## Effect of High-energy Milling on the Solid State Formation of Zinc Manganites $(Zn_xMn_{3-x}O_4, 0.5 \le x \le 1.5)$ from the System $ZnC_2O_4 \cdot 2H_2O$ -*n* MnCO<sub>3</sub> (*n* = 1, 1.5 and 2)

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By combination of TG/DSC and XRPD measurements it has been shown that zinc manganites form  $(Zn_xMn_{3-x}O_4 \text{ with } 0.5 \le x \le 1.5)$  starting from mixtures of zinc oxalate dihydrate and manganese carbonate subjected to mechanical activation by high energy milling. Solid solutions ZnO-Mn<sub>3</sub>O<sub>4</sub>-ZnMn<sub>2</sub>O<sub>4</sub> are the products obtained by the same experimental conditions, when starting from a physical mixture. Furthermore milling, besides changing the enthalpy of dehydration of zinc oxalate, induces a partial formation of amorphous Mn<sub>3</sub>O<sub>4</sub> at r. t. In particular ZnMn<sub>2</sub>O<sub>4</sub> can be prepared by annealing the milled mixture for 18 h at 650 °C while a temperature > 1000 °C is needed to prepare ZnMn<sub>2</sub>O<sub>4</sub> from a physical mixture. Finally, the calorimetric data suggest that the mechanism of the reaction is different in the two kinds of mixtures.

Key words: Zink Manganites, ZnMn<sub>2</sub>O<sub>4</sub>, Mechanical Milling, Simultaneous TG/DSC