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Mechanical properties of polycrystalline $RuSr_2GdCu_2O_8$ superconductor

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ABSTRACT

The main objective of this paper is to report the room temperature hardness and elastic modulus of the $RuSr_2GdCu_2O_8$ superconductor phase by instrumented indentation. Polycrystalline samples were produced by a solid state reaction technique. The samples were also characterized by scanning electron microscopy, X-ray diffraction and electrical resistivity measurements. The influence of porosity on the mechanical properties was avoided by considering only those indentations inside the grains. The hardness and elastic modulus were 8.6 GPa and 145 GPa, respectively. These values are comparable with those of Y-123. The indentation fracture toughness evaluated after conventional Vickers indentation was 1.9 MPa $m^{1/2}$.

1. Introduction

The ruthenocuprate $RuSr_2GdCu_2O_8$ (Ru-1212) was synthesized for the first time by Bauernfeind et al. [1,2] and it has attracted considerable interest because of the coexistence of magnetic order and superconductivity in this phase [3]. The magnetic long-range ordering of the Ru sub-lattice occurs below the transition temperature $T_M \sim 130$ K while the superconductivity arising from the CuO_2 layers occurs below the critical temperature $T_C \sim 40$ K. Ru-1212 is a triple perovskite structure very similar to $YBa_2Cu_3O_{7-\delta}$ (Y-123), with the Y and Ba atoms being replaced by Gd and Sr, respectively, and with the CuO chain being replaced by RuO_2 planes [4]. However, differently in the case of $YBa_2Cu_3O_{7-\delta}$, the magnetic and superconducting properties, and probably the mechanical properties of Ru-1212, are extremely sensitive to the details of sample preparation [5,6].

Some studies have shown that the Ru-1212 is microscopically uniform [5]. However, there are many other studies that indicate a possible phase separation in superconducting and magnetic regions [7–9]. From high-resolution transmission electron microscopy and synchrotron X-ray diffraction analysis, a possible phase separation from the rotation of 14° of the RuO_6 octahedra around the *c*-axis was suggested. Due to this rotation, there is the formation of small domains with characteristic lengths around 200 Å and separated by sharp antiphase boundaries of reversed rotation [10]. Another important point to be considered is the role of adding or removing oxygen atoms from the structure. For example, it was shown that prolonged annealing time at 1060 °C during sample preparation is essential for obtaining superconductivity and to increase the size of domains related to the RuO_6 octahedral [11].

Besides magnetic and superconducting properties, it is also important to know the mechanical properties of these materials and their dependence with the microscopic/mesoscopic granularity. To our knowledge, there is no available study on the mechanical properties of Ru-1212 by instrumented indentation. Therefore, the main objective of this paper is to report the mechanical properties of polycrystalline $RuSr_2GdCu_2O_8$ superconductor samples, namely the hardness (H) and elastic modulus (E), measured by instrumented indentation. Also, the fracture toughness (K_C) was evaluated after conventional Vickers indentation. The samples were also characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and electrical resistivity measurements.

2. Experimental details

Ceramic samples of $RuSr_2GdCu_2O_8$ were synthesized following the standard solid-state-reaction procedure using the mixture of high purity RuO_2 (99.95%), $SrCO_3$ (99.99%), Gd_2O_3 (99.99%) and CuO (99.99%) powders. The powders were first calcinated in air at 950 °C followed by grinding and pressing into cylindrical pellets. Afterwards, the pellets were heated for 20 h in flowing N_2

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atmosphere at 1010 °C. The resulting samples were reground, pressed again into pellets and calcinated again at 1050 and 1055 °C in flowing O_2 for 24 h. Finally, the samples were reground and pressed into the final shape. They were subsequently sintered at 1060 °C in flowing O_2 for 6 days.

The crystal structure was analyzed by X-ray powder diffraction (XRD) using a Shimadzu diffractometer with Cu Kα in θ–2θ configuration. The X-ray diffraction patterns were collected from 10° to 100° in the 2θ range with 0.02° steps and 4 s counting time. The electrical resistivity as a function of temperature was measured using a low-frequency AC technique. Sample dimensions for resistivity measurements were $4 \times 3 \times 2$ mm^3. Sample porosity was measured by Hg porosimetry using an Autopore IV Mercury Porosimeter 9500 model.

Before the indentation tests, the sample surface was previously grounded and polished up to 1 μm diamond paste. The sample dimensions were $6 \times 6 \times 3$ mm^3. Room temperature H and E profiles were determined by instrumented indentation following the Oliver and Pharr method [12]. The indentations were performed using a Nanoindenter XP™. The diamond tip was a Berkovich type and the applied loads ranged from 6.3 to 50 mN. The tests were performed at room temperature in air with 50% relative humidity. Sample porosity decreases the measured H and E. To avoid its effect, a 100 indentations were performed in a matrix of 10×10 spaced by 30 μm. This separation is about 60 times the maximum penetration depth. The maximum load was chosen so that the indentation size would be about 1/5 of the grain size. In this way, we expected that some of the indentations were inside the grains and the measured H and E could be assumed as a value of a full dense material. For that purpose, the 44 indentations with the highest H were examined by SEM and only those that were inside the grain were used for H and E determination. The fracture toughness was obtained by 20 N Vickers indentations and using the relation according to Anstis et al. [13]:

$$K_C = \alpha \left(\frac{E}{H_v}\right)^{1/2} \frac{P}{c^{3/2}}, \quad (1)$$

where α is a geometrical constant equal to 0.016 ± 0.004, c is the radial crack length and P is the applied load. The number of indentations used for calculation of the indentation fracture toughness was 25. Samples surface morphology and Vickers and Berkovich indentations were observed by scanning electron microscopy.

3. Results and discussion

Fig. 1 shows typical SEM of the fracture surface of an as-prepared $RuSr_2GdCu_2O_{8+d}$ sample. Small grain sizes of about 1 μm are observed. Agglomeration of these grains up to a size of 10 μm is also observed. We are not sure if these 10 μm agglomerations are a single grain or an agglomeration of 1 μm grains with grain boundaries. From this figure, we can also observe that the sample is homogeneous with no precipitates. Moreover, no sharp grain facets and boundaries can be seen, possibly indicating the melting of surfaces [14]. The crystallite size distribution and its variation with annealing time were studied by Kumary et al. [15]. The authors reported that the grain size increased from sub-micron for the as-prepared sample to a few microns for well annealed samples. In Fig. 1, we can also observe the presence of many defects such as pores that are created during the heating and cooling process. Their size and quantity depend strongly on the thermal process involved [15].

The sample was characterized by means of X-ray powder diffraction performed in a high resolution diffractometer using Cu Kα radiation as shown in Fig. 2. The most intense diffraction peaks were indexed as belonging to the $RuSr_2GdCu_2O_{8+d}$ tetragonal phase and with *P4/mmm* space group symmetry, with lattice parameters a = 3.843 (1) Å and c = 11.552 (1) Å. These values are in good agreement with those previously reported [1,2]. Also, the sample was found to be nearly single-phase because peaks related to the perovskite-type $SrRuO_3$ and Sr_2GdRuO_6 (2116) were not observed.

Fig. 3 shows the temperature dependence of the electrical resistivity of Ru-1212 at zero external magnetic field. The measured value of $\rho(T) \cong 10$ mΩ cm at room temperature is within the range of the reported values for the Ru-1212 compound [16]. Also, the sample exhibits metallic behavior in the normal state at higher temperature (not shown). The critical temperature T_C, defined as the maximum of $d\rho/dT$, is around 36.5 K and the zero-resistance temperature is $T_{C0} \cong 30$ K. The transition width, ΔT, defined between 5% and 95% of the transition height is approximately 10 K. It was also observed (not shown) a subtle fall in the $\rho(T)$ curve near 130 K, making the onset of magnetic ordering of the Ru sub-lattice and that is in agreement with previous study [16]. Yet, the electrical resistivity displays a shallow minimum near 65 K followed by a slight upturn in $\rho(T)$ close to the onset of the superconductivity, indicative of the increased charge localization.

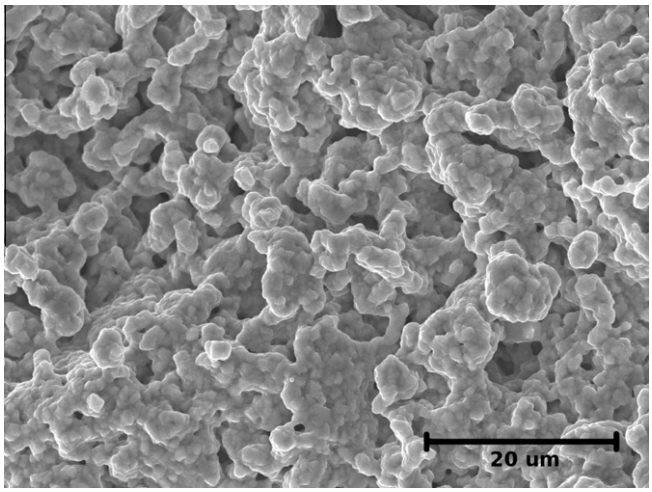

Fig. 1. Scanning electron microscopy of fracture surface of as-prepared $RuSr_2GdCu_2O_{8+d}$ sample.

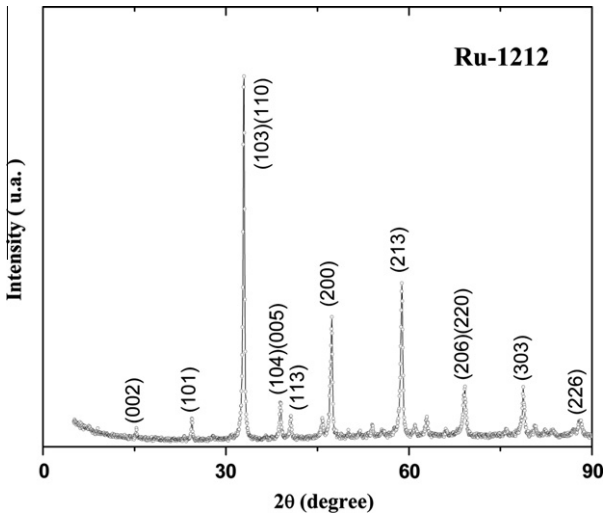

Fig. 2. Room temperature X-ray diffraction of polycrystalline $RuSr_2GdCu_2O_{8+d}$ sample.