Examination of nanostructured $Ca_{1-x}Gd_xMnO_3$ (x=0.05; 0.1; 0.15; 0.2) obtained by modified glycine nitrate procedure

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Introduction

Starting $Ca_{1-x}Gd_xMnO_3$ powders (x=0.05, 0.10, 0.15, 0.20) were prepared by combustion of solutions containing mixture of glycine with metal nitrates in their appropriate stoichiometric ratios. The so-obtained powders were annealed at the temperature of 850 ºC to 950 ºC for 10 minutes to produce final nanostructured samples with the average nanoparticle size of about 20 nm. Properties such as phase evolution, lattice parameters, chemical composition and magnetic properties were monitored by DTA, X-ray diffraction, SEM/EDS and magnetic measurements. The possibility of incorporation of Gd ions in the positions A of the perovskite structure was investigated by X-ray methods. Influence of Gd on unit cell volume of the perovskite compounds, occupation numbers and distances between atoms were analyzed by Rietveld refinement. Microstructure size–strain analysis was performed, as well. The results revealed that Gd entered positions A in the structure. It revealed that synthesized material is single phase of the orthorhombic-perovskite structure described by *Pnma* space group. Differential thermal analysis (DTA) revealed phase transition at ≈ 918 ºC. Magnetic measurements show that electron doping by Gd^{3+} ions substantially changes $CaMnO_3$ antiferromagnetic (AFM) behaviour. After introduction of Gd^{3+} ions, significant ferromagnetic (FM) component appears due to an emergence of double exchange interaction between Mn^{3+}-Mn^{4+} ions. This resulted in appearance of a low temperature plateau in field cooled (FC) magnetization as well as in emergence of hysteresis loop with the relatively high coercivity up to 2300 Oe.

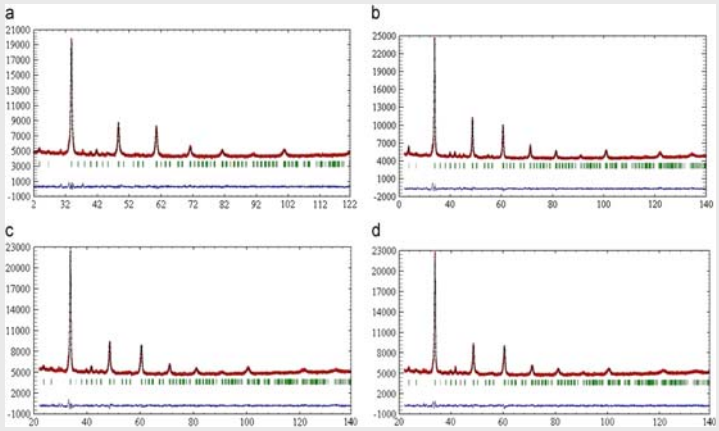

Fig. 3.Results of Rietveld refinement of the samples: (a)$Ca_{0.95}Gd_{0.05}MnO_3$; (b)$Ca_{0.9}Gd_{0.1}MnO_3$; (c)$Ca_{0.85}Gd_{0.15}MnO_3$; (d)$Ca_{0.8}Gd_{0.2}MnO_3$.

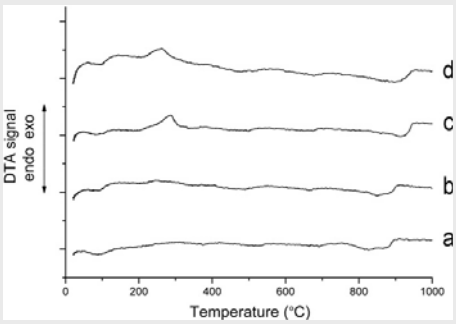

Fig. 1. DTA diagrams of synthesized $Ca_{1-x}Gd_xMnO_3$ (x=0.05; 0.1; 0.15; 0.2) powders: (a) $Ca_{0.95}Gd_{0.05}MnO_3$; (b) $Ca_{0.9}Gd_{0.1}MnO_3$; (c) $Ca_{0.85}Gd_{0.15}MnO_3$; (d) $Ca_{0.8}Gd_{0.2}MnO_3$.

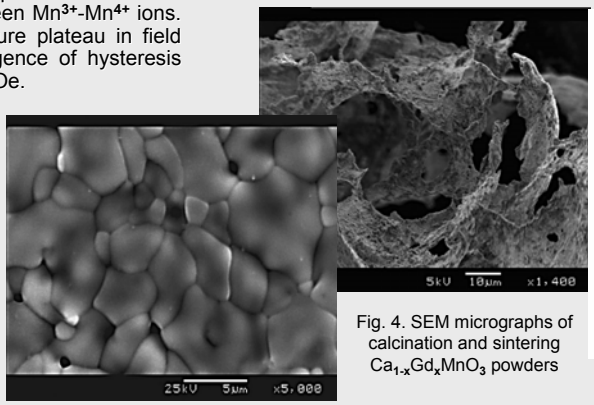

Fig. 4. SEM micrographs of calcination and sintering $Ca_{1-x}Gd_xMnO_3$ powders

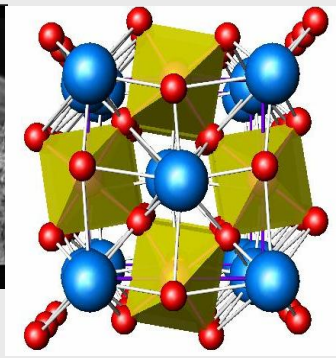

Fig. 5. Crystal structure of $Ca_{1-x}Gd_xMnO_3$.

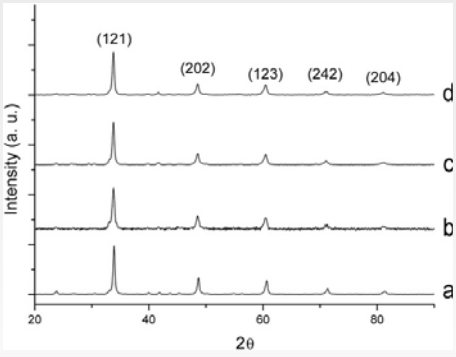

Fig. 2. XRD patterns of $Ca_{1-x}Gd_xMnO_3$ (x=0.05; 0.1;0.15;0.2) powders: (a)$Ca_{0.95}Gd_{0.05}MnO_3$; (b) $Ca_{0.9}Gd_{0.1}MnO_3$; (b)(c) $Ca_{0.85}Gd_{0.15}MnO_3$; (d) $Ca_{0.8}Gd_{0.2}MnO_3$.

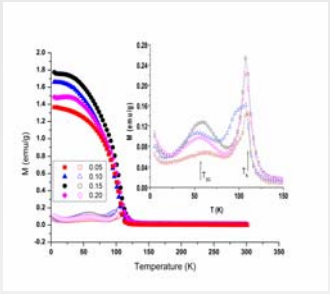

Fig. 6. Temperature dependence of ZFC (open symbols) and FC magnetization (full symbols) of $Ca_{1-x}Gd_xMnO_3$ in the magnetic field of 100 Oe. Inset: Details of ZFC magnetization; spin-glass transition and Néel temperature are denoted by arrows.

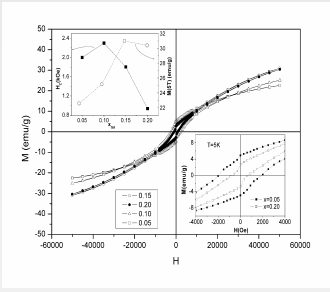

Fig. 7. Hysteresis curves of $Ca_{1-x}Gd_xMnO_3$ at 5K. Insets:below-details for x=0.05 and x=0.20; above-coercitivityvs.concentration.

Conclusion

Innovative materials processing techniques, such as the modified combustion process described here, seem to hold much promise for the preparation of technologically important perovskite $Ca_{1-x}Gd_xMnO_3$, with "x" ranging from 0.05 to 0.20, owing to the control over stoichiometry, homogeneity and purity.

A major breakthrough in the investigation of this family of oxides has resulted from improved structural descriptions, such as the composite structure model, $Ca_{1-x}Gd_xMnO_3$ and the application of the space group approach towards structure determination.

The Rietveld refinement showed that the obtained powders exhibit a precise stoichiometry compared to the tailored composition. It was found that the crystallite size lies in the nanometric range (26-35 nm). The calculated and measured lattice parameters and average bond distances increase with higher dopant concentration. Magnetic measurements showed that when concentration x increases, magnetization also increases due to the formation of ferromagnetic ordered clusters in antiferromagnetic $CaMnO_3$ matrix.

Acknowledgment

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