Effect of Silver Substitution Threshold on the Superconducting Properties of IG Processed Bulk YBCO/Ag Composite Superconductors

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Abstract: In this article, we report anomalous substitution of Ag in Cu sites in Y-123 lattice during the fabrication of bulk YBCO/Ag composites via the Infiltration Growth Processing technique. We have observed concentration quenching of Ag in the Y-123 unit cell which implies a threshold for Ag substitution in Cu sites. We find gradual variation in properties with increase in Ag content up to a threshold value beyond which the superconducting properties are altered significantly. We discuss the effect of substitution threshold of Ag on the magnetic and superconducting properties of these composites and the optimum substitution level of Ag for enhanced properties.

Keywords: YBCO/Ag composite superconductors, IG processing, Magnetic susceptibility, Critical current density.

INTRODUCTION

Bulk components of YBCO superconductor with transition temperature around 92 K is one of the most vigorously studied materials since the last two and half decades because of several interesting physical properties and a number of potential practical applications such as in electric motors and generators, flywheel systems, levitating systems, field trapping SC magnets etc., [1-10]. Infiltration Growth Processing (IGP) technique is one of the most preferred techniques for fabrication of bulk YBCO superconductors and YBCO/Ag composites. Ag composited YBCO has several advantages over the pure YBCO material such as increased mechanical strength and improved superconducting properties as a result of better microstructure and grain-boundary properties [11-13]. Metallic Ag composited with YBCO acts in reducing porosity, voids and cracks and sealing the grain boundary gaps thereby substantially improving the microstructure of the bulk material. There are several reports suggesting an improvement in the mechanical and superconducting properties of YBCO owing to its composition with Ag resulting in YBCO materials where Ag remains in metallic form as precipitates distributed over the YBCO matrix in the resulting product [14-15]. Several techniques have been used to synthesize YBCO/Ag composites such as conventional sintering techniques and improved melt-growth techniques. Melt growth based techniques offer a lot of advantages over the conventional sintering techniques such as uniformity of distribution of metallic silver (Ag) and non-superconducting Y-211 phase in the superconducting Y-123 matrix[16]. Silver plays the role of a sealing agent leading to improved microstructure with reduction macroscopic defects such as voids, pores and cracks. The inter-grain coupling is improved as a result of silver accumulation at the grain boundaries [17-18]. This also enhances the mechanical properties of the end-product where silver acts as a metallic reinforcement in the ceramic YBCO matrix. Infiltration Growth Processing (IGP) technique was developed as an advancement over the conventional melt growth technique as it is based on the conventional techniques while at the same time provided several additional advantages. Bulk YBCO or YBCO/Ag samples fabricated by conventional melt growth techniques suffered from a few disadvantages such as deformation of the bulk product during synthesis, non-uniformity in the distribution of secondary phases such as Y-211 and metallic Ag, significant amounts of macroscopic defects in the form of voids, pores or cracks etc. In YBCO based materials, it is important to understand the role of defects. The YBCO formation usually occurs via the peritectic reaction

$$2\ Y_1Ba_2Cu_3O_{7-\delta} \rightleftharpoons Y_2Ba_1Cu_1O_5 + Ba_3Cu_5O_8 \quad (1)$$

where Y-211 is the non-superconducting phase which remains as a product of the above reaction. There are several advantages resulting from the Y-211 byproduct in the above reaction [19]. The $Y_2Ba_1Cu_1O_5$ (Y-211) phase, while being non-superconducting, can act as pinning center generator if their size, shape and distribution in the Y-123 matrix is properly controlled. The Y-211 distributed in the Y-123 matrix causes

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among other things, strain effects at the interface between the two phases. Defects of the size of coherence length result from this strain. These microscopic defects and other naturally existing defects in a ceramic material such as YBCO effectively act as pinning centers thereby causing arrest of flux creep in the material leading to improved current carrying properties in the superconductor [20]. Hence, in order to achieve better properties in this material, it is important to obtain defects whose size is of the order of coherence length of YBCO which is around 2 nm in the a-b plane [21-22].

The infiltration growth processing (IGP) technique developed as an alternative to the conventional melt-based techniques provides solution to several of the problems mentioned above. The samples synthesized by the IGP technique have near-net shape as they do not suffer from any deformation during the synthesis. This is a major advantage of the IGP technique where bulk samples for practical applications can be fabricated requiring little grinding or shaping. Growth of large samples with single grain morphology is possible in IGP with suitable seeding using Seeded Infiltration Growth Processing technique (SIGP). Further, samples synthesized through IGP technique posses minimum number of macroscopic defects and appropriately sized microscopic defects due to uniform distribution of Y-211 particles in the Y-123 matrix. The size and shape of the secondary phase Y-211 are also better controlled using the IGP technique [23-24]. Hence, IGP technique has been established as a superior technique with several advantages over the conventional melt growth techniques since the last 15 years. The IGP technique involves infiltration of the liquid phases present in the source pellet, after decomposition, into a target pellet of Y-211 phase. The peritectic reaction involving Y-123 and Y-211 is dependent on several process parameters such as composition of the precursor powders and their sintering temperatures, heat treatment schedules used during processing and any additives used. For example, it has been reported that silver, added as an additive, has a very significant role in modifying the peritectic transformation temperatures in the YBCO system

In the succeeding sections we discuss the fabrication and superconducting properties of YBCO/Ag superconducting composites via the IGP technique. We report the important observation of Ag substitution in Cu sites in Y-123 lattice and the concentration quenching threshold of Ag in Y-123 matrix for optimally improved properties.

EXPERIMENTAL DETAILS

The Y-123 and Y-211 precursor powders used in making the pellets have been prepared following the citrate synthesis route [25-26]. The technique involved dissolving stoichiometric proportions of starting chemicals in concentrated nitric acid to form nitrate mixtures. Highly pure powders of Yttrium Oxide (Y_2O_3) , Barium Carbonate ($BaCO_3$) and Copper (II) Oxide (CuO) (Merck make, 99.9 % pure) in appropriate amounts of conc. Nitric acid after weighing out the chemicals as per the composition using a high-precision chemical balance (*Mettler –AE 340*). The chemicals were mixed using a magnetic stirrer (*Remi Equipments Inc.*) with a hot plate (*Meta-Lab Sci. Ins.*) to ensure continuous, homogeneous mixing and sustained reaction. Citric acid and ethylene glycol were added to the mixture for gelling and pH of the resulting solution was adjusted to 8. The solution was heated to around 250 C on the hot plate for around 3 hours for combustion reaction to take place. The fine powders from the combustion reaction were sintered at 900° C for Y-123 and 950° C for Y-211 for 24 hour duration. The sintered powders are finely ground using an agate mortar and a pestle. The bulk samples in pellet forms were pressed using a hydraulic press capable with a compaction pressure of 460 MPa, The metallic silver contents used for making YBCO/Ag composites were 2 wt %, 4 wt % and 10 wt % metallic silver added to the precursor Y-123 powders which acted as a liquid source for the peritectic reaction. The metallic silver powder was separately ground in a clean agate mortar in ethanol medium to avoid oxidation of silver. The mixture of Y-213 and metallic Ag powders were mixed and ground thoroughly before pelletization. The resulting pellet will henceforth be referred to as liquid source pellet which is a mixture of Y-123 and metallic Ag powder. The non-superconducting Y-211 phase powders were pressed into green compacts using same compaction pressures without any additives. The Y-211 green compacts would henceforth be denoted as target pellets. The resulting samples made with 540 MPa pressure using 2 wt %, 4 wt % and 10 wt % Ag are coded as Y540-2, Y540-4 and Y540-10. The powders of Yttria (Y_2O_3), Yttria Stabilized Zirconia (YSZ) and Alumina (Al_2O_3) were used to press the support pellets. The Infiltration Growth Processing (IGP) technique involves infiltration of liquid phases, which form after decomposition of Y-123, into the target pellet made of Y-211 precursor powders. This follows from the peritectic reaction given in Eqn. 1. The present work involves fabrication of YBCO/Ag composite

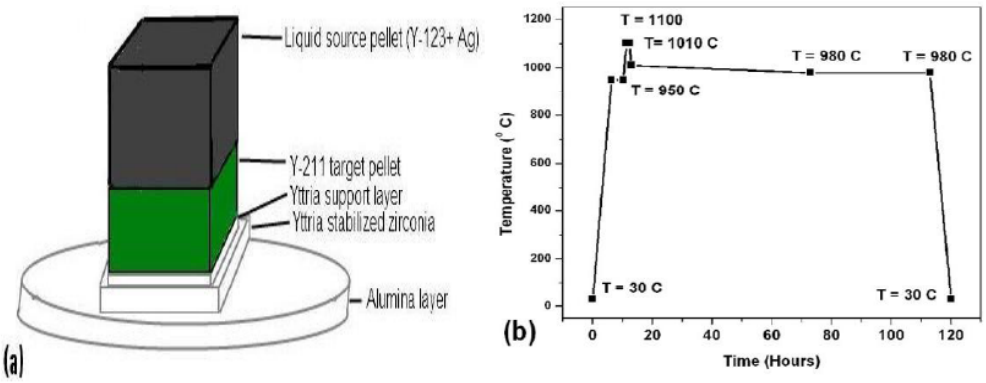


Figure 1: (**a**) Shematic representation of the synthesis configuration of IGP bulk YBCO/Ag composite samples and (**b**) Temperature-Time diagram employed during synthesis.

superconductors using the conventional IGP technique with liquid source on top to achieve infiltration by force of gravity. Here, we have an additional component in silver which is mixed to the liquid source powders.

The samples heat treated as per the schedule depicted in Figure **1** (**b**) were oxygenated at 450° C for 120 hours after separating out the target pellets alone. The samples thus fabricated were used for different characterization techniques such as X-ray diffraction, Field emission scanning electron microscopy (FESEM-EDAX), AC susceptibility (χ(T)) and critical current density $J_c(H)$, the results of which are discussed in the next section.

RESULTS AND DISCUSSION

The x-ray diffraction studies were carried out on the YBCO/Ag samples to probe the role of Ag addition on the structure of the composite material as shown in Figure **2**.

The x-ray diffraction pattern for the three samples with varying Ag content clearly reveals gradual shifts in prominent peaks and suppression of a few other peaks. The lattice parameters and cell volumes were found to show gradual increase with Ag addition indicating some amount of substitution of Ag atoms in Cu sites in the YBCO lattice. The peak indexing and lattice parameter calculations were carried out using *powderx* x-ray

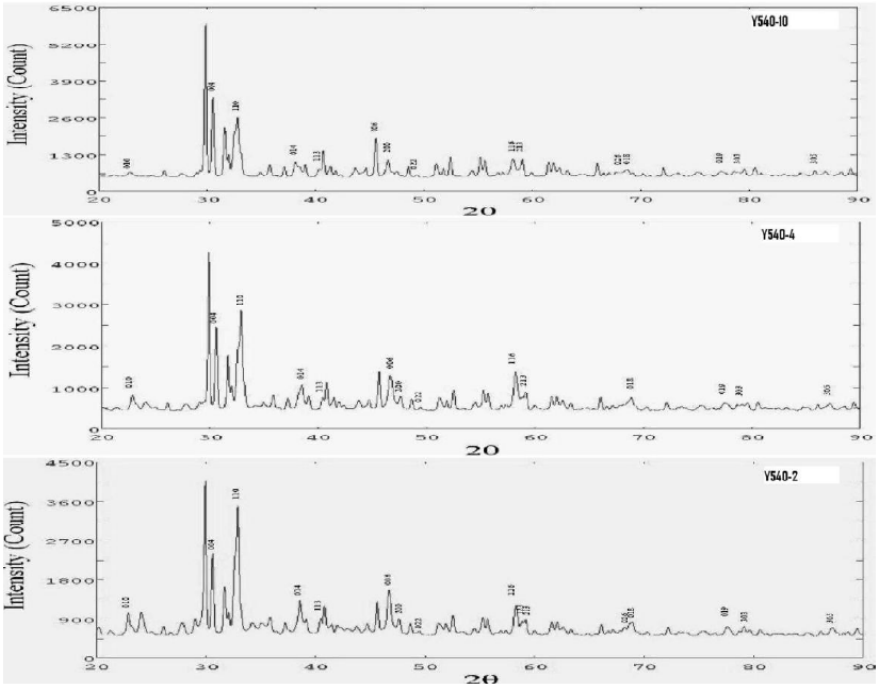


Figure 2: The XRD patterns of the IG processed YBCO/Ag powder speciemens containing 2 wt%, 4 wt% and 10 wt% silver.

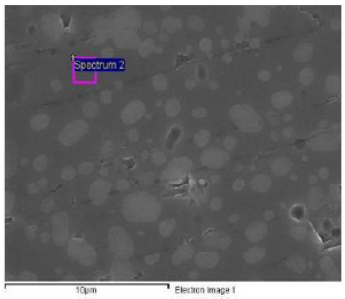
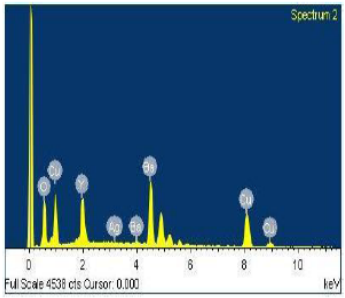
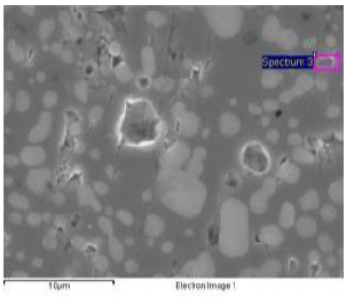
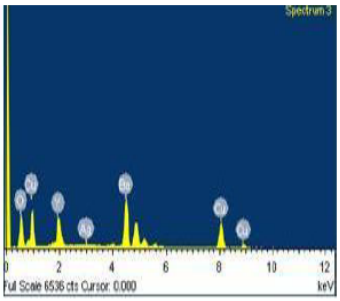
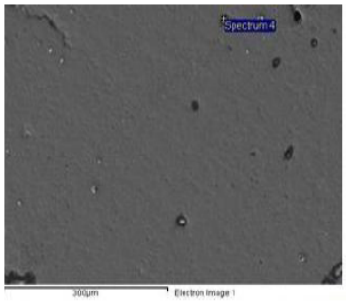
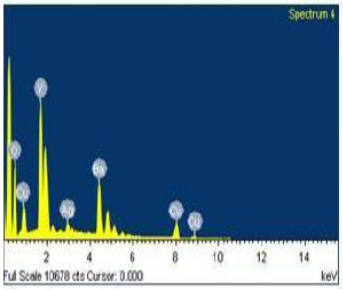
Sample code (Ag content)	Image of the EDAX Spectrum Region	EDAX Spectrum of elements
Y540-2 (2 wt %)		
Y540-4 (4 wt %)		
Y540-10 (10 wt %)		

Figure 3: EDAX images and spectra of the YBCO/Ag composite samples with varying Ag content showing the presence of Ag in the Y-123 matrix indicating possible substitution of Ag for Cu in YBCO lattice.

analysis software employing *cellref* algorithm. The structural analysis revealed systematic variation in lattice parameters with variation in silver content. However, from the XRD analysis, it was not clear as to the amount of Ag substituting for Cu in the Y-123. To further probe this, we carried out detailed microstructural investigations using field-emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDAX) whose results are discussed below. Further, our analysis shows that the amount of Ag in different regions of matrix varies and there are Ag-free regions in the matrix as well, implying that the Ag substitution for Cu in YBCO lattice leading to the $Y_1Ba_2(Cu_{1-x}Ag_x)_3O_{7-\delta}$ composition was inhomogeneous[27]. The Ag substitution for Cu hence is partial and occurs only in certain regions of the sample.

The following table in Figure **4** provides an overall quantitative perspective of Ag substitution from the EDAX measurements and analysis.

From Figure **3** revealing the FESEM-EDAX image and spectra, we observe that the amount of Ag in Y-123 matrix was beyond detectable limits for the Y540-2 sample whereas we could detect presence of metallic silver in the Y-123 matrix for the other two samples namely Y540-4 and Y540-10 with 4 wt % and 10 wt % Ag addition respectively, strongly indicating Ag substitution for Cu sites in YBCO unit cell. We shall discuss the effect of Ag substitution and concentration quenching threshold on the magnetic and superconducting properties of the YBCO/Ag composite superconductors [28, 29].

Sl. No	Sample Code	Amount of Ag Addition	No. of Regions with Ag Presence in EDAX out of 10 Sample Regions	Avg. Amount of Ag Detected in wt %
1	Y540-2	2 wt %	1	0.30 %
2	Y540-4	4 wt %	3	0.65 %
3	Y540-10	10 wt %	7	7.22 %

Figure 4: The amount of Ag present in the Y-123 matrix through EDAX analysis is tabulated for a sample of 10 regions scanned.

The magnetic and superconducting properties of the YBCO/Ag composite superconductors were studied using AC susceptibility and M-H hysteresis techniques. The χ(T) measurements were carried out on a homemade setup whereas the M-H loops were recorded using a Physical Property Measurement System (QD-PPMS) attached with a Vibrating Sample Magnetometer (VSM). The plots of AC χ' (real part) as a function of temperature for the three samples are shown below in Figure **5**. In Figure **5**, the three samples Y5402-, Y540-4 and Y540-10 are labeled as A, B and C respectively

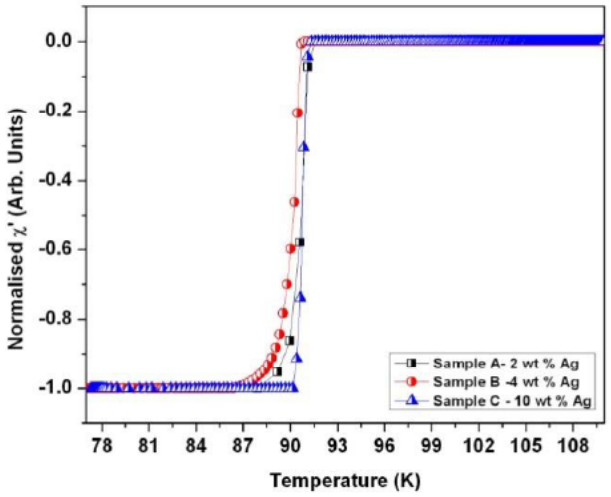


Figure 5: The real part of AC susceptibility as a function of temperature for the three samples revealing minor variations in transition temperatures and transition widths with varying silver content.

The table in Figure **6** below summarizes the results of χ(T) measurements where we can clearly see variations in both transition temperatures and transition widths with varying Ag content in our samples.

It can be seen from the χ(T) behavior that the transition temperatures and widths of transition has an overall improvement with Ag addition across the three samples, though between 2 and 4 %, there is no perceptible improvement. The improvement in T_c and ΔT_c with Ag addition can be attributed to an improved inter-grain coupling and hence a larger unperturbed area for the supercurrent loop which shows up as a marginal improvement in T_c [30]. Though this might appear contradictory to our belief that Ag substitution for Cu sites in Y-123 lattice should cause the secondary phases to broaden the transition width, we observe that concentration quenching occurring beyond 2 wt % silver addition could not result in any additional increase in secondary phase volume as far as Ag substituted phase composition is concerned. The secondary phase composition $Y_1Ba_2(Cu_{1-x}Ag_x)_3O_{7-\delta}$ has a saturation value for x beyond which any further addition of Ag causes it to only appear as precipitates in the matrix rather than to cause any further substitution of Ag for Cu sites. The additional silver also improved the mechanical properties of the system thereby indirectly helping in marginal improvement in T_c and the transition width [29].

Magnetization measurements carried out on the samples to record M-H loops revealed peak effect around the 2T region for samples Y540-2 and Y540-4 which contain low amounts of silver, namely 2 wt % and 4 wt % Ag. This peak is more pronounced for the Y540-4 sample which has 4 wt % Ag and surprisingly this peak vanishes for the Y540-10 containing 10 wt %

Sample Code	Silver Content wt %	Transition Temperature T_c (K)	Transition Width ΔT_c (K)
Y540-2	2 wt %	90.6 K	1.5 K
Y540-4	4 wt %	90.5 K	1.77 K
Y540-10	10 wt %	90.9 K	0.6 K

Figure 6: The variation of transition temperature and width of transition of the three samples as a function of silver content is presented in the table. The variation in T_c across the three samples is minimal.

Ag. This can be explained in terms of concentration quenching of silver that occurs gradually beyond 2 wt % silver addition. The critical current density J_c for all the three samples has been calculated from the M-H loops using Bean's model formula given in equation (2) below [32-33].

$$J_c = 20\frac{\Delta M}{d} A\ cm^{-2} \quad (2)$$

where ΔM is the change in magnetization (in emu/cc units) between the forward and reverse field sweep arms of the M-H loop cycle and 'd' is a geometrical factor involving sample dimensions used for the measurement [34]. The Jc(H) curves are shown in Figure **7** below.

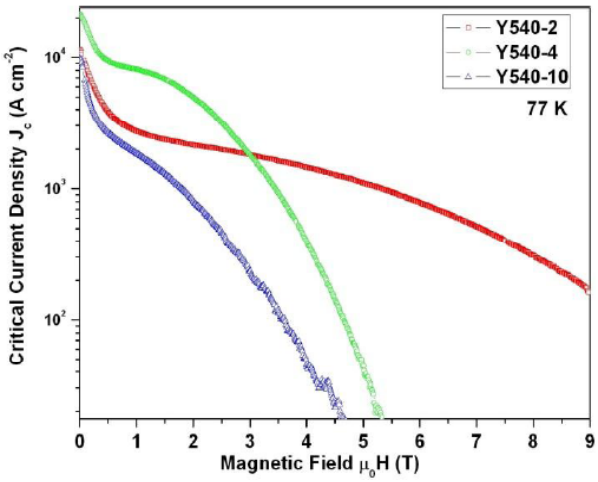


Figure 7: The plot of critical current density J_c of the three samples Y540-2, Y540-4, Y540-10 with varying silver content of 2, 4 and 10 wt % respectively as a function of applied magnetic field calculated from M-H loops recorded at 77 K shows a significant reduction in dependence of J_c on H for the sample Y540-2.

The critical current density J_c of the sample Y540-2 shows significant reduction on its dependence on applied field even up to fields as high as 9 T. The peak effect exhibited by this sample is around 4.5 T magnetic field whereas the peak effect for the sample Y540-4 with 4 wt % Ag is around the 1.5 T field regime which could be due to oxygen deficiencies [35]. The current carrying properties of the three samples vary drastically probably due to the direct role played by silver partially substituting in the Cu sites, thereby causing a lattice mismatch with the cells where Cu has not been substituted by Ag and also mainly due to the indirect role played by silver in modifying the sample microstructure such as Y-211 particles size, distribution etc as revealed from our detailed microstructure analysis.

The addition of silver, obviously, is observed to alter and affect the magnetic and superconducting properties of the samples to different extents depending on the silver content as seen from the data in the previous section. Here, the role of silver is found to be two-fold:

1) a direct role wherein Ag substitutes for Cu sites in the Y-123 lattice thereby possibly causing lattice mismatch effects, low-field pinning behavior, transition width broadening etc.,.

2) an indirect role wherein Ag shows concentration quenching effect beyond 2 wt % addition thereby appearing as precipitates in the Y-123 matrix which while causing an improvement in the mechanical properties also affects the superconducting properties considerably by modifying the microstructure of the non-superconducting secondary phase Y-211 particles to exhibit variation in size, shape, distribution etc which are very crucial aspects for superior performance of the samples.

CONCLUSIONS

We observed an anomalous substitution of Ag in Cu sites in YBCO unit cell in bulk YBCO/Ag superconducting composites fabricate by IGP technique and a concentration quenching of metallic silver above 2 wt %. We studied the effect of Ag substitution on the magnetic and superconducting properties of the samples and we found that there is a substitution threshold for Ag in the Y-123 lattice. We identify the dual roles played by Ag in this system and its impact on the properties. We observed sustained critical current density in our sample with optimum Ag content. The observations reported here are significant from the perspective of practical applications of YBCO/Ag samples with superior superconducting properties.

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