Since the discovery of the high Tc superconductors, many researches have been carried out on the different properties of these materials, especially on the transition temperature into the superconducting state. The rutheno-cuprates belong to a new class of composites, which were synthesized for the first time by Bauernfeind in 1995. Bernhard and collaborators discovered, in 1999, the coexistence of the ferromagnetism and the superconductivity in this phase, which is known as antagonistic phenomenon in the electromagnetism due to spin-charge interactions established in these states. However, the physical nature of the superconducting and magnetic states is still very obscure. The non-stoichiometric (interstitial) oxygen is considered as a possible cause for the non-uniformity of the sample properties. In this paper, results of mechanical spectroscopy in Ru-1212 samples are presented showing complex anelastic spectra, which were attributed to the mobility of the interstitial oxygen atoms in the Ru-1212 lattice.

Keywords: Mechanical Spectroscopy, Ru-1212, Oxygen Mobility

1. INTRODUCTION

The rutheno-cuprate RuSr$_2$GdCu$_2$O$_{8+\delta}$ (Ru-1212) belongs to a class of compounds that were synthesized for the first time in 1995 (1). This material is characterized by a triple perovskite cell similar to YBa$_2$Cu$_3$O$_{7-x}$ (YBCO), in which Y and Ba are substituted for Gd and Sr, respectively, and the CuO$_2$ planes are separated from one another not by means of Cu chains, but by RuO$_6$ octahedra (2). Magnetism and superconductivity can coexist because they are supposed to act in different layers, the first one in the layer containing Ru, and the second in the Cu layer.

The Ru-1212 presents a remarkable development in the study of competition between magnetism and superconductivity (3), this one varying between 0-40 K coexisting with spatially uniform ferromagnetism at 132 K. However this material still presents diverse obscure points about its preparation and characterization, making the sample superconducting or not depending on some “details” during the preparation process (4). This is a critical point. The need to avoid the formation of impurities, such as the ferromagnetic SrRuO$_3$ and to obtain phase as ordered as possible, led to the optimization of the synthesis process, which includes a first calcination, a heat treatment in N$_2$ atmosphere (5,6) and several annealings in flowing O$_2$ (6,7).

The oxygen stoichiometry has been considered as a possible cause for the non-uniformity in the superconducting properties of the samples. Thus, there is a great variety of studies that takes into account the influence of preparation conditions in the oxygen stoichiometry. In the Ru-1212, oxygen vacancies are possibly introduced in the RuO$_2$ planes through vacuum annealing above 600 K (8). The diffusive jumps of the oxygen vacancies are accompanied by changes in the local distortion due to this defect and it can be investigated by mechanical spectroscopy (internal friction) measurements, which are sensitive tools for the study of defects in solids
and allow detailed investigations of the structural and kinetic processes in atomic scale (9).

In this paper, it is reported mechanical spectroscopy study in Ru-1212 samples, in which complex anelastic spectra were found. This was attributed to the interstitial oxygen atoms mobility in the Ru-1212 lattice.

2. EXPERIMENTAL DETAILS

Polycrystalline samples of Ru-1212 were synthesized by the solid-state reactions method, using the mixture of high purity RuO$_2$ (99.99%), Gd$_2$O$_3$ (99.99%), SrCO$_3$ (99.99%) and CuO (99.99%) powders, supplied by Sigma-Aldrich (10). The synthesis process is illustrated in Fig. 1. The heating and cooling rate was 5 K/min.

The structure was determined by powder X-ray diffraction in a Rigaku RINT2000 diffractometer, using CuK$_\alpha$ radiation. The magnetic susceptibility was measured using a quantum design SQUID magnetometer (10).

The mechanical spectroscopy measurements were performed in a torsion pendulum, operating with oscillation frequency around 40 Hz, temperature range between 100 and 400 K, heating rate of 1 K/min and vacuum lower than $10^{-5}$ Torr. This technique allows measuring the elasticity modulus (related to the oscillation frequency) and the elastic energy loss (the internal friction, Q$^{-1}$) as function of the temperature. In mechanical spectroscopy measurements, the samples are made vibrate in the fundamental mode (free vibrations), which gives rise to energy dissipation by heating due to internal friction. In the case of torsion pendulum, this energy loss per cycle is measured by the logarithmic decrement, which is proportional to the internal friction (9).

Aiming at removing the maximum amount of non-stoichiometric oxygen (6), the Ru-1212 samples were annealed twice. The sample was heated up to 773 K at 10 K/min under vacuum lower than $10^{-9}$ Torr. The samples remained at these temperatures for 30 min and soon afterwards they were rapidly cooled by fast cooling of the furnace tube. The second annealing was performed under the same condition, but with temperature of 873 K.

The samples were annealed in oxygen atmosphere in order to recover oxygen content, $\delta$. During the treatment, the samples were placed in equilibrium for 30 min at 973 K with 0.5 Torr of oxygen in a quartz tube connected to an ultra-high-vacuum (UHV) system. After reaching equilibrium, the tube was quenched in water.

3. RESULTS AND DISCUSSION

The X-ray diffraction pattern was analyzed by Rietveld method (10-13) and only the Ru-1212 single phase was showed. This analysis is shown in Fig. 2. The quality refinement indexes are $R_{wp} = 6.85\%$, $R_{F} = 4.06\%$, $R_{F} = 1.40\%$ and $\chi^2 = 1.40$. Table I contains the unity cell parameters, density and weight percentage obtained for the Ru-1212 samples.

In mechanical spectroscopy measurements, a relaxation process gives origin to a peak in the anelastic spectrum in curve for Ru-1212. The superconducting transitions presented the two-step behavior, which is typical of granular high-Tc superconductors (14), as presented in this case.

In Fig. 4 the mechanical spectroscopy curves are presented for the Ru-1212 samples, measured in the as-sintered (as-received) condition and after two heat treatments in UHV. Two relaxation peaks are observed at 210 K and 300 K in the curve for the as-receive sample, which shifts to higher temperature at higher frequencies (not shown here), denoting their thermally activated nature. These peaks disappear after the sample was submitted to heat treatments, showing that the annealing in UHV reduces the excess oxygen. The effect of reducing the amount of excess oxygen is to reduce the peaks, indicating that these peaks are due to excess oxygen.

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The Ru-1212 superconducting samples were analyzed by using mechanical spectroscopy in the Hz range (torsion pendulum). The obtained spectra present at least two relaxation peaks located at 210 and 300 K. The observed peaks are clearly related to the additional oxygen atoms and can be explained by the short-range diffusion of interstitial oxygen in the RuO$_2$ planes.

**4. CONCLUSIONS**

The Ru-1212 superconducting samples were analyzed by using mechanical spectroscopy in the Hz range (torsion pendulum). The obtained spectra present at least two relaxation peaks located at 210 and 300 K. The observed peaks are clearly related to the additional oxygen atoms and can be explained by the short-range diffusion of interstitial oxygen in the RuO$_2$ planes.

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