

GLASS-BONDED COMPOSITES CONTAINING SUPERCONDUCTING $\text{YBa}_2\text{Cu}_3\text{O}_{9-y}$ FOR LEVITATION AND MAGNETIC SHIELDING APPLICATIONS

C.W. Nies, B.E. Smith, J.M. Nickel, W.W. Cao,
T.T. Srinivasan, A.S. Bhalla, R.E. Newnham, and L.E. Cross
Materials Research Laboratory
The Pennsylvania State University
University Park, PA 16802

(Received December 2, 1987; Refereed)

ABSTRACT

The discovery of ceramic superconductors with T_c above 77 K has opened up a wide variety of applications for superconductivity. Unfortunately, the use of these ceramics is limited by their inherent brittleness and chemical instability. To circumvent these limitations, a composite approach is being investigated. Glass-bonded 0-3 composites have been formed using $\text{YBa}_2\text{Cu}_3\text{O}_7$ as a filler. Although these composites do not show zero resistivity, the diamagnetic characteristics of the superconducting filler is preserved. These composites show large diamagnetic susceptibilities and the ability to levitate by repelling magnetic flux.

MATERIALS INDEX: Cuprates, borosilicates, superconductors, composites

Introduction

The recent discovery of oxide ceramic materials which show superconducting behavior at relatively high temperatures has caused a reevaluation of the physical, theoretical and technological aspects of superconductivity. The first of these materials, $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$, was discovered by Bednorz and Muller (1); it possesses the K_2NiF_4 structure and shows zero resistance at 36 K and ambient pressure. More recent discoveries have currently focused attention on the composition $\text{YBa}_2\text{Cu}_3\text{O}_{9-y}$, which exhibits critical temperatures near 90 K (2), well above the boiling point of liquid nitrogen (77 K). These materials have been shown to be an orthorhombic oxygen defect perovskite in their superconducting state (3), and display a high degree of twinning within each grain (4). The oscillation of the twin boundaries has been proposed as a possible mechanism for electron coupling and an increased T_c (5). The superconducting critical temperature has been shown to be intimately related to the oxygen content of the materials, the optimum being near $y = 2$ (6). This oxygen content is obtained by an oxygen annealing step which is generally carried out at temperatures below the normal calcining temperature (7).

The discovery of these materials has opened many possible applications for superconductivity. Because these materials do not require expensive liquid helium coolant, the cost of operating devices based on these oxides can be greatly reduced. Thus, applications for superconductivity that were previously too expensive are suddenly within reach. However, the materials still suffer from the drawback that as ceramic materials, they are inherently brittle and therefore may not be conveniently shaped and handled as ductile materials.

One possible solution to this dilemma is to form a composite of these materials which may be handled in a convenient and inexpensive manner. As an example, grains of carefully processed superconductor could be combined with a matrix material at a temperature below the normal oxygen calcining temperature in order to avoid upsetting the oxygen content of the material. The resulting 0-3 composite may possess many of the original properties of the superconductor, while its shape may be obtained by any convenient process used for the matrix material. Low melting glasses are an interesting choice for the matrix because of their relative stability in a number of environments and their current use in thick film microelectronics.

In this study, composites containing superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ were formed using a low melting lead borosilicate glass as the matrix material. While these composites did not show zero resistance at any temperature tested, a.c. magnetic susceptibility measurements demonstrated a high degree of field exclusion, indicating the superconducting behavior is preserved in the $\text{YBa}_2\text{Cu}_3\text{O}_{9-y}$ filler material. This suggests that these materials may have some use in magnetic shielding or levitation applications requiring reduced processing temperatures.

Experimental Procedure

Superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{9-y}$ for this study was prepared by the citrate processing method (8). In this technique, stoichiometric amounts of Y_2O_3 , BaCO_3 , and CuO were dissolved in an aqueous solution of citric acid monohydrate, nitric acid and ethylene glycol. The solution obtained was dried at 175°C for a period of 15-24 hr, producing a dry cake of predominately purple/brown material. This cake was broken up and calcined in air at $900-925^\circ\text{C}$ for 12 hr, ground and then recalcined in air at 940°C for 12 hr. This produced a single phase material as verified by x-ray diffraction. Following this, the material was ground to a sub-200 mesh ($<75\ \mu\text{m}$) particle size in a mortar and pestle. The oxygen content of the material was corrected by an oxygen anneal at 600°C for 12 hr. This material was then passed through a 200-mesh screen again to verify that no coarsening had occurred. The superconductive nature of this material was confirmed by a.c. susceptibility measurements on an unsintered pressed pellet.

The glass used in this study was a commercial composition (8) listed as 72-78 wt % PbO , 9-12 wt % SiO_2 , and 10-15 wt % B_2O_3 . Its softening temperature is quoted at 475°C , and its thermal expansion is given as $9.0 \times 10^{-6} / ^\circ\text{C}$.

A series of glass-bonded composites was made by dry mixing samples of superconducting and glass powder in nominal compositions ranging from 100 vol % $\text{YBa}_2\text{Cu}_3\text{O}_7$ to 100 vol % glass in 10 vol % increments. Mixing was done in a Spex mill using polymethylmethacrylate media for 10-15 min. The mixed powders were dry-pressed at 140 MPa using a dry lubricant without binder. The samples were then fired on Al_2O_3 substrates at a temperature of 500°C (slightly above the softening temperature of the glass) for 15 min. Following firing, each sample was polished with alumina paper to improve contact for resistance measurements.

Each sample was characterized by green and sintered density measurements, shrinkage measurements, and SEM micrography. In addition, x-ray diffraction was performed on selected samples to detect the formation of any third phase due to reaction of the two components. Electrical characterization was performed using room temperature a.c. resistance and temperature-varying

four point resistance measurements. Magnetic characterization was performed using a.c. susceptibility measurements. The levitating abilities of the composites were tested by a simple pendulum-repulsion experiment, in which the force derived from the field exclusion is indicated by the deflection of a small magnet suspended beside the sample.

Results and Discussion

The results of the x-ray characterization of the materials used in this study are shown in Figure 1. The pattern shown for the $\text{YBa}_2\text{Cu}_3\text{O}_7$ filler indicates that it consists only of the single phase orthorhombic material whose pattern was described by Beyers et al. (3) The sintered glass yields a completely amorphous pattern. The pattern for the composite (nominally containing 50 vol % glass) shows no additional peaks that would indicate development of a third phase. The presence of the glass can only be detected by the increase in the background near the $28^\circ 2\theta$ region, an artifact of the amorphous hump found in the pure glass pattern.

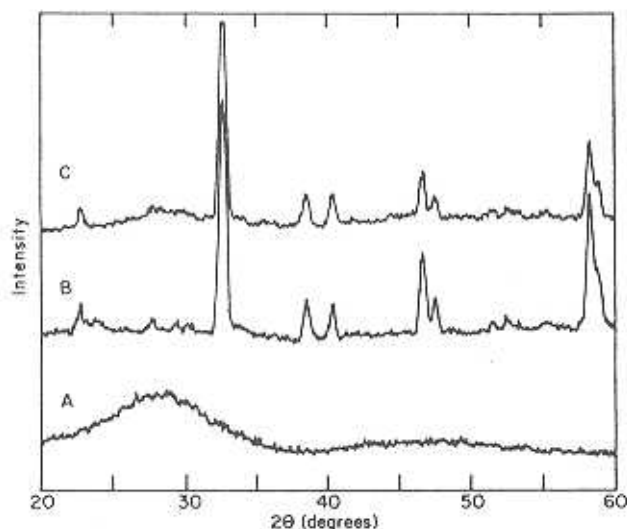


FIG. 1.

X-ray diffraction patterns for a) glass frit, b) $\text{YBa}_2\text{Cu}_3\text{O}_7$ superconductive filler and c) glass bonded composite.

serves to bond particles together locally. At lower loadings where the glass dominates, higher densities were achieved. This shift is to be expected at sintering temperatures above the softening point of the glass. The presence of porosity in all of the samples reduces the actual volume fraction of $\text{YBa}_2\text{Cu}_3\text{O}_7$ found in these samples, as shown in Table 1.

At loadings of 50 and 60 vol % glass, the samples show an anomalous decrease in density and negative shrinkage measurements, indicating swelling of the pellets. This unusual occurrence was explored more fully with scanning electron microscopy. Examples of the microstructure for pellets containing 20, 50 and 80 vol % glass are shown in Figure 4. This series of micrographs

General characteristics, density, shrinkage, and microstructure were also examined for the composites. Observations on the general appearance of the samples are compiled in Table 1. Pure samples of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and those with 10 vol % glass are chalky and have little mechanical integrity. Samples with 20 to 40 vol % glass are well-bonded pellets with smooth surfaces. Samples containing 50 to 60 vol % glass show rippled, uneven surfaces. Samples having 70 vol % glass and above have smooth glassy surfaces. These observations correlate in an interesting manner to the variations of density and shrinkage with composition, shown in Figures 2 and 3. It can be seen that at high loadings of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (<40 vol % glass), little or no densification occurs. This might be expected, as the sintering characteristics of the superconductor dominate the overall densification of the composite, and the glass only

TABLE 1.

General Observations on Sintered Composite Samples

Nominal Vol % Glass	Actual Vol % $\text{YBa}_2\text{Cu}_3\text{O}_{9-y}$	Observations
0	68.32	Pure superconductor; crumbly, chalky surfaces
10	61.10	Less crumbly; chalky, but finer texture surfaces
20	55.66	Well-bonded, no longer chalky; fine surface texture
30	48.13	Well-bonded; fine texture surfaces
40	42.19	Well-bonded; blotchy surfaces
50	28.60	Well-bonded; rippled, shiny surfaces
60	24.80	Well-bonded; rippled, shiny surfaces
70	22.11	Shiny surface; less rippled
80	15.97	Smooth, glassy surfaces
90	7.90	Smooth, glassy surface; curved edges
100	0	Smooth, opaque glass; curved edges

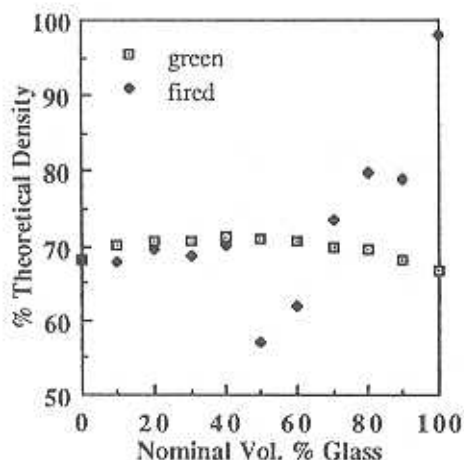


FIG. 2.

Variation of % theoretical density of the glass-bonded composites with composition.

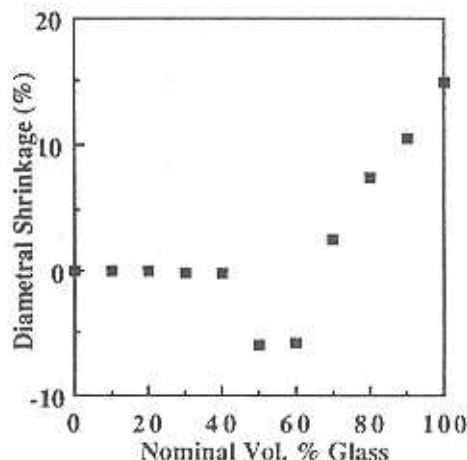


FIG. 3.

Variation of diametral shrinkage with composition for glass bonded composites.

shows the shift in appearance from a continuous matrix of superconducting grains whose pores are ragged in appearance, to a continuous glass matrix with round pores. In the case of the 50 vol % sample, the amount of open porosity is excessive. One hypothesis for the formation of these pores is the entrapment of oxygen released by the superconducting grains during sintering of the composite. If the porosity is closed, the oxygen could then be reabsorbed on cooling. This is supported by the magnetic measurements, which show little loss of the superconductive properties of the grains themselves. At lower volume fractions of glass, enough open porosity exists to allow this oxygen to escape, while at low volume fractions less superconductor exists to release oxygen in the first place. However, in the samples near the middle of the series, conditions may be optimized to impede gas release from the larger amount of $\text{YBa}_2\text{Cu}_3\text{O}_7$, producing the observed swelling. This discovery suggests that low melting glasses may be used to "seal" the surfaces of

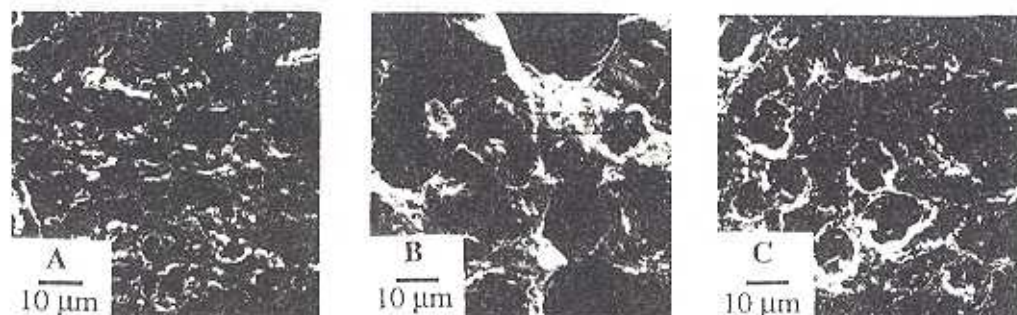


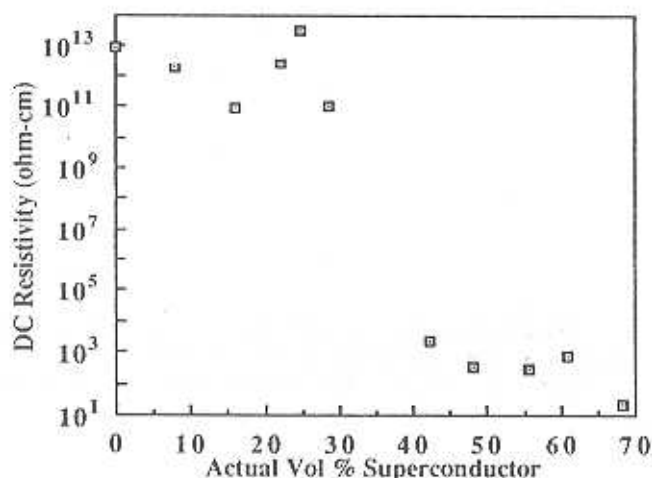
FIG. 4.

SEM micrographs of composites containing a) 20 vol %, b) 50 vol % and c) 80 vol % glass.

these materials, preventing loss of oxygen during firing.

The electrical characterization of these samples was first examined by studying their percolation behavior. The percolation curve for these materials is shown in Figure 5. It can be seen that the resistance becomes very large in the range of 50 to 60 vol % superconductor, with the percolation limit at about 30 vol % (it should be noted that this curve can be expected to change with different particle sizes of the conductive filler). To test these samples for bulk superconductivity, four point measurements were performed on the samples with lower glass loadings (Figure 6). All of the glass bonded samples show a gradual semiconducting behavior. This result suggests that the $\text{YBa}_2\text{Cu}_3\text{O}_7$ grains are not yet in close enough contact to permit bulk superconductivity, though normal metallic conductivity is present.

Representative a.c. susceptibility results for the composites are shown in Figure 7. The measurements taken in this experiment are normalized to the largest value achieved in pure sintered samples of $\text{YBa}_2\text{Cu}_3\text{O}_7$. These plots clearly demonstrate that superconductivity is maintained in the individual $\text{YBa}_2\text{Cu}_3\text{O}_7$ grains, although no bulk zero resistance is observed. As might be



expected, the susceptibility gradually increases with volume fraction of $\text{YBa}_2\text{Cu}_3\text{O}_7$ in the sample. The critical temperature is also shifted, the degree depending on the amount of open porosity in the sample. From an applications standpoint, the most important region of the diagram falls near 77 K, the most likely operating temperature for devices based on liquid nitrogen coolants.

FIG. 5.

Room temperature percolation curve for the glass bonded composites.

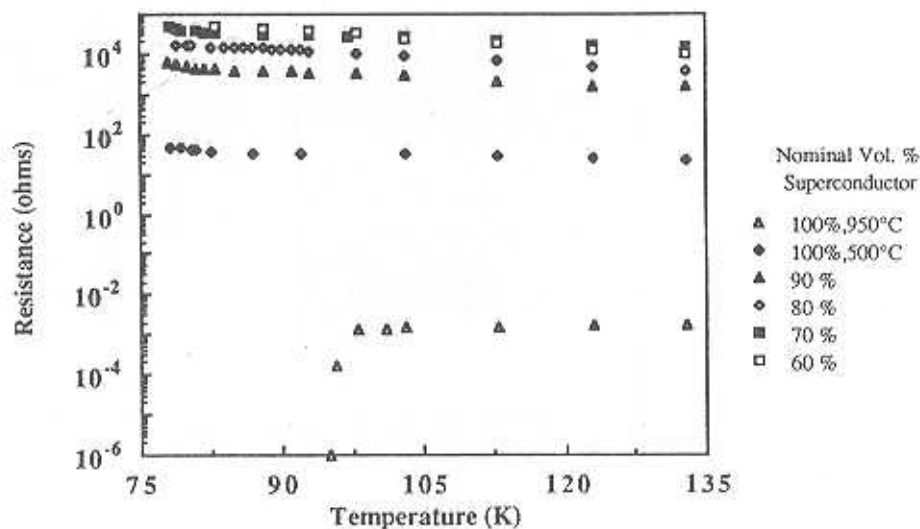


FIG. 6.

Variation of four-point resistance measurements with temperature for composite materials.

A plot of the 77 K susceptibility with temperature (Figure 8) shows the increase more clearly. The linear nature of the plot indicates that the volume susceptibility of a composite with a dispersed superconducting phase may be calculated using a weighted average of the susceptibilities of the components:

$$c_c = v_{f,s} c_s + v_{f,m} c_m$$

where c_c , c_s , and c_m are the composite, superconductor and matrix susceptibilities, and $v_{f,s}$ and $v_{f,m}$ are the volume fractions of superconductor and matrix. If the connectivity of the superconducting phase were changed, e.g. the particles were allowed sinter, this relation may not apply; this fact is indicated by the difference between the susceptibility of the sintered $\text{YBa}_2\text{Cu}_3\text{O}_7$ and that fired at 500°C. To verify this hypothesis, actual susceptibilities of these should be measured, rather than the arbitrary values measured here.

To test the ability of these materials to repel magnetic objects, a small magnetic pendulum was devised (apparatus shown in Figure 9). The force generated by the field on the magnet is given by

$$F_{\text{mag}} = \frac{m g x}{l \cos \theta}$$

where x is the pendulum displacement, g is the gravitational constant, and the other geometric constants are given in Figure 9. For this experiment, samples which were 1.27 cm in diameter and 0.21 cm thick were tested using a neodymium iron boron magnet (mass $m = 0.175$ g) suspended on a thread 22.5 cm long. Each sample was mounted in the sample holder and the displacement of the magnet was zeroed. The sample holder was then filled with liquid nitrogen and the displacement of the magnet was observed. The generated force is plotted with sample composition in Figure 10.

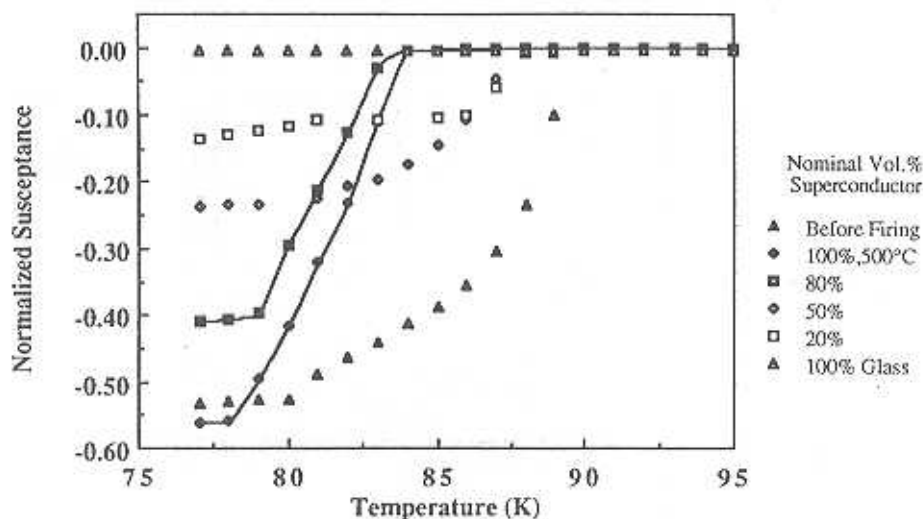


FIG. 7.

A.C. susceptibility measurements for selected composites showing the gradual decrease in susceptibility as volume fraction of $\text{YBa}_2\text{Cu}_3\text{O}_7$ is increased.

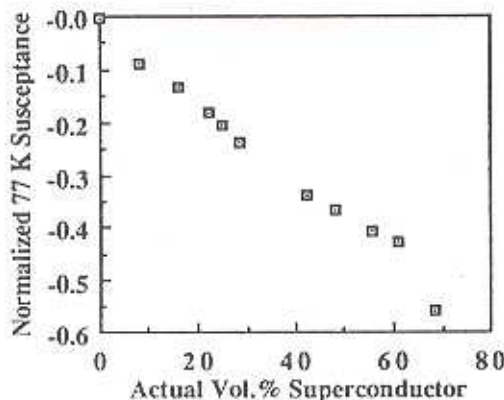


FIG. 8.

Variation of 77 K a.c. susceptibility for glass-bounded composites.

properties which are characteristic of superconductors, as indicated by the susceptibility and repulsion measurements. Some of these composites show porous microstructures which indicate possible oxygen losses during sintering. Normal percolative conductivity could be observed in samples with 40 vol % glass or less, but superconductivity did not occur. The absence of zero resistance in the samples fired at 500°C indicates that intimate contact must exist between the $\text{YBa}_2\text{Cu}_3\text{O}_7$ grains to allow bulk superconductivity.

Interestingly, even the samples containing low amounts of $\text{YBa}_2\text{Cu}_3\text{O}_7$ are capable of producing a measurable force. It can be seen that higher densities of $\text{YBa}_2\text{Cu}_3\text{O}_7$ in the sample create a more concentrated blockade to the magnetic flux. In this respect, the porosity observed in the samples and the dilution of the superconductor by the matrix material necessarily has a detrimental effect on the magnetic properties. The saturation of the curve at high volume fractions of superconductor is probably due to the decrease in the magnetic field at larger separation distances.

Summary

Glass-bounded composites containing $\text{YBa}_2\text{Cu}_3\text{O}_7$ were fabricated which exhibit the magnetic field exclusion

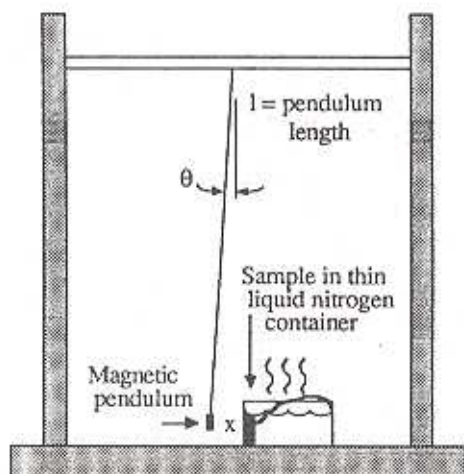


FIG. 9.

Schematic of device used for pendulum repulsion experiment.

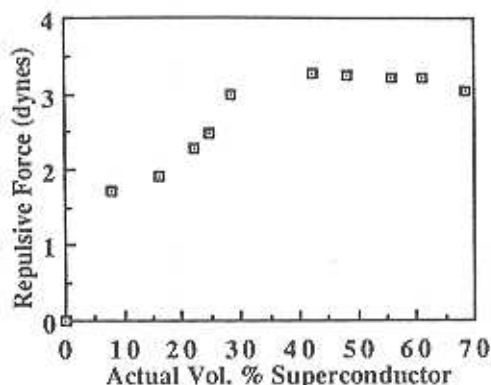


FIG. 10.

Variation of generated force on magnetic pendulum with vol. fraction $\text{YBa}_2\text{Cu}_3\text{O}_7$ in composite.

Acknowledgements

The authors would like to thank the Celanese Research Corporation, Alcoa Research Laboratories, and the Dupont Co. for financial support of this research, and O. Hummel Glass Company for supplying glass frit for this study.

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