EFFECT OF METAL SUBSTITUTION IN BSCCO CERAMIC SUPERCONDUCTORS

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ABSTRACT: The fabrication, electrical, and optical properties of ceramic Bi$_{2-x}$M$_x$Sr$_2$Ca$_2$Cu$_3$O$_y$ (where M=Al or Ni and x=0.3) superconductors are described. Resistivity measurements reveal that when Al is partially substituted at the bismuth site in the BiSrCaCuO compound, $T_c$ decreases to 77 K and the nickel-substituted compound shows a $T_c$ of 70 K, compared to the undoped ceramic BiSrCaCuO samples with $T_c$ of 85 K. Infrared reflectance measurements, which cover the 50-4000 cm$^{-1}$ range, find that the reflectance from the ceramic samples decreases in the metal-doped samples. The observed phonon modes in the infrared conductivity spectra (obtained by Kramers-Kronig analysis) decrease in strength and some features are completely smeared out. Furthermore some of the modes are observed to shift slightly in the frequency on doping, the change in the $T_c$ and vibrational modes is attributed to destabilization of 2223 phase.

Key words: Infrared, reflectance, superconductivity.
Introduction

Since high $T_c$ superconductivity was discovered in the bismuth-containing family, a large number of articles have been published on stabilization and characterization for all the three phases in the BSCCO series [1-10]. In sintered polycrystalline samples the high $T_c$ phase seems to occur in unconnected regions separated by a lower $T_c$ phase, which often prevents the zero resistance of the high $T_c$ phase from being achieved. It has been observed that partial substitution of Bi by Pb helps in stabilization of high $T_c$ phase [11]. Sasakura et al [12] have reported a single phase 2223 sample over a fairly wide range of composition in the formula Bi$_{1.68}$Pb$_{0.32}$Sr$_2$Ca$_2$Cu$_3$O$_y$ can be prepared with a $T_c$ in the range of 105 to 110 K and substantial Meissner fraction.

Basically the phase diagram of HTSC is divided into three different regimes: (1) the underdoped regime, where the superconducting phase is adjacent to the insulating phase and $T_c$ increases with increasing p-type doping; (2) the optimum $T_c$ regime, where $T_c$ reaches the maximum value within a given series; and (3) the overdoped regime where $T_c$ decreases on further doping levels and, at the same time, the material appears to be a better metal.

Using the method described in [11-12] we made an effort to dope BSCCO compound at the bismuth site with aluminum and nickel in Bi$_{2-x}$Sr$_2$M$_x$Ca$_2$Cu$_3$O$_y$ compound. The purpose of this paper is to investigate the effect of aluminum and nickel doping on the electrical and optical properties of the resulting ceramic compounds.

Experimental

Direct solid state reaction of Bi$_2$O$_3$, SrCO$_3$, CaCO$_3$ and CuO in stoichiometric proportions in the range 1113K-1143K is known to yield a major fraction of 2223 phase in the ceramic superconductors. It is also known that the chemical substitution at a crystallographic site other then the Cu site has been found to be extremely useful in the synthesis of HTSC based on bismuth cuprates.

In order to obtain ceramic superconductors, reagent grade Bi$_2$O$_3$, CaCO$_3$, SrCO$_3$, CuO, Al$_2$O$_3$ and NiO$_2$ were weighed in the molar ratio of Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_y$, Bi$_{1.7}$Al$_{0.3}$Sr$_2$Ca$_2$Cu$_3$O$_y$, and Bi$_{1.7}$Ni$_{0.3}$Sr$_2$Ca$_2$Cu$_3$O$_y$. The goal of the process was to produce substitution on the Bi site; however, especially in the case of Ni doping we are unable to rule out substitution on the CuO$_2$ planes. In addition, despite the nominal 2223 stoichiometry, the data suggest that we obtained mostly 2212 composition in these samples. The three samples, named Sample#1, 2, and 3, respectively, were calcined
at 1073 K in a high temperature furnace for 12 hrs. The calcined powders were melted in three different alumina crucibles separately at a temperature of 1473 K, and then the melt was quenched between two steel blocks. Samples of 3 mm thickness and 1 cm diameter were obtained. The three samples so obtained were annealed at 1123 K for 120 hrs. After annealing the samples were cooled slowly to room temperature. Infrared reflectance spectra in the frequency range of 50 to 4000 cm\(^{-1}\), were measured using a Bruker 113v spectrometer. The \( T_c \) of the samples was measured using standard four-probe resistance technique.

**Results and discussions**

Introduction of aluminum and nickel at a trivalent bismuth site is expected to cause a charge imbalance and hence change in the \( T_c \) of the compound. Fig 1 shows the resistivity versus temperature for all the three samples. The observed transition width of Sample#1 is about 5 K and a sharp resistivity drop is observed at 90 K and zero resistance is reached at 85 K as can be seen from Fig 1. There is a small anomaly at 110 K, and the data indicate that there is only a small fraction of the 110 K 2223 phase in this sample. The remainder is presumably the 2212 phase.

Sample#2 has a substantial resistivity drop beginning from 100 K, with zero resistance at 77 K. There is an indication of a second phase in this sample at 105 K, suggesting that Al doping reduces the transition temperature of both 2212 and 2223 phases. Sample#3 also shows a drop in resistivity starting from 100 K, with zero resistance reached at 70 K.

![Figure 1. Resistivity vs. temperature for Bi\(_{2-x}\)M\(_x\)Sr\(_2\)Ca\(_2\)Cu\(_3\)O\(_y\) (M=Al,Ni, x=0.3)](image_url)
The room temperature dc-resistivity is highest for sample#1 and is decreased by the substitution of Al and Ni as it is obvious from Fig 1. This observation suggests that the doped samples are in the overdoped regime.

In the reflectivity spectra for the three samples shown in Fig 2, it was observed that there is a variation in the reflectivity at low frequency between the three samples. For aluminum substituted sample i.e., sample#2 the reflectivity is higher than that of sample#1, this increase in the reflectance in sample#2 could be due to increase in the free carrier response, whereas for the nickel substitution at the Bi site the reflectance of the sample #3 reduces a lot in the whole measured frequency range, indicating a major change in the microstructure has taken place in sample#3 This could be due to large difference between the atomic radii of Bi and Ni, and also could be due to charge imbalance because of different valences of these elements, and finally it could be due to Ni substitution on the copper site.

A phonon peak is clear in the reflectance of all samples, at about 670 cm\(^{-1}\). Although quantitative similarity is seen among all the measured reflectance spectra of the oxides with Bi\(_2\)O\(_3\) layer, their dielectric functions are quantitatively different, which can be seen from the variation in the reflectance of these samples in the measured frequency range.

![Graph](image)

Figure 2. Frequency dependent reflectance of Bi\(_{(2-x)}\)M\(_{x}\)Sr\(_2\)Ca\(_2\)Cu\(_3\)O\(_y\) (M=Al,Ni, x=0.3)

Reflection spectra are needed over a wide frequency range to calculate complex reflectance Kramers-Kronig transformation. Below 50
cm$^{-1}$ we used the Hagen-Rubens approximation for the metallic reflectance spectra. We measured the reflectance in the near-IR and visible up to 20,000 cm$^{-1}$ and used these data to extend the midinfrared measurements. At still higher frequencies we used a power law, i.e.,

$$R(\omega) \propto \omega^{-4}$$

The real part of the frequency dependent conductivity so obtained for all the three samples is presented in Fig. 3.

Studies of BSCCO compounds have shown that strongly pronounced structure due to infrared active phonons are superimposed to broad conductivity spectrum caused by electronic conductivity. We have shown [13] that the normal state data cannot fit with simple Drude model alone; instead, a dielectric function which is sum of lattice vibrations and a generalized Drude term (with frequency-dependent damping and mass in order to give the broad midinfrared absorption) must be used. In polycrystalline ceramic samples, these vibrational modes can mostly be associated with lattice vibration parallel to the c axis [14-15].

![Graph showing conductivity vs frequency for BSCCO samples](image)

**Figure 3.** Frequency dependent Conductivity of Bi$_{2-x}$M$_x$Sr$_2$Ca$_2$Cu$_3$O$_y$ (M=Al, Ni, x=0.3)
A factor-group analysis performed on the vibrations of 15 atoms in the Wigner-Seitz cell of Bi$_2$Sr$_2$Ca$_1$Cu$_2$O$_{8+}$ by [15] leads to the following symmetry characterization and spectroscopic activities [infrared (ir) and Raman (R)] of the 28 optic modes: i.e.,

$$\chi=6A_{2u}(\text{ir})+B_{2u}(\text{inactive})+7E_u(\text{ir})+6A_{1g}(R)+B_{1g}(R)+7E_g(R)$$

This shows that there are 7 $E_u$ (c-axis polarized) infrared active phonon modes in the BSCCO compound.

The peaks of the optical conductivity spectra that arise from the weak features in the reflectance spectra below 700 cm$^{-1}$ can be assigned to phonon features. We observe 5 $E_u$ phonon vibrations for sample#1 [15]. The assignment of these vibrational modes can be based on the infrared spectra of the parent materials i.e., Bi$_2$O$_3$, SrCO$_3$, CaCO$_3$, CuO, including the dopant at the bismuth site, also using the calculations made in Refs. [10-12]. The 168 cm$^{-1}$ vibrational mode may have been originated from CuO structure, whereas the 210±4 cm$^{-1}$ feature is close to the IR vibrational mode of SrCO$_3$.

There is a strong mode in CaCO$_3$ vibrational spectra at about 302±4 cm$^{-1}$; thus, the mode around 305 cm$^{-1}$ in the optical conductivity spectra of sample 1 may be originated from Ca-O vibration with the contribution of O vibration of CuO$_2$ planes similar to those in YBa$_2$Cu$_3$O$_x$ compound. The other two modes, at 358 cm$^{-1}$ and around 440 cm$^{-1}$, seen in all three samples, originate from Bi-O and Cu-O vibrations. The slight shift in these modes among the samples is due to partial substitution of Bi by Aluminum and Nickel at the Bismuth site. The strong vibrational mode, around 580 cm$^{-1}$, is assigned by various authors [14-16] as Cu-O (1) in-plane stretching $E_u$ vibrations of CuO$_2$ layers. All the observed phonon modes for the three samples are listed in table I. It was noticed that the intensities of most of the modes in sample#1 are stronger than in sample#2 and 3. The variation in the mode strength of the dopant material is due to a number of factors. First, there can be a change in the effective mass of the resultant composite formed due to Al and Ni substitution. Probably more important is the amount of disorder in the crystal structure, which can result in the vibrational frequencies being broadened enough that the vibrational spectral weight blends with the electronic background. Characteristics of phonon modes were also observed in other measurements, such as tunneling conductance [17-18], neutron scattering [19] and electron-energy-loss spectroscopy [20] measurements.
<table>
<thead>
<tr>
<th>Sample 1</th>
<th>168</th>
<th>213</th>
<th>307</th>
<th>358</th>
<th>580</th>
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<tbody>
<tr>
<td>Sample 2</td>
<td>185</td>
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<td>351-438</td>
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<td>573</td>
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<tr>
<td>Sample 3</td>
<td></td>
<td>216</td>
<td>310</td>
<td>360-451</td>
<td>584</td>
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</table>

In summary we have prepared the $\text{Bi}_{2-x}\text{M}_{x}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ ceramic superconductors and measured resistivity and infrared reflectance spectra, from which the conductivity spectra were derived. From resistivity measurement we observed a formation of weak second phase in the undoped and the aluminum-doped sample. The $T_c$ of the parent sample was observed to decrease on doping. From the IR measurements we observed that the vibrational frequencies do not shift appreciably on doping. Finally, we have given tentative assignments to some of ir-active phonon modes in the bismuth-based superconductors.

References


