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Raman Microscopy Identification of Secondary Spurious Phases in Molten $GdSr_2RuCu_2O_{8-\delta}$ Superconductor for Photonics and Plasmonic Applications

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Abstract. Plasmonic and Photonics applications of superconducting materials, suggested at first by the necessity to minimize the dissipative losses of conventional metals in the high frequency ranges, are topics of growing interest in Optics. In this perspective, $GdSr_2RuCu_2O_{8-\delta}$ (Gd1212) Rutheno-Cuprate Superconductor presents very promising properties, showing both superconducting and magnetically ordered phases coexisting in the same cell. To investigate its features, the fabrication of macroscopic crystallographically oriented samples is necessary. The use of melt texturing techniques has shown to be among the most effective ways to achieve the best characteristics, although the fabrication of high-quality Gd1212 samples is intrinsically difficult.

To reach a better understanding of Gd1212 incongruent melting reaction, a series of bulk samples annealed at temperatures below and above the melting temperature was prepared. Raman Microscopy and Mapping performed on molten and re-solidified samples revealed the presence of different phases, corresponding to those identified in our previous studies. These observations were also confirmed by XRD, TGA-DTA, and SEM+EDS characterisations. Secondary phases formation showed a strong dependence on the temperature of the annealing treatments.

Susceptibility and magnetization measurements show both superconducting and magnetic transitions and a contribution of different spurious magnetic phases as suggested by EDS.

1 Introduction

The research on metamaterials and Photonics applications of High Temperature Superconductors (HTSC) is, nowadays of great interest [1,2]. HTSC are studied because they promise to allow and realization of a wider range of innovative metamaterials characterised by a lower dissipation even at higher frequencies. In particular, research on Gd1212 is focused on understanding the coexistence of magnetic order and superconductivity observed in its unit cell [3], so that both features may be exploited in the design of new materials and devices. Top-Seeding Melt-Textured Growth (TSG) technique allows the fabrication of Gd1212-based samples presenting very good features [4], many of which likely correlated to the presence of secondary phases, both added in the initial mixtures and produced during the melting process. By the observation of differences in secondary phases composition depending on initial mixtures composition, some alternative peritectic reaction have been proposed in previous works [5,6]. More light should be shed then on the chemistry of Gd1212 melting processes, in view to fabricate nanoscale structures integrated on silicon.

2 Experiment

Raman microscopy is a powerful tool that allows to identify and map all the phases appearing on a sample surface. Raman imaging provided us spectroscopic

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information on Gd1212 samples and a complete mapping of phases. In previous works we have analysed Top-Seeded Melt-Textured Gd1212 with different starting powder mixture compositions [7,8]. In this work we analysed pure Gd1212 samples annealed in pure oxygen flow for 10 hours at different temperatures both below and above Gd1212 melting Temperature T_m. (from 1045°C to 1135°C) Samples annealed below Tm appeared as pure Gd1212 sintered pellets. Samples annealed at higher temperature showed, instead a more complex composition. Highest temperature annealed samples' images correctly identified the presence of the Gd1212 matrix and of the predominant Gd1210 precipitates, the ones predicted by the standard melting reaction, but showed also more precipitates, identified as SrRuO3, Gd2CuO4 and CuO, [5], suggesting that composition fluctuations of the starting powders, with a local higher CuO content, may cause the material to follow a different peritectic reaction.

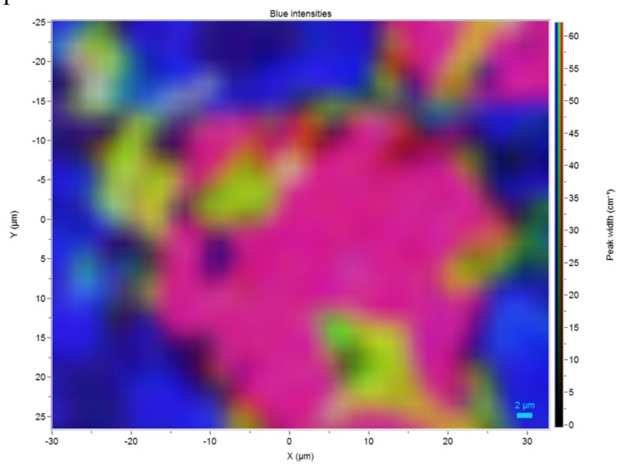

Fig. 1. Raman image of a Gd1212 sample, oxygen annealed at a Ttemperature above T_m showing Gd1212 matrix (blue), Gd1210 precipitate (pink), and other precipitates (green).

3 Other Measurements

We also performed TG-DTA in O_2 atmosphere, showing a complex oxygen absorption behaviour and a reaction peak, associated to decomposition, near 1070°C. SEM-EDS study revealed partial melting and the presence of different phases depending on the annealing temperature. XRD identification of which was also performed. Susceptibility and magnetization measurements show Gd1212 superconducting and magnetic transitions, but also Gd2CuO4 (Gd214) magnetic transition. Gd214, coming from Gd1212 decomposition, likely plays a role in vortex generation.

4 Conclusions

In this work, Gd1212 ruthenocuprate superconductor was analyzed by means of Raman microscopy.

Gd1212 bulk pellets, oxygen annealed at different temperatures, above and below T_m, were prepared.

Previous analysis had suggested different chemical reactions occurring at melting temperature in dependence on the starting mixture composition, due to local CuO excess.

Raman measurements, performed on pure Gd1212 oxygen annealed pellets, allowed a more detailed mapping of these samples, confirming the observed chemical variability and confirming that different melting reactions should be hypothesized for Gd1212 samples in dependence of local composition fluctuations. More quantitative Raman analyses of the samples are in progress.

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