

## Chemical interactions between $\text{Bi}_2\text{Sr}_3\text{CaO}_7$ (Bi-2310) and $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Dy}_{0.2}\text{Cu}_2\text{O}_8$ (Bi-2212(Dy))

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### Abstract

The chemical interactions between  $\text{Bi}_2\text{Sr}_3\text{CaO}_7$  (Bi-2310) and  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Dy}_{0.2}\text{Cu}_2\text{O}_8$  (Bi-2212(Dy)) at 965°C were investigated by means of: (i) an interdiffusion couple and (ii) layers deposited by dip coating on oxidized nickel substrates. The samples were characterized by optical and electron microscopies, energy-dispersive x-ray (EDX) analysis and x-ray diffraction. It turns out that at the peritectic temperature of Bi-2212(Dy), the Bi-2310 phase reacts with the liquid phase resulting from the peritectic decomposition of the Bi-2212(Dy) phase. Dissolution of Bi-2310 leads to an enrichment in Sr and an impoverishment in Cu of the liquid phase, resulting in a shift of the composition of the insoluble phase towards the Ca-rich end of the (Ca, Sr)O solid solution.

### 1. INTRODUCTION

Bi-2212 tapes are usually prepared on silver substrates or in silver sheaths, e.g. by the powder-in-tube (PIT) technique [1-7]. Several attempts to use other metals (such as Ni, in place of Ag) as alternative substrates resulted in deterioration of superconducting properties due to diffusion of the substrate metal ions into the Bi-2212 layer [8]. These observations add practical interest to fundamental studies investigating the chemical interactions of Bi-2212 with other Bi-containing phases.

The present work is devoted to the study of the interactions between Bi-2212(Dy) [9-14] and a Bi-Sr-Ca-O phase often obtained as a by-product during the cooling of a Bi-2212 melt [15]. The existence of a yellow monoclinic phase was reported independently in 1990 by Hong *et al* as the '9115 phase' ( $\text{Bi}_9\text{Sr}_{11}\text{Ca}_5\text{O}_z$ ) [16] and by Roth *et al* as the '2310 phase' ( $\text{Bi}_2\text{Sr}_3\text{Ca}_1\text{O}_x$ ) [17, 18]. Although most composition analyses point to a composition closer to the Bi-2310 formula [19], the alternative nomenclature 9115 has persisted [20] and can create confusion. In 1999 Monnereau *et al* [21] showed that the Bi-2310 phase can be used as an additive to enhance the mechanical properties of Bi-2212 ceramics. They also found that Bi-2310 was unreactive to Bi-2212 below its peritectic temperature: large amounts of the yellow Bi-2310 phase (up to 70 vol%) could be added to the Bi-2212 phase without significant alteration of the superconducting properties. However, the interactions between Bi-2212 and Bi-2310 at the peritectic temperature were not investigated by these authors.

In the present paper we report the results of our study concerning the chemical interactions between  $\text{Bi}_2\text{Sr}_3\text{CaO}_7$ , synthesized with Bi, Sr and Ca in stoichiometric ratios 2:3:1 and  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Dy}_{0.2}\text{Cu}_2\text{O}_8$ .  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Dy}_{0.2}\text{Cu}_2\text{O}_8$  (Bi-2212(Dy)) was used throughout the present study instead of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  (Bi-2212), so that magnetic texturation of the tapes under 1.2 T was possible [22-26]. We have studied different configurations: (i) a Bi-2212(Dy) and Bi-2310 phase interdiffusion couple, (ii) a Bi-2310 pellet sintered at 1000 °C and (iii) Bi-2212(Dy) deposited by dip coating on oxidized nickel tapes with or without a Bi-2310 'buffer layer'.

### 2. EXPERIMENTAL DETAILS

The  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Dy}_{0.2}\text{Cu}_2\text{O}_{8+\delta}$  powder (Bi-2212(Dy)) [27] was synthesized by solid state reaction. Stoichiometric amounts of  $\text{Bi}_2\text{O}_3$ ,  $\text{CaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{CuCO}_3$  and  $\text{Dy}_2\text{CO}_3$  were ground together and thermally treated at 850 °C for 48 h with a heating rate of 200 °C h<sup>-1</sup>, including an intermediate grinding after 24 h.

The 'yellow' 2310 phase ( $\text{Bi}_2\text{Sr}_3\text{CaO}_7$ ) was prepared in two steps [21]. Stoichiometric amounts of  $\text{CaCO}_3$  and  $\text{SrCO}_3$  were mixed together and calcined at 900 °C for 48 h with intermediate grinding.  $\text{Bi}_2\text{O}_3$  was then added to the calcined powder and a second thermal treatment was carried out at 850 °C for 24 h. The heating rate was 200 °C h<sup>-1</sup> up to 700°C and 5 °C h<sup>-1</sup> between 700 and 850 °C. All thermal treatments were performed in air.

Pellets of the two powders (Bi-2212(Dy) and Bi-2310) were uniaxially pressed. A Bi-2310 pellet was sintered at 1000 °C for 12 h (heating rate: 150 °C h<sup>-1</sup>). A Bi-2212(Dy) pellet and a Bi-2310 pellet were sintered at 850 °C for 12 h (heating rate: 150 °C h<sup>-1</sup>), then the Bi-2212(Dy) pellet was put on top of the Bi-2310 pellet and this interdiffusion couple was treated at 965 °C for 12 h (heating rate 150 °C h<sup>-1</sup>).

Bi-2212(Dy)/Bi-2310/NiO/Ni tapes were prepared by dip coating [28]. The Bi-2310 powder was added to an aqueous solution containing 20 gl<sup>-1</sup> of agar-agar. The powder represented 40% of the total mass of the slurry. After mixing vigorously for 12 h, a viscous slurry was obtained and deposited by dip coating on an oxidized nickel substrate. The tapes were dried in air and calcined at 1000 °C for 12 h to densify the layer. The Bi-2212(Dy) layer was deposited on top of the Bi-2310/NiO/Ni structure. The preparation of the slurry was similar to that of Bi-2310 but the thermal treatment was different: the tape was calcined at 965 °C for 12 h under a 1.2 T magnetic induction in order to texture the Bi-2212(Dy) layer. The tape was finally annealed at 750 °C for 24 h to recombine the secondary phases formed during the recrystallization process. Bi-2212(Dy)/NiO/Ni tapes free from Bi-2310 were also prepared by this method for comparison purposes.

The different powders were characterized by x-ray diffraction with a Siemens D5000 diffractometer (Cu K $\alpha$  radiation). Fragments of the tapes as well as the interdiffusion couple were put into resin and polished cross-sections were analysed using energy-dispersive x-ray (EDX) spectroscopy in an environmental scanning electron microscope (Philips XL-30 FEG ESEM, coupled to a Phoenix EDAX system). The temperature dependence of the electrical resistance was measured using the standard four-probe method in a Physical Property Measurement System (PPMS) from Quantum Design.

### 3. RESULTS

#### 3.1. Interdiffusion couple

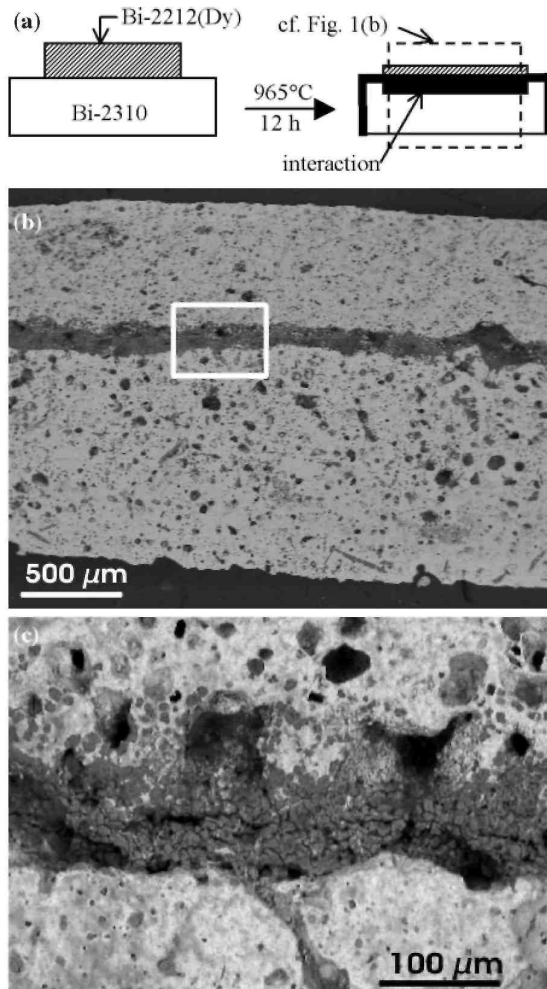
The Bi-2212(Dy)/Bi-2310 interdiffusion couple was heated up to 965 °C, i.e. slightly above the peritectic temperature of the Bi-2212(Dy) phase. Figure 1(a) displays a schematic diagram of a section through the interdiffusion couple. Experimentally, the liquid phase resulting from the peritectic decomposition of Bi-2212(Dy) penetrated by infiltration into the Bi-2310 pellet, as sketched in figure 1(a). It also spilled over onto the surface of the Bi-2310 pellet. Figures 1(b) and (c) present electron micrographs of a polished cross-section through the interdiffusion couple. Figure 1(c) shows part of the interaction zone at higher magnification. The contrast due to the back-scattered electrons reveals that the thermal treatment has promoted the formation of an interphase of approximately 100  $\mu$ m thickness at the limit of the infiltration of the liquid phase.

The different zones of the interdiffusion couple were characterized by EDX analysis. The typical cationic composition of the dark interphase (see figure 1(c)) is 90% calcium and 10% Sr. In the 'Bi-2310' pellet, the composition of the main phase is actually close to a ratio Bi:Sr:Ca of 2:3:0.5. Secondary phases containing Ca, Sr and Cu in variable ratios were also found in that pellet. In the case of the zone above the interphase, the cationic composition was analysed at different distances from the interphase. The Sr/Bi ratio increases from 1.2 to 1.6 while the Cu/(Sr + Bi) ratio decreases from 0.56 to 0.27 when the distance from the interphase decreases from 200 to 5  $\mu$ m.

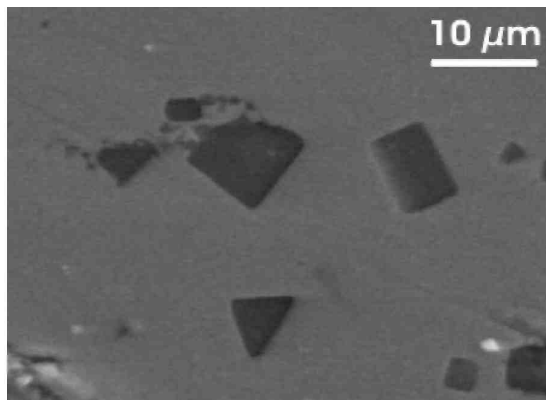
#### 3.2. Bi-2310 pellet

Figure 2 shows an electron micrograph of a Bi-2310 pellet sintered at 1000 °C. Secondary phases with rectangular or triangular shapes can be observed. It was found by EDX analysis that these secondary phases contain ~90% Ca and ~10% Sr. The composition of the main phase is Bi:Sr:Ca 44:66:12. The pellet was also characterized by means of x-ray diffraction. The observed x-ray pattern shows a good agreement with the JCPDS reference pattern of Bi<sub>2</sub>Sr<sub>3</sub>O<sub>6</sub> (No 46-0497), although a small shift of the peak positions is observed at high  $2\theta$ .

**Figure 1:** Cross-section through the Bi-2212(Dy) and Bi-2310 pellet interdiffusion couple: (a) schematic diagram; (b) back-scattered electron micrograph of the polished cross-section; (c) back-scattered electron micrograph presenting part of the interaction zone at higher magnification.



**Figure 2:** Electron micrograph of a polished cross-section through a Bi-2310 pellet sintered at 1000°C.



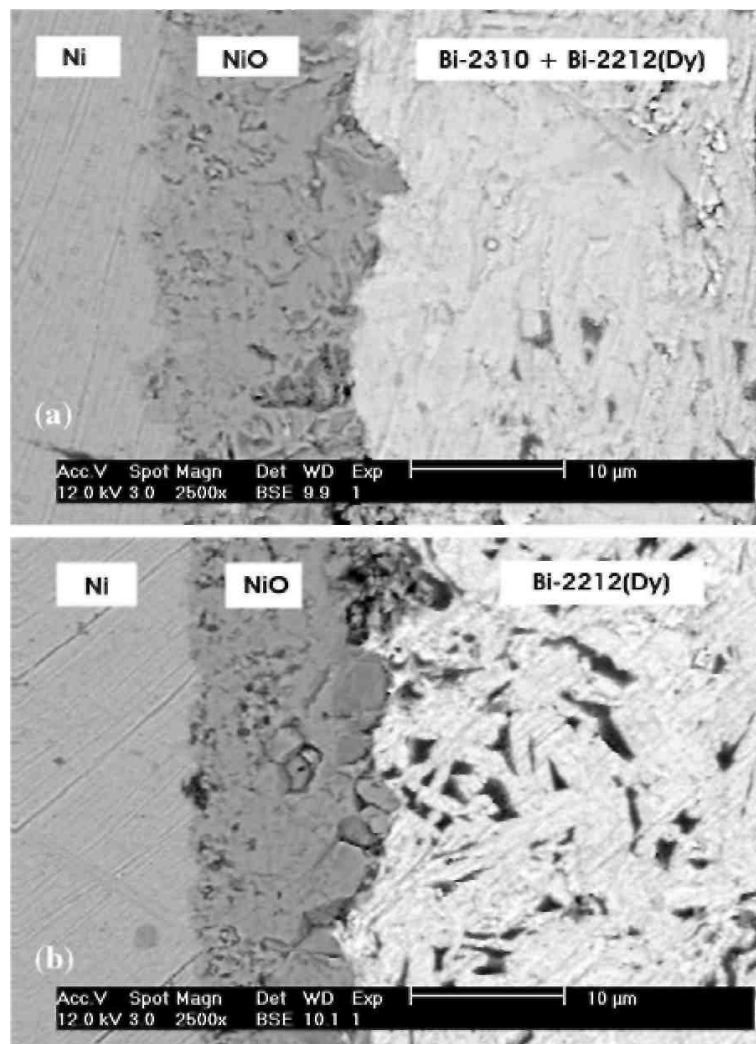
### 3.3. Tapes on Ni substrates

Several tapes were prepared by dip coating on nickel substrates. The different steps of the synthesis were detailed in the experimental section.

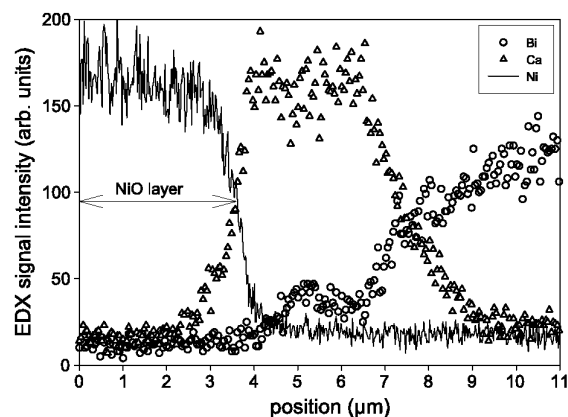
The thickness of the Bi-2310/NiO/Ni tape after thermal treatment at 1000 °C was approximately 80  $\mu\text{m}$  but the density was extremely poor. The sintering temperature was kept below 1000 °C in order to prevent the Ni substrate from becoming brittle.

Figure 3(a) shows a back-scattered electron micrograph of a polished cross-section through the Bi-2212(Dy)/Bi-2310/NiO/Ni tape, put into resin after thermal treatment up to 965 °C and annealing at 850 °C. That tape is much denser than the Bi-2310/NiO/Ni tape, due to the appearance of a liquid phase during the peritectic decomposition of Bi-2212(Dy). The thickness varies between 10 and 50  $\mu\text{m}$ , with an average around 20  $\mu\text{m}$ . The Bi-2310 layer could not be distinguished. Besides this, no *continuous* interphase layer between NiO and the oxides deposited by dip coating could be observed. However, a *local* interphase could be detected in one of the thickest regions of the tape. Figure 4 displays the results of EDX line scans performed across that interphase. For the sake of clarity, only the Ni, Ca and Bi signals are plotted in the graph. As can be seen, a  $\sim 2 \mu\text{m}$  thick Ca-rich layer has formed between the NiO and the 'Bi-Sr-Ca-Dy-Cu-O' phase. EDX point scans were carried out in the interphase zone in order to determine the typical cationic composition: Bi 1.5, Sr 15.8, Ca 43.3, Dy  $\sim 0$ , Cu 27.8, Ni 11.6.

**Figure 3:** Back-scattered electron micrographs on polished cross-sections of the tapes: (a) Ni/NiO/Bi-2310/Bi-2212(Dy) and (b) Ni/NiO/Bi-2212(Dy) put into resin after thermal treatment up to 965 °C and annealing at 850°C.

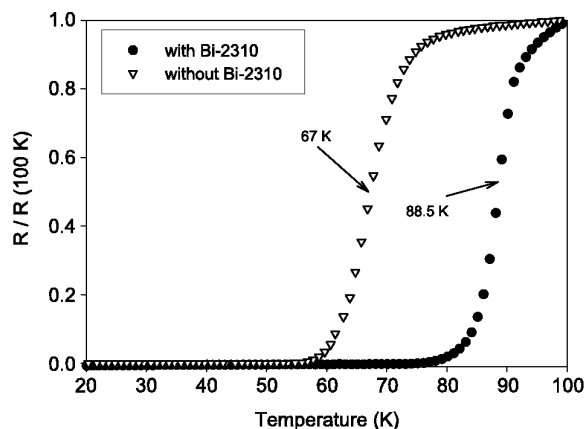


**Figure 4:** EDX line scan across the interface between NiO and the dip-coated layers for the Ni/NiO/Bi-2310/Bi-2212(Dy)tape. For the sake of clarity, only Ni, Bi and Ca signals are shown in the figure.



A tape without the Bi-2310 layer was also prepared for comparison of the superconducting properties. The microstructure of that tape is shown in figure 3(b). It is less dense than that of the Bi-2212(Dy)/Bi-2310/NiO/Ni tape. It is also thinner (average thickness  $\sim 10 \mu\text{m}$ ). Figure 5 shows the temperature dependence of the electrical resistance for both tapes. A resistive transition is observed in both cases. The temperatures of the inflexion point in the transition are respectively 88.5 and 67 K for the Bi-2212(Dy) tapes produced with and without the Bi-2310 layer.

**Figure 5:** Temperature dependence of the normalized electrical resistance  $R/R_{(T=100\text{ K})}$  for the Bi-2212(Dy) tapes produced with (circles) or without (triangles) a Bi-2310 buffer layer.



#### 4. DISCUSSION

The Bi-2310 and Bi-2212(Dy) interdiffusion couple was heated up to 965 °C, i.e. slightly above the peritectic temperature of the Bi-2212(Dy) phase [29]. At that temperature, the Bi-2212(Dy) phase partially melts and penetrates into the Bi-2310 pellet by infiltration. The micrographs presented in figures 1(a)-(c) of the 'results' section indicate that the liquid phase does not simply fill the pores of the Bi-2310 pellet, but also reacts with the Bi-2310 compound. Before attempting to discuss the experimental results, it is worth examining how each component of the interdiffusion couple is expected to behave at 965 °C.

The pseudo-binary phase diagram of the Bi-2201-CaCuO<sub>2</sub> system published by Suzuki *et al* [30] can be used to get information about the behaviour of pure Bi-2212 phase. When heated in air above its peritectic temperature

(887 °C), Dy-free Bi-2212 first decomposes into solid (Sr, Ca)CuO<sub>2</sub>, solid Bi-2201 and a liquid phase. Above 894°C, Bi-2201 dissolves into the liquid phase and finally, above 960 °C, (Sr, Ca)CuO<sub>2</sub> releases its copper in the liquid phase and turns into solid (Sr, Ca)O. This reaction sequence has to be adapted to take into account the presence of dysprosium. The peritectic temperature of the Bi-2212 phase, where 20% of the calcium ions are substituted by dysprosium ions, is approximately 965°C, significantly higher than the peritectic temperature of Dy-free Bi-2212. Previous results from our group have indicated that dysprosium ions tend to concentrate into the liquid phase [31]. As a result, once the peritectic decomposition has occurred, Dy-free (or Dy-poor) Bi-2201 and (Sr, Ca)CuO<sub>2</sub> are not stable at 965 °C and can be expected to decompose into liquid phase and solid (Sr, Ca)O. In conclusion, phase diagram analysis indicates that alkaline-earth ions are the least soluble cations in the Bi-Sr-Ca-(Dy)-Cu-O system. As for Bi-2310, analysis of the pellet sintered at 1000 °C has revealed a tendency towards decomposition into a Ca-rich (Ca, Sr)O phase and a phase with a Bi:Ca:Sr ratio close to 2:3:0.5.

With these data in mind, we now turn to the analysis of the EDX results concerning the interdiffusion couple. On the Bi-2212(Dy) side, it was shown that the Cu content decreases and the Sr/Bi ratio increases significantly when the distance from the interphase decreases. This strongly suggests that the Sr-rich Cu-free Bi-2310 phase dissolves into the liquid phase created by the peritectic decomposition of the Bi-2212(Dy) phase. The segregation of a Ca-rich phase at the limit of the progression of the liquid phase into the Bi-2310 pellet indicates that the modification of the liquid composition leads to a shift of the composition of the insoluble phase, from a Sr-rich (Sr, Ca)O for Bi-2212(Dy) to a Ca-rich (Ca, Sr)O when the liquid composition becomes richer in Sr and poorer in Cu. This is just another example of the well-known sensitivity of the phase equilibria in these materials with respect to small shifts of the system's overall composition [32],

The rest of the Bi-2310 pellet appeared to have turned into a main phase with a Bi:Ca:Sr ratio close to 2:3:0.5 and secondary phases containing Sr, Ca and Cu in variable ratios. The presence of copper results from the infiltration of Cu-containing liquid from the Bi-2212(Dy) phase into the Bi-2310 pellet.

The information gathered during the study of the interdiffusion couple can now be used in order to analyse the results concerning the Bi-2212(Dy)/Bi-2310/NiO/Ni tape. After the heat treatment at 965 and 850 °C, the Bi-2310 layer is no longer distinguishable. The Bi-2310 layer was indeed very porous and easily infiltrated by the liquid phase resulting from the peritectic decomposition of the Bi-2212(Dy) phase. Similarly to what happens in the case of the interdiffusion couple, the Bi-2310 phase reacts with the Bi-2212(Dy) phase. However, the amount of Bi-2310 is too small for a Ca-rich interphase to segregate, except in the thickest part of the tape. During the annealing at 750 °C, the (Ca, Sr)O phase recombines with copper (and perhaps nickel) to yield a Ca-Sr-Cu-(Ni) phase, as predicted by the phase diagram of Suzuki *et al* [30]. The exact composition is unknown; it could be a mixture of several phases [33]: (Sr, Ca)CuO<sub>2</sub>, (Sr, Ca)<sub>2</sub>CuO<sub>3</sub>, SrCu<sub>0.75</sub>Ni<sub>0.25</sub>O<sub>2</sub> (JCPDS 72-0852; 78-2284; 72-0852 respectively).

The reaction of Bi-2310 with Bi-2212(Dy) has not formed a continuous buffer layer between the NiO and the superconducting layer. However, the electrical properties of the Ni/NiO/Bi-2310/Bi-2212(Dy) tape are much better than those of the tape without Bi-2310 deposition. The transition temperature  $T_C$  increases from 67 to 88.5 K. The transition width is reduced from 7.5 to 5 K. Nevertheless the larger thickness and better density of the tape with Bi-2310 would suffice to explain these better properties. Further investigations are needed to determine whether the small modification of the overall composition resulting from the dissolution of Bi-2310 can improve the superconducting properties.

## 5. CONCLUSION

The chemical interactions between Bi<sub>2</sub>Sr<sub>3</sub>CaO<sub>7</sub> (Bi-2310) and Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>0.8</sub>Dy<sub>0.2</sub>Cu<sub>2</sub>O<sub>8</sub> (Bi-2212(Dy)) at 965 °C were investigated using an interdiffusion couple and layers deposited by dip coating on oxidized nickel substrates.

The samples were characterized by optical and electron microscopies, energy-dispersive x-ray (EDX) analysis and x-ray diffraction. At the peritectic temperature of Bi-2212(Dy), the Bi-2310 phase reacts with the liquid phase resulting from the peritectic decomposition. It has not been possible to prove at this stage that a small modification of the overall composition resulting from the dissolution of Bi-2310 can improve the superconducting properties. However, we have shown that dissolution of Bi-2310 leads to an enrichment in Sr and an impoverishment in Cu of the liquid phase, resulting in a shift of the composition of the insoluble phase towards the Ca-rich end of the (Ca, Sr)O solid solution.

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