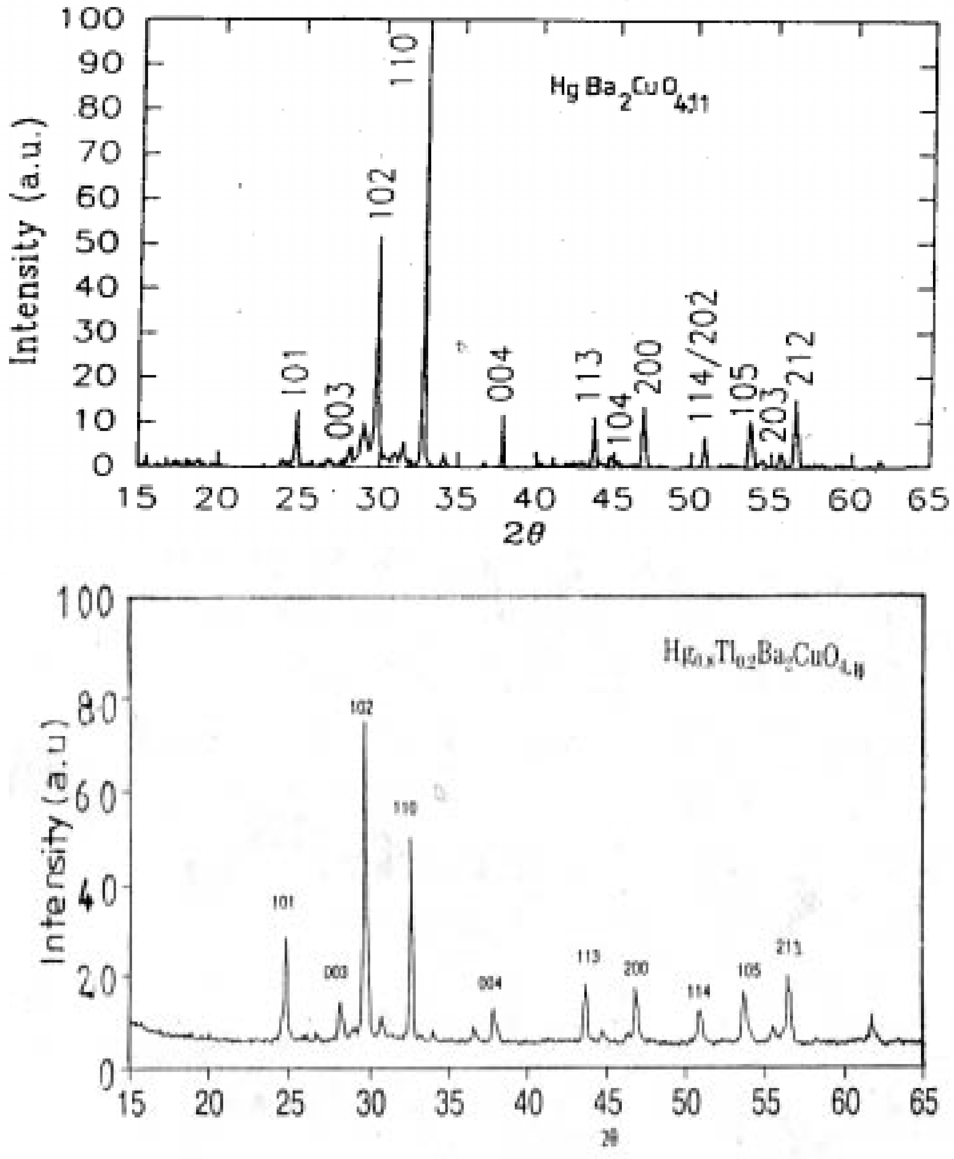

Figure 1. X-ray diffraction patterns for Hg Ba_2 Cu $O_{4.11}$ and $Hg_{0.8}$ $Tl_{0.2}$ Ba_2 Cu $O_{4.11}$ samples at room temperature

EPR measurements were performed on powdered samples at room temperature using JEOL X-band spectrometer with 100 kHz field modulation at 9.24 GHz. The EPR signal intensity was evaluated using the relation [19] $I = K(\delta H)^2L$, where δH is the peak to peak linewidth, L is the peak- to peak height and K is constant depending on the lineshape (the assumption is made that all x-band resonances have the same value of K).The Spin density of Cu^{2+} in the samples at room temperature is estimated by comparing the intensity of the EPR signal with that of a known amount of spins in the standard $CuSo_4 . 5H_2O$ crystal.

Results and Discussion

Fig.1. shows X-ray diffraction pattern at room temperature for $Hg\ Ba_2\ Cu\ O_{4.11}$ and $Hg_{0.8}\ Tl_{0.2}\ Ba_2\ Cu\ O_{4.11}$ samples without appreciable impurity phases. The peaks index are confirmed with the literature data in such system using p4/mmm tetragonal structure as observed in all Hg-1201 cuprates [6,7] with lattice parameters a = 3.877 Å and c = 9.508 Å . The dependence of lattice parameters on Tl-content for such compound is presented in reference [5]. Figure 2. shows the (onset) values of T_c determined from electrical resistivity measurements plotted as a function of Tl content. It is evident that T_c is nearly constant around 94 ^oK up to x=0.5 and the sudden drop to 83 ^oK at x=0.6 agrees with the observation of Noda et.al. [20]. However, Nakajima et al . [21] observed a continuous change of T_c vs Tl content. The change of T_c with Tl content may be due to the change in oxygen content in the sample and then to the concentration of charge carriers . These results can be described according to the charge transfer model [22] and will be published elsewhere.

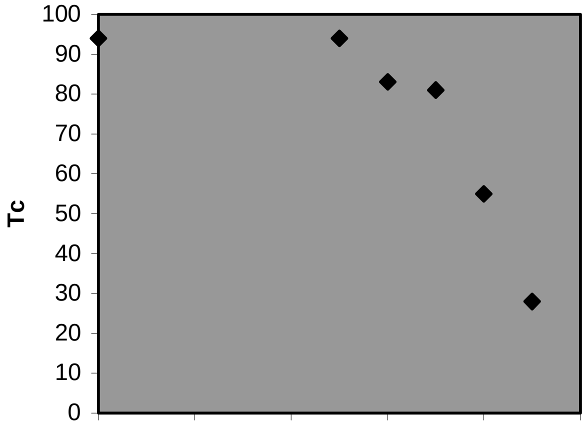

Figure 2: The dependence of T_c on Tl content of $Hg_{1-x}\ Tl_x\ Ba_2\ Cu\ O_{4.11}$ ceramics.

Figure 3. shows the Cu^{2+} EPR spectra of $Hg_{1-x}\ Tl_x\ Ba_2\ Cu\ O_y$ at room temperature just after the quenching process. These signals correspond to the powder–like spectrum of divalent copper ion ($3d^9$, s = ½ , I = 3/2) . The EPR spectrum of $Hg\ Ba_2\ Cu\ O_y$ (at x=0) consists of only one strong signal of Lorentzian lineshape, suggesting

an averaging of g-tensor by strong exchange coupling between Cu^{2+} ions ($g_{av} = 2.106$ and linewidth $\delta H = 23.2mT$. This broad line was fitted to a spin Hamiltonian in the form :

$$\hbar = g\beta H.S + J (S_i. S_j) , \qquad (1)$$

where the first term is the Zeeman term and the second term is the exchange interaction. The fitting line gives an average exchange integer J with the value +0.65 cm^{-1} . This value is small with respect to weak ferromagnetic coupling. The spin relaxation time can be estimated from the observed linewidth to be $1.25x10^{-11}$ sec, which is in the same order of magnitude for most HTSC materials. However, the EPR spectrum of $Tl Ba_2 Cu O_{4.56}$ (at x=1) consists of three signals, indicates a rhombic symmetric environment as explained below . These spectra are described by a spin Hamiltonian of the form :

$$\hbar = \beta[g_xH_x.S_x + g_yH_y.S_y + g_zH_z.S_z] +J (S_i. S_j), \qquad (2)$$

with $g_x = 2.034$, $g_y = 2.106$, $g_z = 2.233$ and unresolved hyperfine structure . The central line in the spectrum has the same position of $HgBa_2 Cu O_{4.11}$ signal (i.e. $g_{av} = g_y$) . Figure 3. shows also the variation of EPR spectra of $Hg_{1-x} Tl_x Ba_2 Cu O_{4.11}$ with Tl content . It can be seen that these spectra consist of three signals each with the same g-values of that spectrum of $Tl Ba_2 Cu O_{4.56}$ (at x=1) .The outer two signals in these spectra are decreasing in intensities with decreasing of Tl content, then heading in the central signal. At x = 0.5 , the feature of the spectrum consists of two signals with $g_1 = 2.106$ and $g_2 = 2.034$. When x becomes less than 0.5 , (i.e in the HTSC region), the spectrum shows only one strong signal which is the superposition of the EPR signal of $Hg Ba_2 Cu O_{4.11}$ (at x=0) . From neutron diffraction measurements by Wagner et.al. [7] , the crystal structure of $Hg Ba_2 Cu O_{4.11}$ indicates the existence of partial substitution of Cu(II) in the site of Hg in the structure. The EPR spectra of Cu(II) probe in $Hg_{1-x} Tl_x Ba_2 Cu O_{4.11}$ samples represent a central signal with two outer signals as shown in Figure 3. The spectra can be attributed to the presence of two Cu(II) sites in the structure. As Tl^{3+} cations prefer a distorted octahedral coordination [7], this gives a probability of chain – plane interaction with Cu(II) defect in the Cu(I)-O plane [23] . Therefore, the Cu(II) center in the position of (Hg/Tl)–O(4) plane may be coordinated in low symmetry five coordination . This represents a rhombic g-tensor as shown in Figure 3. On the other hand, Cu^{2+} site in Hg position, coordinated in three –fold octahedral site symmetry, represents an isotropic EPR signal of Lorentzian lineshape. A decrease of Tl content (i.e going to HTSC regime) leads to a shift of the structure toward the higher symmetry with only one isotropic EPR signal . The low symmetry phases of the structure of $Hg_{1-x} Tl_x Ba_2 Cu O_{4.11}$ compounds observed by EPR measurements (rhombic g-tensor) are reflected in the study of stabilization of superconductivity in this system [5]. Those phases show a decrease in T_c with the increase of Tl content.

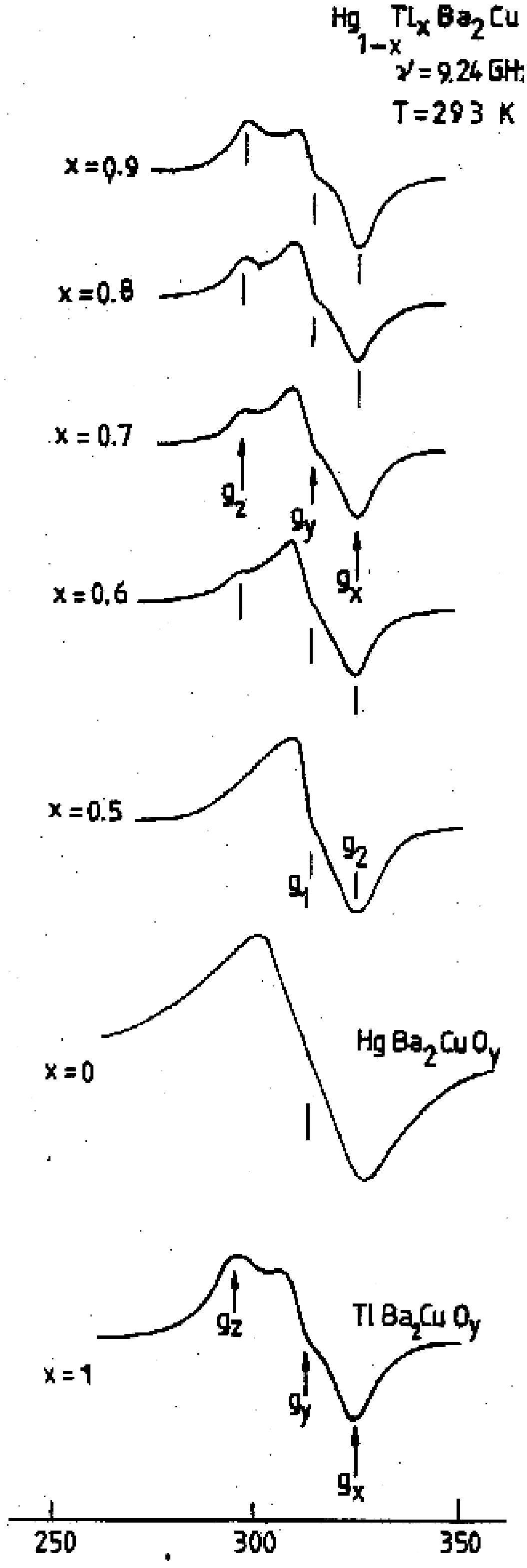

Figure 3: The EPR derivative spectra for Hg_{1-x} Tl_x Ba_2 Cu O_y ceramics at room temperature. The g-values are marked.

Finally, the number of spins are calculated from the intensity of the recorded EPR spectra. The calculated numbers of copper ions in Hg Ba_2 Cu $O_{4.11}$ and in Tl Ba_2 Cu $O_{4.56}$ were $1.0x10^{21}$ and $9.88x10^{20}$ per gram respectively. More than half of these values are expected to be paramagnetic Cu^{2+} with S =1/2 . As shown in Figure 4. , the recorded spectra indicate that the number of spins is much lower than that expected and inversely proportional to Tl content. This reflects a reduction of spin susceptibility by increasing Tl content. The increase of Tl content will then causes : i) a decrease of T_c due to an increase of Cu valence state ii) lowering the symmetry of the structure which may be due to chain – plane interaction ,during mechanically processing of the samples as discussed by Stankowski et.al., [23]. iii) a decrease of the number of spins , which reflects the fluctuation of valence state of Cu ions.

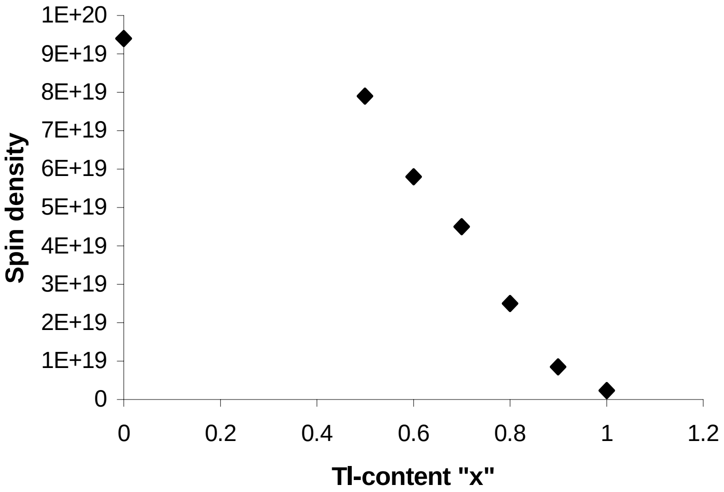

Figure 4: Variation of spin-density (per gram) with Tl content for Hg_{1-x} Tl_x Ba_2 Cu $O_{4.11}$ samples at room temperature.

Conclusion

Superconductivity in Hg_{1-x} Tl_x Ba_2 Cu $O_{4.11}$ is believed to be originated from the presence of holes in the CuO_2 structure sheets in this compound. This can be assigned in the consequence of cation substitution of Hg^{2+} instead of Tl^{3+}. The EPR studies reflect the symmetry variation in the structure. This is related to the variation of oxidation state of Cu in the compound. EPR of Cu^{2+} signal observed in this system is due to Cu^{2+} defects in (Hg/Tl)-O_4 plane and/or plane-chain interaction.

In case of Tl Ba_2 $CuO_{4.56}$, EPR signal shows rhombic symmetry with $g_x = 2.034$, $g_y = 2.106$ and $g_z = 2.233$. The signal may be attributed to some defects of Cu^{2+} in Tl^{3+} site or the presence of plane-chain interaction between Tl/CuO(2) and CuO(1) planes. Whenever, substitution of Hg in Tl Ba_2 $CuO_{4.56}$, the symmetry shifted towards a higher ordered tetragonal symmetry up to $Hg_{0.5}Tl_{0.5}$ Ba_2 $CuO_{4.11}$ compound. The central signal in the spectrum of Hg_{1-x} Tl_x Ba_2 Cu $O_{4.11}$ is the superposition of Cu(II) signal in the Hg Ba_2 $CuO_{4.11}$ compound. The outer signals g_x and g_z behave dynamic character as Hg^{2+}concentration is increased . Increasing of Hg^{2+} above 50%, refines the Hg Ba_2 $CuO_{4.11}$ structure with only one isotropic EPR signal of Lorentzian lineshape with g = 2.106 .

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