11th International Conference on Advanced Materials
Rio de Janeiro Brazil
September 20 - 25
ICAM2009

Synthesis and quantitative metal content by complexometric analysis and X ray diffraction in (Ni, Cu, Co)$_{1+x}$Mn$_{2-x}$O$_y$ nanosize samples

R. A. Ferreira[(1)*], C. Morilla-Santos[(1)], P. N. Lisboa Filho[(2)]

(1) UNESP – Universidade Estadual Paulista, Programa de Pós-Graduação em Ciência e Tecnologia de Materiais, Bauru, SP, Brazil, * frafael@fc.unesp.br
(2) UNESP – Universidade Estadual Paulista, Departamento de Física, Faculdade de Ciências, Bauru, SP, Brazil, plisboa@fc.unesp.br.

Abstract – Manganese based magnetic materials present a rich magnetic phase diagram. The magnetic response of these materials is very sensitive to metal content and oxygen stoichiometry and have been analyzed by several different wet chemical methods. In this contribution it is presented an analyses procedure based on complexometric titration and X ray diffraction associated to Rietveld analyzes. Nanosized ceramic samples of (Ni, Cu, Co)$_{1+x}$Mn$_{2-x}$O$_y$ were prepared by a modified polymeric precursors method and the relative amounts of the metals and oxygen stoichiometry were determined by complexometric analyses. Also, the crystallographic phase evolution was traced by x ray diffraction studies.

Advanced oxide materials with nominal composition (Ni, Cu, Co)$_{1+x}$Mn$_{2-x}$ O$_y$ with perovskite or spinel structures present crystallographic properties and consequently magnetic response largely influenced by the oxygen stoichiometry and valence states of manganese, which causes Jahn-Teller effects [1].

Samples were synthesized by a of polymeric precursors method. Stoichiometry amounts of the chemicals, $MnCO_3$ (99,9%), CuO (99,99%), $Co(NO_3)_3.6H_2O$ (98%) and Ni_2O_3 (99,99%), were weighted and diluted in a nitric acid solution with constant stirring at temperature of 70°C. After the formation of homogeneous and clear aqueous metals solution citric acid and ethylene glycol was added and a polyester is formed in a polymeric gel. Further, the polymeric gel obtained is dried at 250°C for 4 hours for a subsequent heat treatment in different atmospheres was performed.

As mentioned before, it is fundamental to perform a quantitative chemical analyses of the material in order to determine the relative amounts of the metals Cu^{n+}, Co^{n+} and Ni^{n+}, as well as of Mn in it equivalent oxidation states III and IV.

Andersen et al. described [2] a method of analysis of the total manganese amount (Mn_t) that consisted in the reduction of Mn^{+3} and Mn^{+4} to Mn^{+2} in acid solution and a subsequent potenciometric titration, however such method is very expensive with a high consumption of materials and chemicals. The authors also described a simple and inexpensive method that allows the quantification of the relative amounts of manganese in the oxidation states III and IV (Mn_{oxi}), for the methods iodometric titration.

Our contribution consists in develop a procedure for the analysis of Mn_t, Cu^{n+}, Co^{n+} and Ni^{n+} in samples prepared by chemical synthesis using complex titration that consists in the reaction among the free metal present in a previously prepared solution for the reaction of the material in acid solution with a EDTA and after that by a well-controlled pH adjustment a stable chelate coordination complex is formed. In addition, X ray diffraction studies associated to Rietveld refinement method are performed to determine the occurrence of secondary phases.

It is expected that such conjugated procedure o wet chemical and diffraction studies allow determining the real amounts of metals ion (Cu^n+, Co^n+ and Ni^n+), of Mn_t and of Mn_{oxi}, oxygen stoichiometry and the number of vacancies to better explaining the magnetic behavior of the samples.

References

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[2] Andersen et al, Journal of Solid State Chemistry 113 (1994) 320-326.