

**Study of Ag:(Bi,Pb)<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> Composite Precursor Powders  
Obtained by Spray Pyrolysis**

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## Abstract

Ag-BPSCCO composite precursor powder was prepared by spray pyrolysis and the as-prepared and thermally treated (750°C (1 h) and 780°C (3 h)) powders were characterized by ambient X-ray Diffraction, *In Situ* X-ray Diffraction, Transmission Electron Microscopy, Magnetic susceptibility measurement and Differential Thermal Analysis. The as-prepared powder exhibited submicron polycrystalline and multiphasic particles containing the phases Bi-2212, Bi-2201, cuprate 14:24 ( $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ ), CuO and Ag. After thermal treatment the particles become mainly Bi-2212 submicronic single-crystals. The heat treated precursors possess also 14:24,  $\text{Ca}_2\text{PbO}_4$ , 3321, CuO and Ag. The magnetic susceptibility measurements showed that traces of the phase Bi-2223 are already present after thermal treatment. A combination of DTA and *in situ* X-ray diffraction experiments showed that in the precursor St1,  $\text{Ca}_2\text{PbO}_4$  phase decomposes in the a large temperature range 780°C-830°C. It was observed that at 840°C, just after the decomposition of  $\text{Ca}_2\text{PbO}_4$  phase, a new cuprate 2:1 phase was started to form. For the same precursor, the incipient melting of Bi-2212 is located at around 845°C. The complete melting of Bi-2212 in St1 powder occurs at about 875°C.

**Keywords:** spray pyrolysis, metal – metal oxide composite powder, Ag:(Bi,Pb)-2223 powder, *in situ* X-ray diffraction, TEM.

## Introduction

There are just a few reports on metal – metal oxide composite powders, prepared by spray pyrolysis route<sup>1-3</sup>. For example, Majumdar et al.<sup>2</sup> described formation of Ag-CuO composite powder, while Matsumoto et al.<sup>3</sup> demonstrated viability of preparation of Ag-TiO<sub>2</sub> composite powder. At the same time, there is just one brief report on metal – complex oxide composite powder synthesis by spray pyrolysis<sup>4</sup>, that the authors are aware of. In this article<sup>4</sup>, the authors gave an evidence of Ag-BPSCCO (BiPbSrCaCuO) precursor powder synthesis. This kind of composite powder has a great potential utilization as the precursor powder in technologies for obtaining superconducting tapes, bulks or foams. Actually, the preparation of a high quality precursor powder is the first critical step in the development of high-temperature superconducting devices. Aerosol decomposition routes, such as spray-pyrolysis, possess several advantages (chemically homogeneity, uniform submicron particles, etc.) over conventional solid-state techniques<sup>5</sup>. The quality of the powders obtained by spray-pyrolysis can be additionally improved by urea addition to metal nitrates precursor solution<sup>6</sup>.

In this paper we report on preparation of Ag-BPSCCO composite powder by spray pyrolysis applying somewhat different parameters than used in reference 4, as well as, on characterization of this powder in as-prepared form and after one rapid thermal treatment, at 750°C (1 hours) and 780°C (3 hours).

## Experimental

Composite particles of Ag:(Bi,Pb)-2223 stoichiometry were synthesized from a mixed nitrate solution with the appropriate ratio of the cations necessary to produce the (Bi,Pb)-2223 phase (Bi:Pb:Sr:Ca:Cu=1.8:0.2:2:2:3). The nominal concentration corresponds to 100g of mixed metal oxides accomplished through dissolving of nitrates into 1000ml of a 5 wt% HNO<sub>3</sub> water solution with 2 wt% urea and 20 wt% Ag (in the form of AgNO<sub>3</sub>). The precursor solution characteristics (density, pH, viscosity, and surface tension) were

measured and used to calculate<sup>7</sup> the average droplet size (2725 nm), the mean particle size (318 nm) and the aerosol droplet density ( $<10^{14}$  droplets/m<sup>3</sup>). The solution was atomized using an ultrasonic atomizer with the working frequency of  $1.7 \cdot 10^6$  Hz. Aerosol decomposition was carried out in a tubular flow reactor in argon gas at temperatures up to 840°C. The details of the synthesis process are given elsewhere<sup>6</sup>. The aerosol flow rate is determined by the argon flow rate ( $1.7 \cdot 10^{-6}$  m<sup>3</sup> s<sup>-1</sup>) and the reactor geometry (quartz tube characteristics: inner diameter  $3.6 \cdot 10^{-2}$  m, length  $6 \cdot 10^{-1}$  m), therefore the residence time of a droplet/particle at the maximum reaction temperature was 5s. Two kind of as-prepared powders were obtained from this process: S1, collected at the end of the high temperature tubular flow reactor, where the temperature is maintained at 200°C, and S2, which is carried by the argon flow to a receiving flask where it is trapped in distilled water. These two as-prepared powders were further thermally treated in air at 750°C (1 h) and 780°C (3 h) and were denominated St1 and St2.

Phase analysis of the as-prepared and heat treated powders was completed using a Siemens D-5000 diffractometer. CuK $\alpha$  radiation and graphite monochromator were used with a 0.02 scanning step and a step time of 25s. Quantitative phase analysis was carried out using the Rietveld method and the software Topas 2.1<sup>8</sup>. Particle structure was characterized by transmission electron microscopy (TEM), using a JEOL 2010 operated at 200kV. Magnetic susceptibility measurement was performed by an AC susceptometer Lake Shore 7000 (magnetic fields and frequency between 1Oe and 100Hz, respectively) in the temperature range of 80K – 130K.

Differential Thermal Analysis (DTA) and *in situ* X-ray diffraction were used to determine decomposition temperature of a plumbate secondary phases, as well as, incipient melting temperature of Bi-2212 superconductor phase, both present in the powder St1. DTA of the sample St1 was carried out under static air atmosphere up to 920°C in a Perkin-Elmer

DTA-7. The heating rate was 10°C/min. *In situ* X-ray diffraction experiments of the powder St1 was performed at the XRD1 beamline of the Brazilian National Synchrotron Light Laboratory (LNLS). The powder was heated from room temperature up to 740°C at a rate of 20°C/min. From this temperature up to 830°C, one pattern was taken every 5°C. The exposure time for every pattern was about 10 minutes. From 830°C a temperature-time schedule was applied up to the highest measuring temperature of 875°C, Figure 1. One pattern was taken every 10 minutes in this range of temperature. The step size was of 0.02° (2 Theta). The wavelength was 1.54068 Å ( $\Delta\lambda=0.001617$ ) and it was calibrated with highly crystalline silicon standard.

## Results and Discussion

The phase compositions of two as-prepared powders, S1 and S2, are qualitatively exactly the same, as it is followed from Figure 2(a,b). They consist of five phases: Bi-2212, Bi-2201, cuprate 14:24 ( $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ ), CuO and Ag. Quantitative analysis of these diffractograms performed by Rietveld method demonstrated, however, that there are some quantitative differences between the phase contents of those two powders, Table 1. The major one is related to the content of Bi-2212. It appears that the powder S2 is somewhat richer in Bi-2212 phase than the powder S1.

One can observe that both as-prepared powders do not possess Pb-rich phases (plumbates) such as  $\text{Ca}_2\text{PbO}_4$  (CP) or  $(\text{Pb,Bi})_3(\text{Sr,Ca,Bi})_5\text{CuO}_{12+x}$  (3321). This could mean that Pb is located in the Bi-2212 phase. Figure 3 confirms this, exhibiting the characteristic asymmetry of the diffraction peak situated at about  $2\theta=33.2^\circ$ . This peak consists of two Bi-2212 diffraction lines: (200) and (020). Therefore, when this one is asymmetric it means that the orthorombicity (defined as  $z=b-a/b+a$ ; a and b are unit-cell parameters) is more pronounced ( $z=2.6\times 10^{-4}$ ), indicating that the phase Bi-2212 possesses Pb, forming (Bi,Pb)-2212. TEM micrographs, Figure 4(a,b), show that particle structure of the two as-prepared

powders is similar. The particles in both powders are polycrystalline and multiphasic, as it can be seen in the selected area diffraction patterns (SADP), Figure 4(c,d). The SADP exhibit diffraction rings corresponding to Bi-2201, Bi-2212 and 14:24 phases. Particles dimension vary between 300nm and 500nm.

It generally occurs that the particles in the as-received powders change rapidly its phase composition after exposure to electron beam. This can be illustrating for the region marked in Figure 4a, and showed with higher magnification in Figure 5a. Its first SADP, exhibited in Figure 4c, is multiphasic showing three phases: Bi-2201, Bi-2212 and 14:24. After the exposure to electron beam this pattern change to the one showed in Figure 5b. It is still polycrystalline, but consists almost completely of Bi-2212 phase. A displaced-aperture dark field (DF) image, Figure 5c, taken from spot (corresponding to Bi-2212 phase) indicated in Figure 5b, demonstrates that the particle is predominantly composed of very small Bi-2212 crystals with dimensions around 5nm to 10nm.

Magnetic susceptibility measurements of as-received powders indicate that there is no traces of Bi-2223 phase and that the (Bi,Pb)-2212 phase present in both powders is not superconducting or that its critical temperature is lower than 80K.

After brief thermal treatment of as-prepared powders at 750°C (1h) and 780°C (3h), the powders St1 and St2 were formed. Their X-ray diffraction patterns are exhibited in Figure 6(a,b). It can be noticed that there are considerable qualitative differences between these two patterns. In the diffraction pattern of the St1 powder one can identify four phases: Bi-2212, 14:24,  $\text{Ca}_2\text{PbO}_4$  and Ag, while the St2 powder contains one more phase: CuO. Quantitative analysis of these two diffraction patterns, Table 1, carried out by Rietveld method, showed that both powders contain about 60wt% of Bi-2212 phase. The St1 powder is rich in 14:24 cuprate ( $\approx 15\text{wt}\%$ ) and also possesses about 7wt% of  $\text{Ca}_2\text{PbO}_4$  together with 19wt% of silver. The St2 powder contains only 5wt% of 14:24 cuprate phase. However, it possesses about

7wt% of CuO and two plumbate phases: 3321 (5wt%) and  $\text{Ca}_2\text{PbO}_4$  (1.6wt%). The presence of 3321 phase can only be verified by Rietveld method because its diffraction lines overlap with diffraction lines of other secondary phases. Thus, the St1 powder possesses two ceramic secondary phases (14:24 and  $\text{Ca}_2\text{PbO}_4$ ), while the St2 powder contains four (CuO, 14:24, 3321 and  $\text{Ca}_2\text{PbO}_4$ ), although the total percentage of ceramic secondary phases in the St1 powder is somewhat higher ( $\approx 22\text{wt}\%$ ) in comparison with St2 powder ( $\approx 18\text{wt}\%$ ). The lack of asymmetry of the diffraction peak at about  $2\theta=33.2^\circ$ , Figure 3, suggests that Bi-2212 is more tetragonal ( $z=4\times 10^{-5}$ ) than in the as-received powders. Therefore, the Bi-2212 formed after thermal treatment in the powders St1 and St2 is Pb-free and the Pb is situated in the phases  $\text{Ca}_2\text{PO}_4$  and 3321.

The powders St1 and St2 showed mainly agglomerated single crystal, monophasic Bi-2212 submicronic particles, Figure 7(a,b). The SAD pattern in Figure 7c, corresponding to the particle in 7b, was indexed for the [001] Bi-2212 zone axis and the modulation wave vector,  $\lambda$ , was determined to be  $26.78\text{\AA}$  (4.89b). This value of  $\lambda$  confirms that there is no Pb in the Bi-2212 structure [9].

Magnetic susceptibility curves of the powders St1 and St2 are presented in Figure 8(a,b). The curves revealed a drop of magnetic susceptibility at 109K indicating that the powders St1 and St2 possess a small quantity of Bi-2223 phase, which can not be detect by X-ray diffraction technique.

In order to determine the temperature range for conversion of the thermally treated powders into (Bi,Pb)-2223, the powder St1 was analyzed by DTA. The DTA curve, Figure 9, exhibited two endothermic peaks in the temperature range between  $700^\circ\text{C}$  and  $900^\circ\text{C}$ . The first one, with onset at  $790^\circ\text{C}$ , could be related to the decomposition of  $\text{Ca}_2\text{PbO}_4$  phase and the second one, with onset at  $845^\circ\text{C}$ , should be associated to the incipient melting of Bi-2212.

Therefore, the ideal temperature range for conversion to Bi-2223 should be around 840°C (few degrees below the onset of Bi-2212 melting).

*In situ* X-ray diffraction experiments confirm the observation from DTA that  $\text{Ca}_2\text{PbO}_4$  starts to decompose at around 780°C-790°C, Figure 10a. This decomposition can be followed by gradual reduction of intensity of  $\text{Ca}_2\text{PbO}_4$  diffraction line situated at 17.8° (2Theta). The process of  $\text{Ca}_2\text{PbO}_4$  decomposition was very sluggish for the phase assemblage in St1 powder and therefore the decomposition involved a large temperature range of about 50°C, ending almost completely at 830°C. However, one can notice that there is still a trace of the  $\text{Ca}_2\text{PbO}_4$  diffraction line at about 17.8°, even at temperatures over 830°C up to 845°C. This means that a very small quantity of  $\text{Ca}_2\text{PbO}_4$  still exists in the range of 830°C-845°C. The diffraction patterns taken at temperatures above 845°C did not show this line and therefore it can be concluded that  $\text{Ca}_2\text{PbO}_4$  phase was completely decomposed.

At around 840°C-845°C, the diffraction patterns started to alter their background. It can be seen that the background, previously completely linear, Figure 10b, formed a hump in the 2Theta region 25°-35°, Figure 10c. This is a region rich in Bi-2212 diffraction lines, Figure 10. The hump grows as the temperature increases. At the same time, the total intensity of Bi-2212 diffraction lines decreases, Figure 10a. At 860°C some diffraction lines of Bi-2212 phase, for example (002) and (113), had their intensities significantly reduced in comparison with other Bi-2212 diffraction lines. The events like modification of background, reduction of total intensity of Bi-2212 diffraction lines and alteration of intensity relations between some diffraction lines of Bi-2212 phase, can be interpreted as a sign of the incipient melting of Bi-2212. At 840°C one can, also, observe formation of a new cuprate phase 2:1 ( $\text{Ca}_{2-x}\text{Sr}_x\text{CuO}_3$ ) through appearance of a diffraction line at 14.4°(2Theta), Figure 10a. At 875°C the phase Bi-2212 started to melt completely, Figure 10a.



## Conclusions

Two Ag-BSCCO composite precursor powders were prepared by spray-pyrolysis. One was collected at the end of the high temperature tubular flow reactor (powder S1), where the temperature is maintained at 200°C and the second was carried by the argon flow to a receiving flask where it is trapped in distilled water (powder S2). Both as-prepared Ag-BSCCO powders consist of a submicronic, polycrystalline, multiphasic particles and are highly reactive. Their phase assemblage consists of (Bi,Pb)-2212, Bi-2201, 14:24, CuO and Ag. After rapid thermal treatment at 750°C (1h) and 780°C (3h) these powders transform to a precursors (St1 and St2) containing predominantly (60%wt) Bi-2212 phase, which appears in agglomerated single crystal submicronic particles. The precursor St1 possesses also 14:24, Ca<sub>2</sub>PbO<sub>4</sub> and Ag, while St2 contains 14:24, Ca<sub>2</sub>PbO<sub>4</sub>, Ag, CuO and plumbate 3321. Magnetic susceptibility measurements indicated that both thermally treated powders contain a small percentage of Bi-2223 phase.

A combination of DTA and *in situ* X-ray diffraction experiments showed that in the precursor St1, Ca<sub>2</sub>PbO<sub>4</sub> phase decomposes in the a large temperature range 780°C-830°C. It was observed that at 840°C, just after the decomposition of Ca<sub>2</sub>PbO<sub>4</sub> phase, a new cuprate 2:1 phase started to form. For the same precursor, the incipient melting of Bi-2212 is located at around 845°C. The complete melting of Bi-2212 in St1 powder occurs at about 875°C.

## Acknowledgements

This research was partially financially supported through the NEDO International Joint Research Grant Program 01MB7: "Wetability of solid by liquid at high temperatures", as well as Republic of Serbia Science Foundation.

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## Figure Captions:

Figure 1. Temperature-time schedule between 830°C-875°C applied for *in situ* X-ray diffraction of St1 powder.

Figure 2. X-ray diffraction patterns of the two as-prepared powders a) S1 and b) S2.

Figure 3. A comparison of the Bi-2212 diffraction peak situated at about  $2\theta = 33.2^\circ$  for the as-prepared powder S1 to the heat treated powder St1.

Figure 4. TEM images of the as-prepared powders a) S1, b) S2; c) and d) SAD patterns of marked areas in Figures 4a and 4b, respectively. (1: Bi-2201, 2: Bi-2212, c: 14:24).

Figure 5. a) Higher magnification bright field TEM image of a region of the as-prepared powder S1 marked in Figure 4a; b) SAD pattern of this region after a longer exposure to the electron beam; c) Displaced-aperture dark field (DF) image taken from spot, corresponding to Bi-2212 phase, indicated in Figure 5b. (1: Bi-2201, 2: Bi-2212).

Figure 6. X-ray diffraction patterns of the two heat treated powders a) St1 and b) St2. (2\*: incommensurate Bi-2212 diffraction lines).

Figure 7. TEM images of the heat-treated powders a) St1, b) St2, c) SAD pattern of the particle in Figure 7b.

Figure 8. Magnetic susceptibility curves for the heat-treated powders a) St1 and b) St2.

Figure 9. DTA curve of the heat treated powder St1.

Figure 10. a) X-ray patterns of the St1 powder taken at different temperatures between 740°C and 875°C, b) X-ray pattern taken at 740°C, c) X-ray pattern taken at 845°C. (Pb – Ca<sub>2</sub>PbO<sub>4</sub>, 2:1 - Ca<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>3</sub>).

Table 1. Weight percentages of the phases present in as-prepared and heat treated powders

	Powder - S1	Powder - S2	Powder - St1	Powder - St2
<b>Bi-2212 (%)</b>	31.8	38.8	59.1	62.4
<b>Bi-2201 (%)</b>	17.5	19.9	-	-
<b>14:24 (%)</b>	19.2	14.6	15.3	5.0
<b>CP (%)</b>	-	-	6.6	1.6
<b>3321 (%)</b>	-	-	-	5.1
<b>CuO (%)</b>	7.8	7.2	-	6.9
<b>Ag (%)</b>	23.7	19.5	19.0	19.0

Figure 1

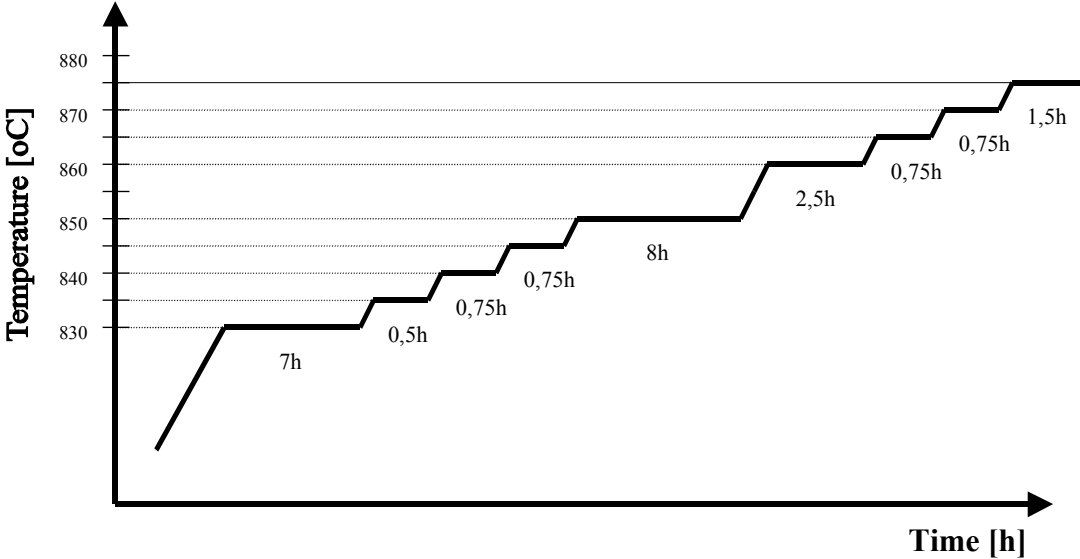


Figure 2

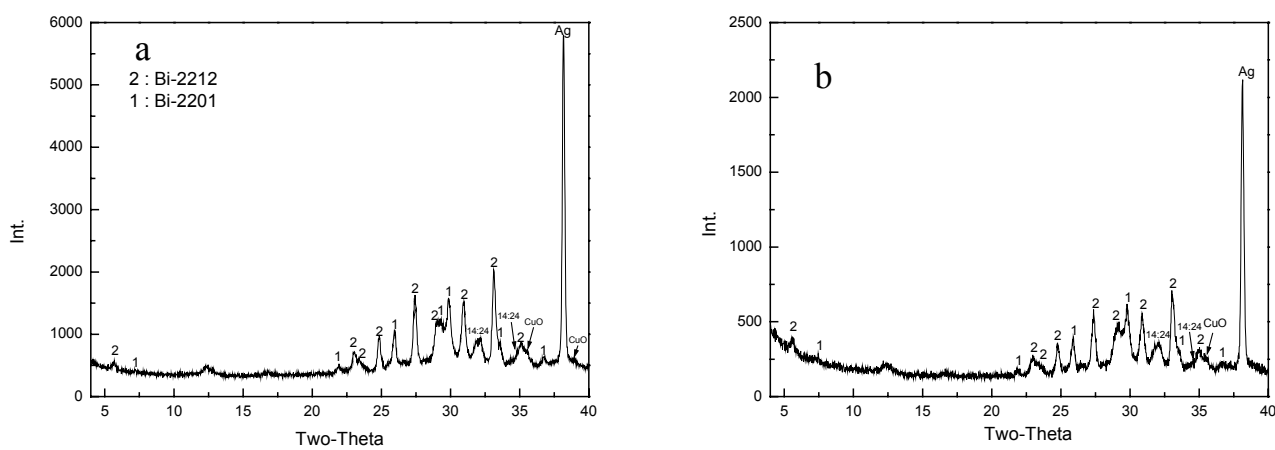


Figure 3

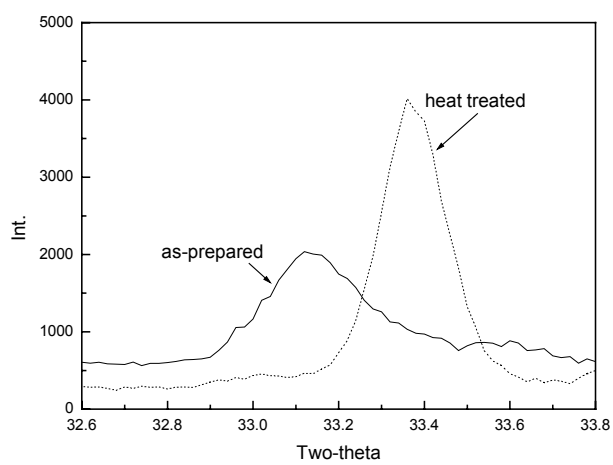


Figure 4

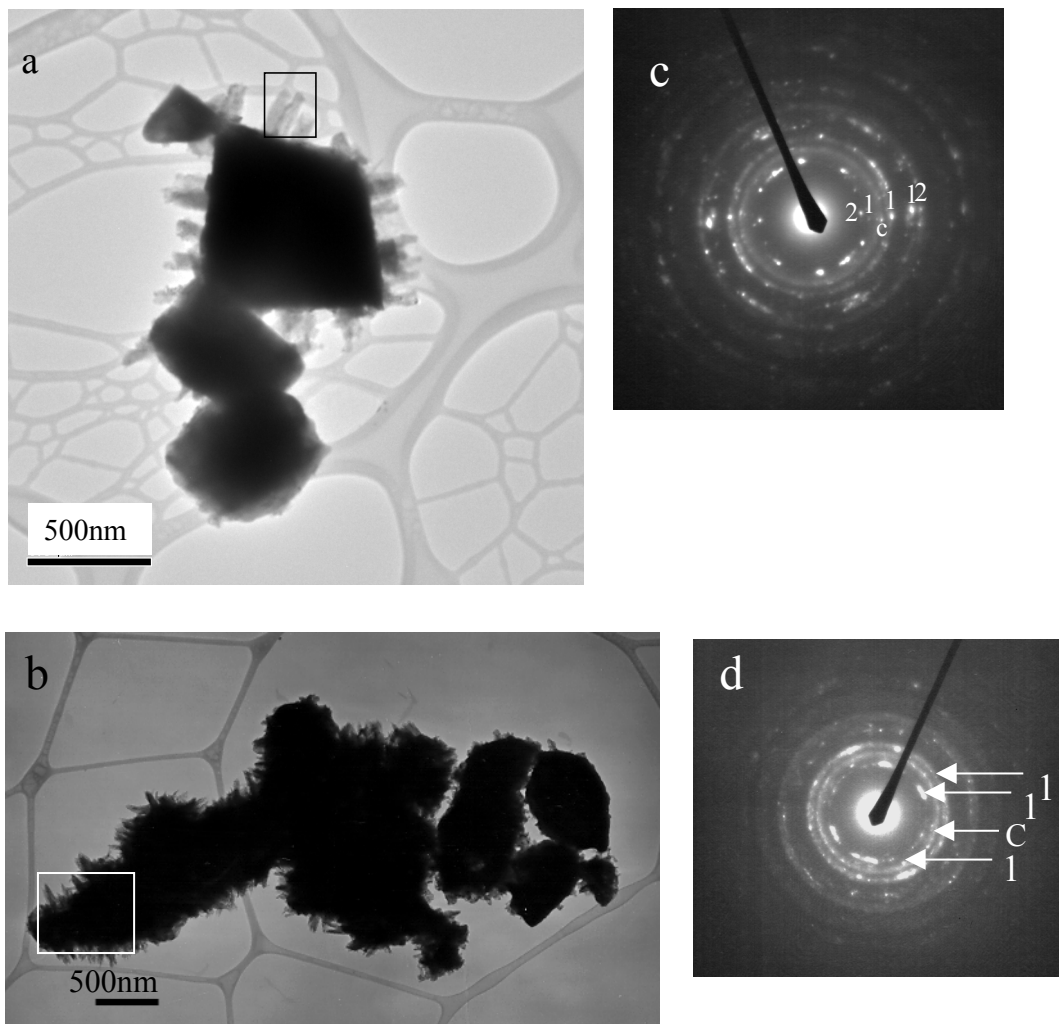


Figure 5

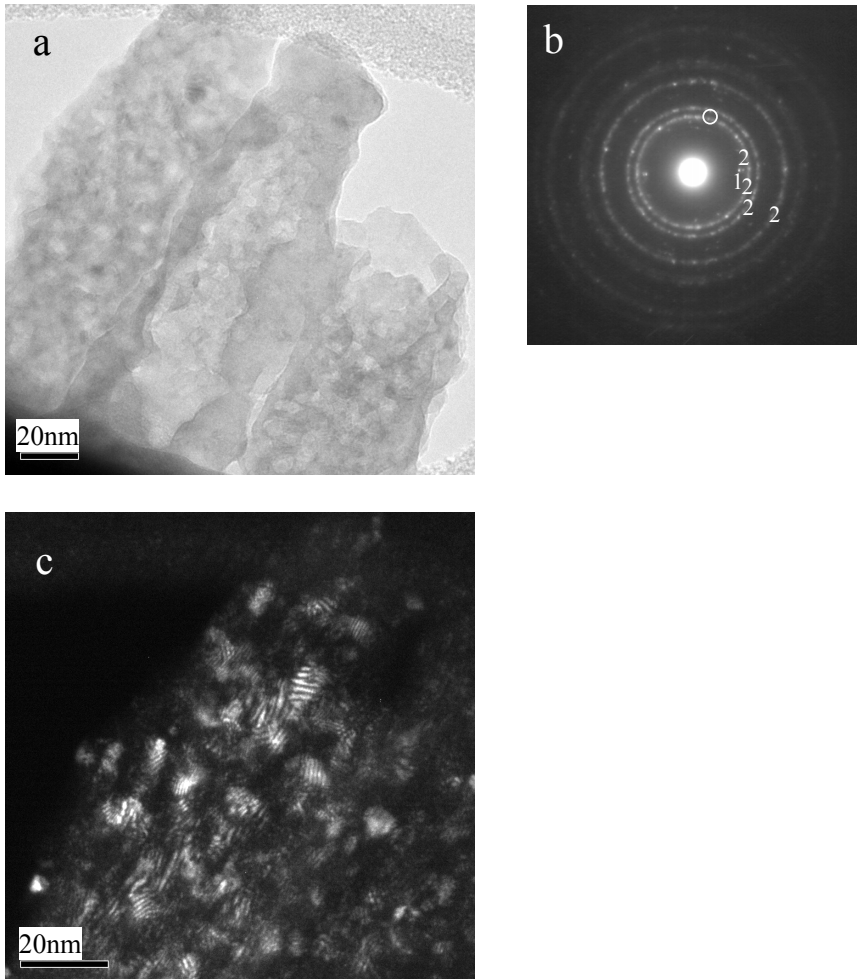


Figure 6

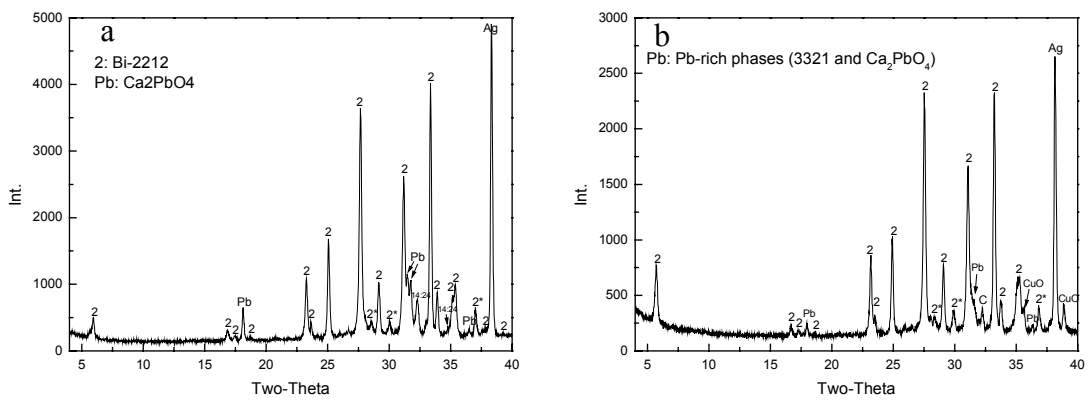


Figure 7

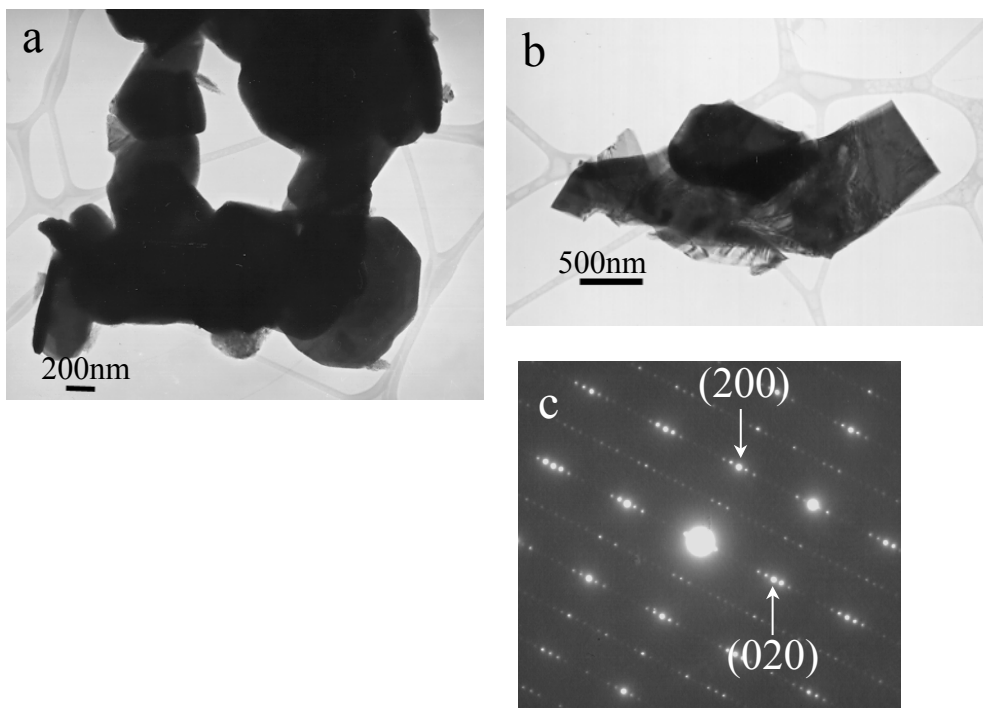


Figure 8

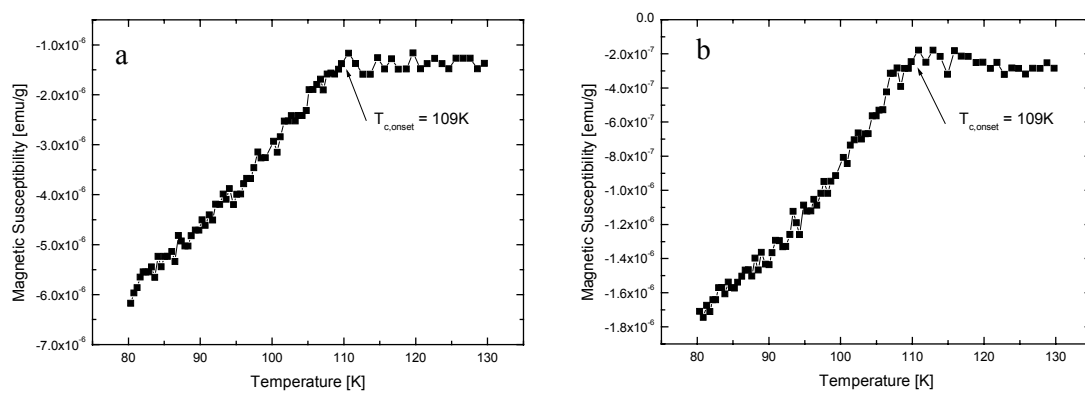




Figure 9

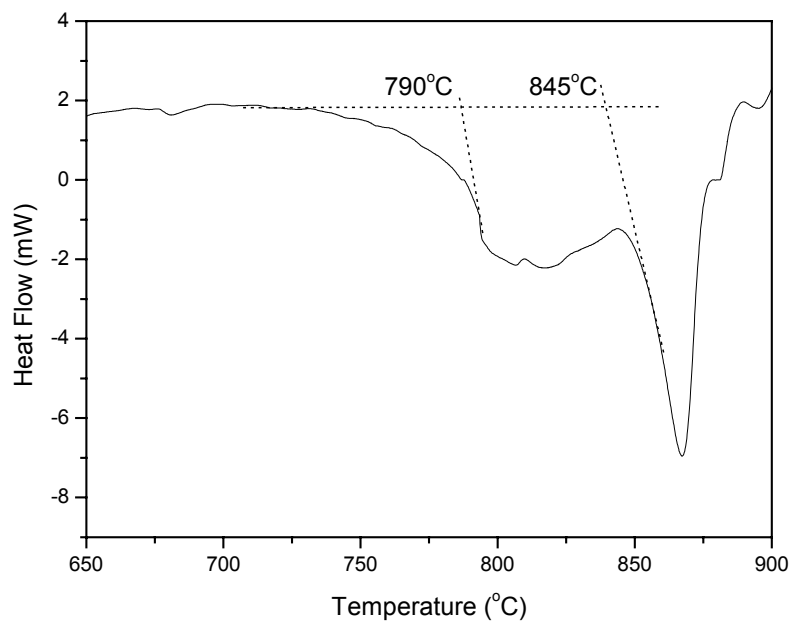


Figure 10

