Effects of oxygenation processes on (Nd,Gd)-$Sr_2RuCu_2O_x$ synthesis

Antonio Vecchione[1, a] Marcello Gombos [a] Consiglia Tedesco [b] Daniela Sisti [b]
Sivaperumal Uthayakumar[2, c] Sandro Pace [c]

[a] *I.N.F.M.-Coherentia U.d.R. Salerno and Dipartimento di Fisica "E. R. Caianiello", Universitá di Salerno, via Salvador Allende, I-84081 Baronissi (Salerno), Italia.*
[b] *Dipartimento di Chimica, Università di Salerno, via S. Allende, I-84081 Baronissi (Salerno), Italia.*
[c] *I.N.F.M. U.d.R. Salerno and Dipartimento di Fisica "E. R. Caianiello", Università di Salerno, via Salvador Allende, I-84081 Baronissi (Salerno), Italia.*

Abstract

In this work we report on the effect of oxygenation processes on the structure and composition of $GdSr_2RuCu_2O_x$ and $NdSr_2RuCu_2O_x$ compounds. By x-ray diffraction analysis it results that the tetragonal Gd-based compound begins to form after prolonged time, while a progressive improvement of cubic Nd-based samples is observed as impurity peaks disappear. Evolution of crystalline structure after oxygen annealing treatments has been studied too.

Key words: rutheno-cuprate materials, synthesis processes, X-ray powder diffraction

1. Introduction

$RESr_2RuCu_2O_x$ (RE-1212) rutheno cuprates have attracted much attention due to the co-existence of ferromagnetism and superconductivity in these new class of compounds [1,2]. After the report by Bauernfeind et al. [3], many efforts are being made to synthesize these compounds. We have already reported that absence of superconductivity in the $NdSr_2RuCu_2O_x$ (Nd-1212) compound is due to the intermixing of cations of Cu/Ru site as well as Nd/Sr ions producing disordered network of CuO_2 and RuO_2 planes [4]. This disordered network inhibits superconductivity and magnetic ordering. The establishment of the superconducting state has turned out to be strongly dependent on the sample quality [1]. A better understanding of the relation between the phase formation and the oxygenation process is necessary in order to improve the reliability and repeatibility to synthesize these new class of compounds. In this report, we investigate the effect of oxygenation on the structural properties of (Nd,Gd)-1212 to get more insight into the phase formation of these compounds.

2. Results and discussion

Polycrystalline samples of Nd and Gd-1212 were prepared by mixing the stoichiometric amounts of Gd_2O_3 or Nd_2O_3 and $SrCO_3$,CuO_2 and RuO_2. We have prepared two batches of Gd-1212 samples. The first batch of Gd-1212 sample was calcinated in air for 10 hours at 960°C and a second batch of Gd-1212 was calcinated at 960°C for 17 hrs. After the calcinating the two batches the samples were reground, milled and annealed in argon flow at 1020°C for 10 hours. Finally the samples were oxygenated with a procedure made by several cycles of heating at temperatures ranging from 1050°C

[1] Corresponding author: Antonio Vecchione, Dipartimento di Fisica "E. R. Caianiello", Università di Salerno, via Salvador Allende, I-84081 Baronissi (Salerno), Italia. E-mail:vecchione@sa.infn.it
[2] Permanent address: Crystal Growth Centre, Anna University, Chennai 600 025, India

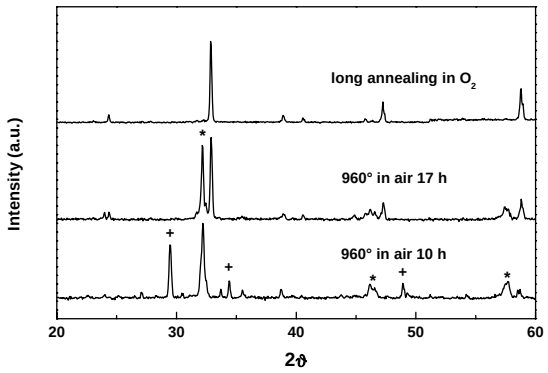

Fig. 1. XRD patterns for Gd-1212 at different preparation stages.

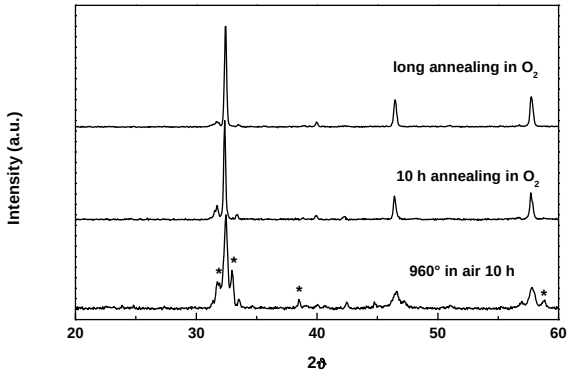

Fig. 2. XRD patterns for Nd-1212 at different preparation stages.

to 1080 °C (hereafter called "long annealed samples"). The same thermal procedure carried out for the Gd-1212 was repeated for the Nd-1212. The phases produced after each step were monitored by X-ray diffraction by means of Philips PW-1700 diffractometer using Ni-filtered Cu Kα radiation. Fig.1 shows X-ray diffraction patterns of Gd-1212 samples at different preparation steps. It can be inferred that the formation of Gd-1212 phase (main reflections at $2\theta = 32.9°$, $47.2°$ and $58.8°$, marked by stars) occurs only after several hours of thermal treatment in air at 960°C. In particular, even after 10 h the Gd-1212 phase is not yet formed. At this stage, the main reflections can be attributed to $SrRuO_3$ and to an unidentified phase containing Gd and Cu (marked by crosses). Also, thermal analysis has been carried out by TGA performing on stoichiometric mixtures of precursor oxides. TGA spectrum shows a continuous weight loss occurs at 960°C and the process does not appear complete even after 10 hours at this temperature [5]. The tetragonal Gd-1212 phase begins to form only after prolonged time at 960°C. Several annealing cycles in oxygen at different temperatures are needed to obtain a pure Gd-1212 phase (top diffractogram in Fig. 1).

Fig.2 shows X-ray diffraction patterns of the grown Nd-1212 sample (Fig. 2). The bottom pattern shows the 10 h calcinated Nd-1212 sample. Secondary phases can be detected and are partially overlapped to Nd-1212 reflections. Extra peaks are observed around the main reflection at $2\theta = 32.4°$. The formation of Nd-1212 phase follows a pathway different from that of Gd-1212. In fact, as results also from TGA profile performed on stoichiometric mixtures of precursor oxides of Nd-based compound, the phase is formed after 3 hours at 960°C. At this stage, no significant amounts of precursors are detected, and Nd-1212 is the most abundant phase present although the composition of the aggregates is not homogeneous. Further oxygenation of the Nd-1212 sample shows no change in the phase except a suppression of the impurity phases (middle pattern of Fig.2). Very long annealing cycles at 1050-1080 °C both in inert and oxidizing atmospheres are needed for obtaining a homogeneous Nd-1212 cubic phase (top pattern of Fig.2).

In conclusion, our study points out that the formation of tetragonal Gd-1212 phase and Nd1212 follows two different pathways. In the case of Gd-1212 solid state reaction from precursor oxides leads to intermediate compounds which transforms in the desired tetragonal phase after prolonged oxygen thermal treatments. On the contrary, Nd-1212 disordered cubic phase readily forms together with spurious compounds and long oxygen annealing results effective only in suppressing them. The observed differences have a deep effect on physical properties of the two materials. In fact, Gd-1212 shows a coexistence of superconductivity and magnetic ordering, while Nd-1212 is paramagnetic and not superconducting.

References

[1] C. Bernhard, J.L.Tallon, Ch. Niedermeier, Th. Blasius, A. Golnik, E. Brücher, R.K. Kremer, D.R. Noakes, C.E. Stronach, E.J. Ansaldo: Phys. Rev. B **59**, 14099 (1999).

[2] J. Tallon, C. Bernhard, M. Bowden, P. Gilberd, T. Stoto, D. Pringle: IEEE Trans. on Appl. Superc. **9**, 1696 (1999).

[3] L. Bauernfeind, W. Widder, H.F. Braun: Physica C **254**, 151 (1995).

[4] A. Vecchione, D. Zola, M. Gombos, S. Pace, L. Marchese, G. Cerrato, C. Tedesco, P. W. Stephens, C. Noce: Eur. Phys. J. B **26**, 51 (2002).

[5] C.Tedesco, A.Frache, M.Gombos, H.O.Pastore, L.Marchese, to be submitted to Chem. Phys. Lett.