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Surface Fourier transform-infrared spectral study of the effect of silver and carbon in $Tl_{0.5}Pb_{0.5}Sr_2CaCu_2O_{7-\delta}$

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The relation between the effect of silver on the amount of residual carbon and the rate of carbonate build-up on the surface of the particles of Tl1212 and Bi2212 was studied by infrared spectroscopy using a diffuse reflectance infrared–Fourier transform (DRIFT) cell. The result showed that appreciable amounts of carbonate still remained after calcination at 940 °C when carbonates were used as starting materials. Samples prepared using oxides also showed the presence of carbonate that originated from the CO_2 adsorption at the surface during processing. The small amounts of surface carbonates were below the detection limit of X-ray diffraction. However, the DRIFT technique has been found to be a convenient and effective method for qualitative and semi-quantitative analysis of carbonate formation on the powder surface and atmospheric degradation of thallium- and bismuth-compound superconductors. The presence of silver decreased the rate of the carbonate formation on the Tl1212 and Bi2212 particle surface influencing the degradation process. Carbonate formation was more sensitive to the presence of silver in Tl1212 than in Bi2212. The presence of silver appeared to change the hydroxylation kinetics of calcium and/or strontium, which was directly related to the carbonate forming process.

1. Introduction

One of the major problems in the practical application of high-temperature superconductors (HTSCs) is associated with the chemical stability against the environmental conditions under which a good deal of H_2O and CO_2 are always ready to react. $YBa_2Cu_3O_7$ (YBCO) is known to be very sensitive to water [1–3]. The reaction of YBCO with atmospheric CO_2 generates degradation products, including $BaCO_3$ according to the reaction [1, 2]

$$2YBa_2Cu_3O_7 + 3CO_2 \rightarrow Y_2BaCuO_5 + 3BaCO_3 + 5CuO + 0.5O_2 \quad (1)$$

This reaction is strongly catalysed by water vapour, and YBCO ceramics have been observed to disintegrate after hours of soaking in water-vapour-saturated air at room temperature.

Although the Bi–Sr–Ca–Cu–O (BSCCO) system is known to be less sensitive to water than YBCO, it has been shown in the literature that BSCCO thin films degrade upon exposure to water for several hours [4]. Sintered BSCCO bulk also showed a tendency towards a decrease in the T_c and J_c with water soaking time [5].

Atmospheric degradation products, which are mainly composed of carbonates built up on the surface or in the grain boundaries, can be partly responsible for limiting the current-carrying capacities of these materials. Carbon contamination can occur if the calcination of the starting materials is not completed. A more common source of contamination is the reaction of the surface of the powder with atmospheric CO_2, which is particularly likely to be a problem when fine powders are used. Therefore, the problems associated with the stability against water and CO_2, should be important, especially in the industrial application of these materials. The influence of residual carbon impurities, however, has often been overlooked, and therefore not many related studies have been carried out for the YBCO and BSCCO systems [4, 6, 7].

Studies on residual carbon and carbon adsorption on the surface of thallium-compound superconductors are completely absent. In this system, the reaction is usually carried out in a sealed condition, in which case the carbon introduced through the incomplete calcination of precursors and/or carbon adsorption from the atmosphere cannot be easily removed. Also, thallium compounds respond very sensitively to a change in oxygen and thallium pressure. Therefore, if the presence of residual carbon does influence superconducting properties of thallium compounds, as it does for YBCO and BSCCO, thallium compounds may be more sensitive than YBCO and BSCCO.

In the course of investigating the effect of silver in the $Tl_{0.5}Pb_{0.5}Sr_2CaCu_2O_7$ (Tl1212) system, it was found that using different starting materials (oxides versus carbonates) can lead to different sintering behaviours [8]. The purpose of this work was to investigate the effect of silver when different amounts of carbon (mostly present as carbonate) are present in the Tl1212 system. Different starting materials were used to make the Tl1212 compound with different silver and carbon contents. The relation between the effect of silver on the amount of residual carbon (or adsorbed carbon-containing species) and the rate of carbonate build-up on the surface of the particles was studied by infrared spectroscopy using a diffuse reflectance infrared–Fourier transform (DRIFT) cell. The DRIFT method is a very surface-selective technique, and its resulting infrared bands indicate the state of the surface of the particle. $Bi_2Sr_2CaCu_2O_8$ (Bi2212) and $Bi_2Sr_2CaCu_2O_8$–20 wt % Ag powders were also prepared and analysed to investigate the same effect.

2. Experimental procedure

Powder specimens with a nominal composition of $Tl_{0.5}Pb_{0.5}Sr_2CaCu_2O_7$ (Tl1212) and Tl1212–0.37 Ag were prepared by solid-state reaction using two kinds of starting materials ($SrCO_3/CaCO_3/CuO/(Ag_2O)$), and $SrO/CaO/CuO/(Ag_2O)$)). Mixtures having nominal compositions of $Sr_2CaCu_2O_y$–($Ag_{0.37}$) were calcined at 940 °C for 20 h. The reacted precursors were mixed with an appropriate amount of Tl_2O_3 and PbO, and then reacted in the form of powders in sealed silver tubes at a temperature of 850 °C for 6 h. Heating and cooling rates of 10 $°C\,min^{-1}$ were used. The weights of the silver tubes containing the samples before and after sintering were used to check the loss of thallium. All of the samples were kept in a desiccator except while processing, to minimize the exposure time to air.

The residual carbon concentrations in the precursor powders were determined by a combustion method using a LECO 4000A carbon determinator. Powder X-ray diffraction (XRD) data were collected using a Siemens D500 diffractometer. DRIFT spectra were obtained for the powders using a Nicolet 60 XSR FT–IR spectrometer equipped with a Spectra-Tech diffuse reflectance accessory. The powder was placed in a sample holder with KBr as a diluent. Each spectrum was scanned 4096 times to increase the signal-to-noise ratio.

For the ageing experiment, sample powders prepared from oxide starting materials were used. Samples were put in a water-vapour-saturated closed container. Deionized water was used. The powders were not immersed in the water, and there was no direct contact between the liquid water and the samples. The temperature of the water was 22 ± 3 °C. Infrared reflectivity spectra were obtained for the powders aged for a certain amount of time to monitor the amounts of carbonate species built up on the powder surface.

$Bi_2Sr_2CaCu_2O_8$ (Bi2212) and Bi2212–20 wt % Ag powders were prepared using SrO and CaO as starting materials, and applying the same method as was used to make Tl1212 powders. The reaction was carried out at 865 °C for 24 h in open atmosphere with flowing oxygen. The sample powders were aged under the same conditions as the Tl1212 powders. XRD and DRIFT were used to analyse the powder samples before and after ageing.

3. Results and discussion

3.1. Silver–residual carbon relation

Table I lists the residual carbon contents in the precursor powders measured by the combustion method, together with the notation used to indicate materials prepared with different starting materials. Those powders starting with oxides contain less carbon, as expected. Those with added silver show less carbon than those without silver. This result indicates that 940 °C–20 h treatment will not guarantee carbon-free precursor powders. Even when starting materials do not contain carbon, the calcined precursors contain detectable amounts of carbon. Repeating calcination after re-grinding reduces the amount of carbon but does not completely remove it. Precursor powders calcined at 940 °C–20 h were used for the following work because this calcination condition has been and is frequently used to prepare precursor powders for thallium-compound superconductors.

Fig. 1 illustrates the XRD patterns of precursor powders calcined at 940 °C–20 h and the Tl1212 –(0.37 Ag) powders sintered at 850 °C–6 h. A, B, C, and D are explained in Table I. The major phases in the precursor powders are $(Ca, Sr)CuO_2$ and $(Ca, Sr)_2CuO_3$ (see Fig. 1a). Small amounts of CaO and CuO are also present. No appreciable difference in the XRD patterns can be found for powders prepared with different starting materials. A metallic silver peak appears in XRD patterns for A and C.

Tl1212–(0.37 Ag) powders are almost X-ray phase-pure, except for a small amount of $Tl_{0.5}$–$Pb_{0.5}$–Sr_2CuO_5 (Tl1201) (see Fig. 1b). As in the case of the precursor powders, XRD patterns show little difference when different starting materials are used. For both precursor and Tl1212–(0.37 Ag) powders, no $SrCO_3$ nor $CaCO_3$ peaks can be identified in the XRD patterns.

Fig. 2 illustrates the DRIFT spectra obtained for the precursor and the Tl1212–(0.37 Ag) powders. The three investigated band areas are indicated as b1, b2,

TABLE I Residual carbon content in the precursor powder measured by the combustion method

Starting materials	Notations used	Carbon content (wt %)
$SrCO_3$, $CaCO_3$ CuO, Ag_2O	Carbonate–0.37 Ag (A)	0.15
$SrCO_3$, $CaCO_3$ CuO	Carbonate–no Ag (B)	0.35
SrO, CaO CuO, Ag_2O	Oxide–0.37 Ag (C)	0.05
SrO, CaO CuO	Oxide–no Ag (D)	0.07

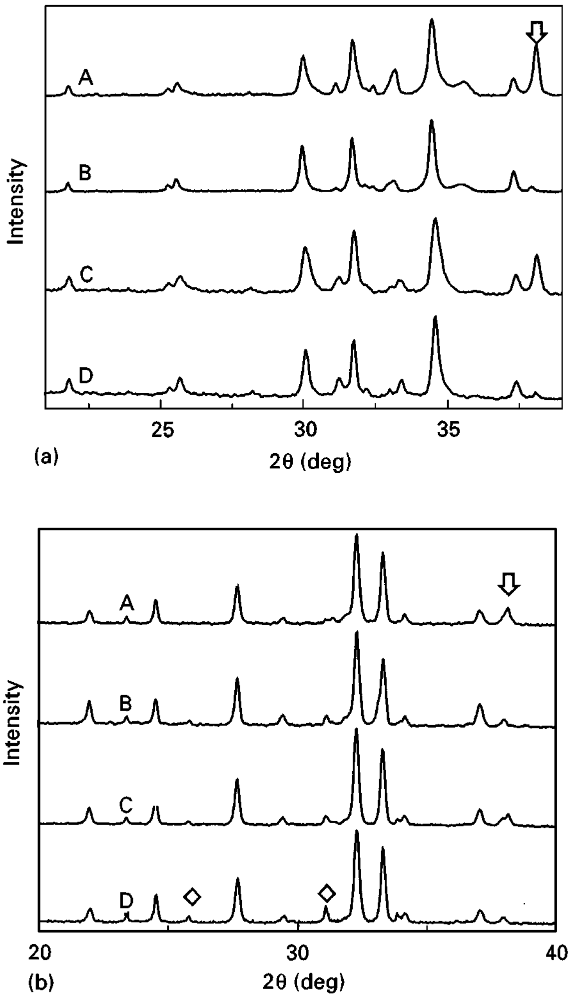

Figure 1 XRD patterns of (a) precursor powders, and (b) Tl1212–(0.37 Ag). The arrows and diamonds indicate the peaks of Ag and Tl1201, respectively. A–D, see Table I.

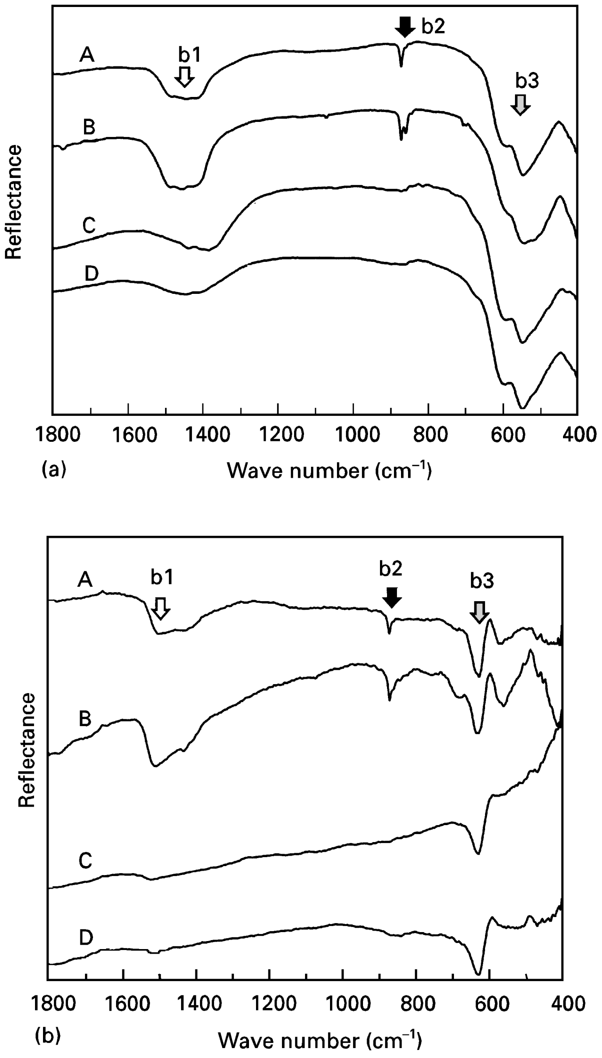

Figure 2 DRIFT spectra for (a) precursor powders, and (b) Tl1212–(0.37 Ag). A–D, see Table I.

and b3. The scales of reflectance were adjusted in each spectrum to make the band intensities of the spectral region b3 about equal. Bands corresponding to the asymmetric stretching vibrations of CO_3^{2-} of $CaCO_3$ and $SrCO_3$ are seen as a doublet in the spectral region b1 [9, 10]. The bands associated with the out of plane bending vibration of CO_3^{2-} for both of the carbonates are seen overlapping in the spectral region b2. The bands in the spectral region b3 are different in Fig. 2a and b. In Fig. 2a, the multiple bands in the spectral region b3 result from the convolution of bands corresponding to the stretching vibrations of Cu–O in the CuO planes in different kinds of copper-containing oxides in the precursor ($(Ca, Sr)CuO_2$, $(Ca, Sr)_2CuO_3$, and CuO). In Fig. 2b, the band in the spectral region b3 is associated with a Cu–O stretching vibration in the CuO planes of Tl1212 phase.

Assuming that the bands at the spectral region b3 in Fig. 2a come from the Cu–O stretching vibration alone, the whole band area of the spectral region b3 can be used as a reference, in combination with that of the carbonate bands in the spectral region b2, to estimate the relative amount of total carbonates on the surface of the precursor powders. The ratio of the band area of b2 to that of b3 ($b2/b3$) was used to compare the relative amount of total carbonates on the surface of the precursor powders. A higher value of $b2/b3$ indicates a larger amount of carbonates on the powder surface compared to that of Cu–O containing phases. Table II lists the $b2/b3$ values calculated from the DRIFT spectra shown in Fig. 2a. The ratios are normalized with respect to that of sample D (oxide–no silver).

TABLE II Band area ratio of the spectral region b2 to the spectral region b3 calculated from the DRIFT spectra. The ratios are normalized with respect to that of oxide–no silver samples

	Precursor	Tl1212
Carbonate–0.37 Ag (A)	5.8	1.9
Carbonate–no Ag (B)	12.1	4.2
Oxide–0.37 Ag (C)	1.3	0.6
Oxide–no Ag (D)	1.0	1.0

It should be noted that the values in Table II are not perfectly quantitative but will give qualitative estimates. Different powder particle size which generates different surface area per unit weight can also result in some errors. However, the powder samples were prepared by following the same procedure, and went through the same steps. Therefore, the particle-size effect should not be appreciable, and it should be perfectly reasonable to compare the band areas corresponding to vibrations of different phases for semi-quantitative comparison of the amounts of the phases. The band area for the spectral region b1 in Fig. 2a was not used because the band-shape was such that a different selection of the starting and ending positions of the bands could result in different band areas.

When carbonates were used as starting materials (see A and B in Fig. 2a), the band intensities of the carbonates are lower for the samples with added silver. In the case of C and D in Fig. 2a, smaller amounts of residual carbon are detected in the precursor powders by the combustion method as compared to A and B in Fig. 2a (Table I). The band positions of the spectral region b1 in C and D (see Fig. 2a) are slightly shifted to lower wave number, and the shapes of the bands are different from those of A and B in Fig. 2a. This difference can be caused by the difference between the carbonates introduced through the carbonate starting materials (which are in the bulk and on the surface) and carbonates formed as the result of the CO_2 adsorption on the surface. Almost all of the carbonates in C and D come from the CO_3^{2-} adsorbed on the surface of the particles during processing. Carbonates can also form from CO_2–adsorption in A and B. However, the following conditions would exist: (1) the presence of pre-existing carbonates may lead to a lesser extent of surface adsorption; and/or (2) the pre-existing carbonates may dominate the band position leading to less band shift to lower wave number.

In Fig. 2b, the bands in the spectral regions b1 and b2 of A and B spread out to lower wave number like those of C and D in Fig. 2a, indicating more CO_2-adsorption during further processing of the precursor powders. The band in the spectral region b3 was used as a reference for relative comparison of the amounts of carbonate as was done for the precursor powders. The results are given in Table II. As with the precursor powders, the presence of silver seems to reduce the amount of carbonate when carbonates are used as starting materials (see A and B in Fig. 2b). For both the precursor and reacted Tl1212 powders, the effect of silver is not clear in the case of C and D because the amount of carbonate is so small.

Appreciable amounts of carbonate still remain in the precursor powders after single calcination when $SrCO_3$ and $CaCO_3$ were used as starting materials. These starting materials are commonly used to synthesize thallium-compound superconductors. Repeating calcination after re-grinding reduces the amount of carbonate but does not completely remove it. Calcining at higher temperature can reduce the residual carbon content. Calcining $2SrCO_3$–$CaCO_3$–$2CuO$ mixtures at temperatures higher than 1000 °C causes total melting of the mixture, which makes regrinding for mixing with Tl_2O_3/PbO very difficult. The melting temperatures of $SrCO_3$, $CaCO_3$, and CuO are much higher than 1000 °C (1497, 1339 and 1326 °C, respectively), but mixtures of those phases in Sr : Ca : Cu = 2 : 1 : 2 stoichiometry melt at far lower temperature, probably because of the presence of a eutectic. When silver is added, the melting point of silver (~962 °C) can also limit the calcination temperature, because silver melting could lead to inhomogeneous distribution of silver throughout the precursor powder.

Samples prepared using oxides also show the presence of carbonate that originated from the CO_2 adsorption at the surface during processing. The small amounts of surface carbonate cannot be detected with XRD, but DRIFT spectroscopy is very sensitive to its presence, allowing both the identification and a rough estimate of its concentration. The presence of silver seems to affect the residual carbonate content when carbonate starting materials are used. For both precursor and Tl1212 powders, the relative intensities of carbonate bands were lower when silver was added.

3.2. Effect of silver on the carbonate formation on the surface of $Tl_{0.5}Pb_{0.5}Sr_2CaCu_2O_7$

To investigate further the effect of silver on the surface carbonate formation, infrared spectral analysis of the powders treated in humid air was conducted. Samples C and D in Fig. 2b, which were prepared from oxide starting materials and have low carbon content, were used for the ageing experiment. Fig. 3 illustrates the DRIFT spectra of Tl1212 and Tl1212–0.37 Ag powders aged in water-saturated humid atmosphere at room temperature. Ageing was carried out for 6, 24, and 48 h. Appreciable amounts of carbonates are built up on the surface of silver–free powders after 6 h ageing. For both the silver-added and silver-free powders, the bands corresponding to carbonates grow as ageing time increases. The same method that was used in the previous section was also used to compare semi-quantitatively the amounts of carbonates built up on the powder surface.

The effect of silver is obvious from the comparison of the bands in b2 and b3 in Fig. 3. In spectra of the silver-added samples (see Fig. 3b), the b2 bands are not as strong as the b3 bands, while the b2 bands grow more rapidly and are more intense than b3 bands in silver-free samples (see Fig. 3a). The ratio of band area of b2 to that of b3 of silver-added $((b2/b3)_{Ag})$ and silver-free $((b2/b3)_{no})$ samples were calculated and listed in Table III together with $((b2/b3)_{no})/((b2/b3)_{Ag})$ values. $((b2/b3)_{no})/((b2/b3)_{Ag})$ was calculated to quantify the effect of silver to reduce the rate of carbonate formation on the powder surface and indicates how fast carbonates are built up on the silver-free sample compared to the silver-added sample at each ageing time. Carbonates are formed in the silver-free sample ~1.6 times faster than in the silver-added one.

3.2.1. $Bi_2Sr_2CaCu_2O_8$

The samples reacted at 865 °C for 24 h are almost phase-pure Bi2212 with a small amount of $Bi_2Sr_2CuO_6$ (Bi2201) present. Fig. 4 illustrates DRIFT spectra of Bi2212 and Bi2212–20 wt % Ag powders aged in the water-saturated humid atmosphere,

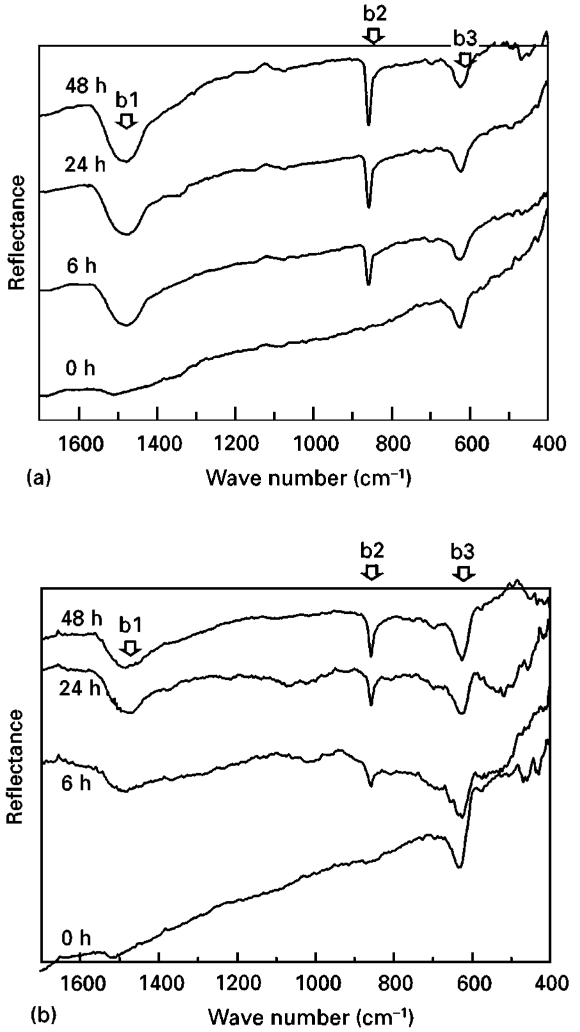

Figure 3 DRIFT spectra of (a) Tl1212, and (b) Tl1212–(0.37 Ag) powders aged in the water-saturated humid atmosphere.

TABLE III Band area ratio of the spectral region b2 to the spectral region b3 ($(b2/b3)_{no}$ and $(b2/b3)_{Ag}$) calculated from the DRIFT spectra of Tl1212 and Tl1212–0.37 Ag, respectively

Ageing time (h)	$(b2/b3)_{no}$	$(b2/b3)_{Ag}$	$((b2/b3)_{no}/(b2/b3)_{Ag})$
6	0.45	0.27	1.7
24	0.57	0.36	1.6
48	0.59	0.39	1.6

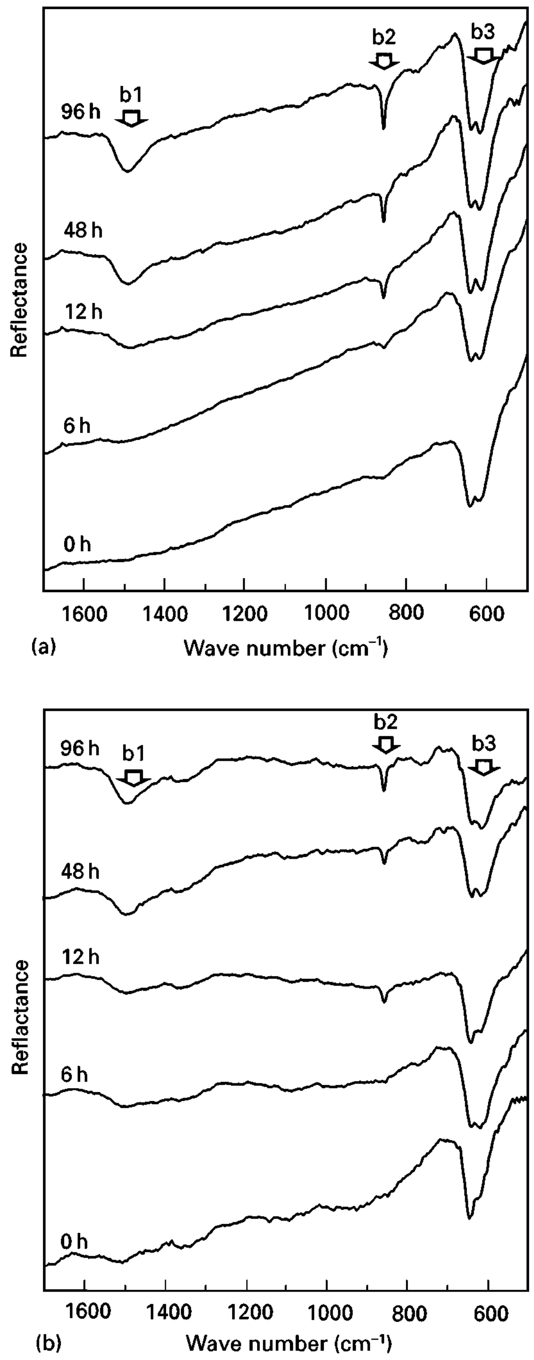

Figure 4 DRIFT spectra of (a) Bi2212, and (b) Bi2212–20 wt % Ag powders aged in the water-saturated humid atmosphere.

respectively. The observed bands in the b1 and b2 spectral regions correspond to the same vibrations that were assigned to the bands in Fig. 2b. The bands in the spectral region b3 are associated with a Cu–O stretching vibration in the CuO planes of Bi2212 phase [11].

Carbonate bands grow as ageing time increases in both silver-free and silver-added Bi2212 samples. The trend observed for Tl1212 is also found for Bi2212 system: the b2 bands of silver-free Bi2212 grow more rapidly compared to the band areas of b3 than those of silver-added Bi2212 (see Fig. 4). However, the growth rates of carbonates were not as different in the two cases as those observed in the Tl1212 system (see Fig. 3). $(b2/b3)_{Ag}$, $(b2/b3)_{no}$, and $((b2/b3)_{no})/((b2/b3)_{Ag})$ values calculated from the spectra are listed in Table IV. Carbonates are formed in the silver-free sample faster than in the silver-added one, but carbonate formation on the surface of the Bi2212 system is less sensitive to the presence of silver than that of the Tl1212 system.

There have not been many reports regarding the carbonate build–up in HTSCs. Cummins *et al.* [12] have used specular infrared reflection spectroscopy to study the atmospheric degradation of YBCO and $YBa_2Cu_4O_8$ in the presence of silver by comparing the rate of carbonate build-up in those systems. Similar studies have never been carried out for bismuth- or thallium-compound superconductors.

TABLE IV Band area ratio of the spectral region b2 to the spectral region b3 ($(b2/b3)_{no}$ and $(b2/b3)_{Ag}$) calculated from the DRIFT spectra of Bi2212 and Bi2212–20 wt %Ag

Ageing time (h)	$(b2/b3)_{no}$	$(b2/b3)_{Ag}$	$((b2/b3)_{no}/(b2/b3)_{Ag})$
6	0.01	0.006	1.7
12	0.03	0.03	1.0
48	0.04	0.03	1.3
96	0.06	0.06	1.0

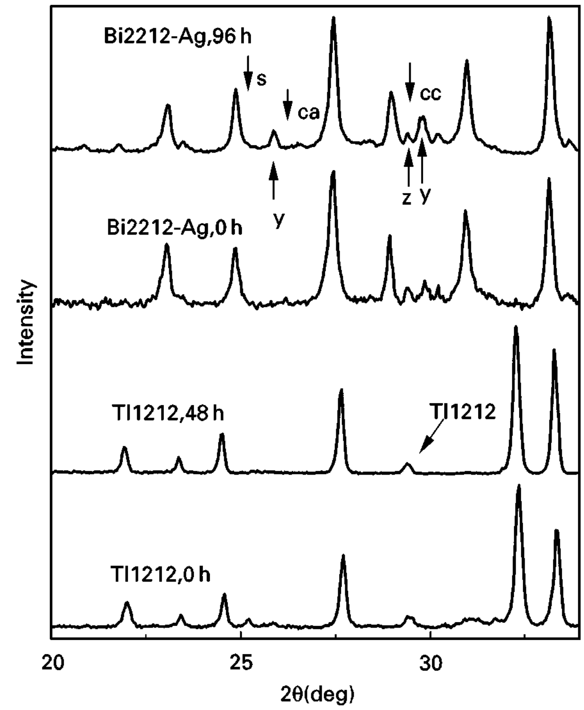

Figure 5 XRD patterns of Bi2212–(20 wt % Ag) aged for 96 and 0 h, and Tl1212 aged for 48 and 0 h. The arrows s, ca, and cc indicate the location of 100% peaks of $SrCO_3$, $CaCO_3$ (aragonite), and $CaCO_3$ (calcite) respectively.

The presence of silver has been reported to decrease the rate of degradation of YBCO in a humid atmosphere [12, 13]. Gao and Vander Sande [5] reported the water-resistance of Bi–Pb–Sr–Ca–Cu–O/Ag superconducting system by observing the microstructure of a sintered bulk body. They found that the presence of silver hinders the contact between the water and the calcium (or strontium)-rich oxides which dissolve easily in water, resulting in less damage from the water.

In the present work, Tl1212 and Bi2212 powders were studied instead of a bulk body. The DRIFT spectra were used to identify and to compare semi-quantitatively the amounts of carbonates built up on the powder surface. The level of concentrations of those carbonates is below the detection limit of XRD. Fig. 5 shows the XRD patterns of Bi2212–(20 wt % Ag) aged for 96 and 0 h, and Tl1212 aged for 48 and 0 h. The arrows s, ca, and cc indicate the location of 100% peaks of $SrCO_3$, $CaCO_3$ (aragonite), and $CaCO_3$ (calcite), respectively. Samples in which the presence of carbonates were observed using DRIFT spectroscopy, do not show peaks of strontium or calcium carbonates in XRD patterns. The peaks indicated as y belong to Bi2201. The peak z is a Bi2201 peak overlapping with a peak from an unidentified phase.

The DRIFT spectra also show that the presence of silver can influence the CO_3^{2-} formation on the Tl1212 and Bi2212 particle surface, and so influence the degradation process. The reactions forming calcium and strontium carbonates from adsorbed CO_2 are strongly catalysed by water vapour. The first stage of the reaction involves the hydroxylation of calcium and/or strontium. The presence of silver appears to change the hydroxylation kinetics of calcium and/or strontium, which is directly related to the carbonate-forming degradation process.

The calcium and strontium-carbonate formation on the powder surface accompanies the formation of other copper- or thallium/lead-rich non-superconducting phases. The grain boundaries of sintered material which usually originate from the powder surface, will be more contaminated with impurity phases when more carbonates form on the surface of the powder, and this will result in more weak links between the grains and limit the current-carrying capacity of the superconductors.

Shaw *et al.* [6] studied the effect of residual carbon on the T_c of YBCO using electron energy loss spectroscopy (EELS) and X-ray photoelectron spectroscopy (XPS) to estimate the carbon content. They found that residual carbon content in the range 0.5–1.2 wt % dropped T_c to ~50 K from 91 K of the almost carbon-free sample. Flükiger *et al.* [7] studied the influence of carbon impurities on J_c in $Bi_2Sr_2Ca_2Cu_3O_{10}$ (Bi2223) using Auger electron spectroscopy. They used the same starting materials with different calcination steps to change the carbon content of Bi2223 powder-in-tube tapes and reported that J_c (77 K, 0 T) decreased from 20 000 to 1500 A cm^{-2} when carbon content increased from < lat % to 10 at %.

Therefore, the different amounts of carbonates formed as the result of the presence of silver observed in this study, will influence the superconducting properties of thallium-compound superconductors. The oxycarbonate phase $Tl_{0.5}Pb_{0.5}Sr_4Cu_2(CO_3)O_7$ [14] which is known to have a T_c of 70 K and has a structure very similar to that of $Tl_{0.5}Pb_{0.5}Sr_2Ca_2Cu_3O_9$, may form when the carbon content exceeds a critical value. It should be noted that the absence of carbon does not guarantee a high J_c value, but its presence can act as a limiting factor. The absolute carbon content and the superconducting properties of the samples were not measured in this study, but their relations will be important in practical application of thallium-compound superconductors.

4. Conclusion

Silver, when added to HTSCs or when used as substrates/containers of HTSCs, is believed to affect the properties of the materials in multiple ways. The relation between the silver and carbon was investigated using Tl1212 and Bi2212 superconductors with different silver and carbon contents. Materials with different carbon contents were prepared by using different starting materials (oxides versus carbonates).

It is not simple to work with problems associated with residual carbon because (1) the atmospheric carbon source (CO_2) is insidious, and the residual carbon content is not easy to control, and (2) determination of carbon content (especially on the surface) is not simple. To detect and determine the amount of residual carbon in HTSCs, Auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS), etc., have been used. In this study, a DRIFT technique, which has not been applied to the study of surface carbonate formation in HTSCs, was used.

The DRIFT spectra of precursor powders (Sr–Ca–Cu–O) showed that appreciable amounts of carbonate still remain after calcination at 940 °C when carbonates are used as starting materials. Samples prepared using oxides also showed the presence of carbonate that originates from the CO_2 adsorption at the surface during processing. Although the small amounts of surface carbonates are below the detection limit of XRD, the DRIFT technique has proved to be a convenient and effective method for qualitative and semi-quantitative analysis of carbonate formation on the powder surface and atmospheric degradation of thallium- and bismuth-compound superconductors.

The study of the effect of silver on the rate of carbonate build-up on the powder surface, showed that the presence of silver can decrease the rate of the carbonate formation on the Tl1212 and Bi2212 particle surface influencing the degradation process, and that carbonate formation is more sensitive to the presence of silver in Tl1212 than in Bi2212. The presence of silver appears to change the hydroxylation kinetics of calcium and/or strontium, which is directly related to the carbonate-forming process.

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