# Moderate-pressure Synthesis and Neutron Diffraction Study of New Metastable Oxides

Jose Antonio Alonso[a], Javier Sánchez-Benítez[b], Horacio Falcón[a], Maria Jesus Martínez-Lope[a], and Angel Muñoz[c]

[a] Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, E-28049 Madrid, Spain
[b] Centre for Science at Extreme Conditions and School of Engineering and Electronics, University of Edinburgh, King's Buildings, Mayfield Road, Edinburgh EH9 3JZ, UK
[c] Dpto. de Física Aplicada, EPS, Universidad Carlos III, Avda. Universidad 30, E-28911, Leganés-Madrid, Spain

Reprint requests to Prof. Dr. J. A. Alonso. E-mail: ja.alonso@icmm.csic.es

Z. Naturforsch. **61b,** 1507 – 1514 (2006); received July 6, 2006

We have synthesized two new series of metastable oxides, namely $RE\mathrm{Mn_2O_5}$ and $RE\mathrm{Cu_3Mn_4O_{12}}$ ($RE$ = rare earths) under moderate pressure conditions. A novel series of ferrimagnetic oxides has been obtained by replacing $\mathrm{Mn^{3+}}$ by $\mathrm{Fe^{3+}}$ in the parent $RE\mathrm{Mn_2O_5}$ compounds ($RE$ = Y, Dy, Ho, Er, Tm, Yb). The crystal structure has been studied by neutron powder diffraction (NPD); it contains chains of edge-linked $\mathrm{Mn^{4+}O_6}$ octahedra connected *via* dimeric groups of $\mathrm{Fe^{3+}O_5}$ square pyramids. The magnetic susceptibility and the thermal evolution of the NPD patterns reveal the onset of a ferrimagnetic structure below $T_C \approx 165$ K, characterized by the propagation vector $k = 0$. Immediately below $T_C$, the $\mathrm{Fe^{3+}}$ and $\mathrm{Mn^{4+}}$ moments lie in an antiparallel arrangement along the *c*-axis direction. At lower temperatures, the magnetic moment of the rare-earth cations also participates in the magnetic structure, adopting a parallel arrangement with the $\mathrm{Fe^{3+}}$ spins.

Some new derivatives of $\mathrm{CaCu_3Mn_4O_{12}}$ have been prepared at moderate pressures of 2 GPa by replacing $\mathrm{Ca^{2+}}$ by $RE^{3+}$ cations in the series $RE\mathrm{Cu_3Mn_4O_{12}}$ ($RE$ = Pr, Sm, Eu, Gd, Tb, Dy, Ho, Tm, Yb); the concomitant electronic injection leads to a substantial contribution to $T_C$. The crystal structures of the new materials were refined in the space group $Im\bar{3}$ from NPD data for the non-absorbing $RE$ cations. The unit cell parameters are considerably expanded with respect to $\mathrm{CaCu_3Mn_4O_{12}}$, as a result of the electronic injection. The r. t. magnetic structure displays a ferrimagnetic coupling between $\mathrm{Mn^{3+/4+}}$ and $\mathrm{Cu^{2+}}$ spins; at low temperatures there is an antiferromagnetic coupling of the $RE^{3+}$ moments with the Mn substructure, which substantially reduces the susceptibility and the saturation magnetization.

*Key words:* Perovskite Oxide, Colossal Magnetoresistance, Ferrimagnetic Oxide, Neutron Powder Diffraction, Unusual Oxidation States