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ScienceDirect
Journal of the European Ceramic Society 27 (2007) 3873–3876
www.elsevier.com/locate/jeurceramsoc

The effect of manganese substitution to gallium on the physical properties of $MgGa_{2-x}Mn_xO_4$ spinel type ceramic thermistors

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Available online 2 May 2007

Abstract

Structural, electric and magnetic properties of $MgGa_{2-x}Mn_xO_4$ based spinel type ceramic compounds have been studied. The samples, prepared by a solid state reaction method, were characterized by X-ray diffraction (XRD), temperature dependent resistivity measurements $\rho(T)$ and magnetic measurements $M(T)$. Mono-phase solid solutions were obtained for all samples in which magnetic ions interact antiferromagnetically at low temperature. For all samples NTC type behaviour is evidenced. The sensitivity range of these thermistors can be tuned by varying Mn content. The values of the effective magnetic momentum (μ_{eff}) seem to confirm the well-known electron "hopping" mechanism of electrical conduction, which is believed to act in this kind of materials.

Keywords: Powders-solid state reaction; Spinels; Electrical conductivity; Magnetic properties; Thermistors

1. Introduction

Ceramic materials showing thermistor type behaviour are being used over 15 years in many applications related to the thermal control or fire detection (thermal sensors).[1] For these materials the temperature dependence of the resistivity being characterized by a high thermistor constants β ($\beta = E_a/k_B = 2727$–$4227\,^{\circ}C$ (3000–4500 K), where E_a is the activation energy and k_B is the Boltzmann constant).[2]

Electrical resistance dependence versus temperature is usually written as:

$$R_T = R_{T_O} \exp\left[\frac{\beta(T_O - T)}{T_O T}\right] \quad (1)$$

where (R_T) is the resistance for an absolute temperature (T), (β) the "beta constant" or "thermistor constant" and R_{T_O} is the resistance at a specified temperature, T_O.[3]

Beside perovskite-type ceramics, as we pointed out elsewhere,[4] the most often used materials for thermistor applications are spinel-like ceramics. Materials from this last system may have very attractive B values, have good thermal stability,[5] and may be readily sintered in air atmosphere.[6]

The electrical conduction in these materials is of hopping type and occurs when electrons jump between neighbour ions of the same type and having different valences.[7] The most used ions to play the described mechanism are the manganese ions.[8]

In this study, we substitute the gallium by manganese in $MgGa_2O_4$ compound, the resulted family of compounds being generally described using a formula like: $MgGa_{2-x}Mn_xO_4$.

The structural and morphological properties together with its electrical and magnetic behaviour were studied in order to better understand the effect of the substitution and its consequences on the electrical conduction mechanisms.

2. Experimental

The ceramic phases of $MgGa_{2-x}Mn_xO_4$ ($x = 0$, 0.1, 0.25, 0.50, 0.75 and 1) were synthesized in air in two steps. Intimate mixtures of, MgO, Mn_2O_3 and Ga_2O_3 (purity > 99.9%), were weighed in stoichiometric proportions and heated in alumina crucibles at 1100 °C for 24 h. The powders were then manually ground again, pressed into cylindrical pellets and sintered in air at 1500 °C for 2 h. In order to avoid as possible the manganese diffusion at high temperature, platinum supports were

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0955-2219/$ – see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.jeurceramsoc.2007.02.129

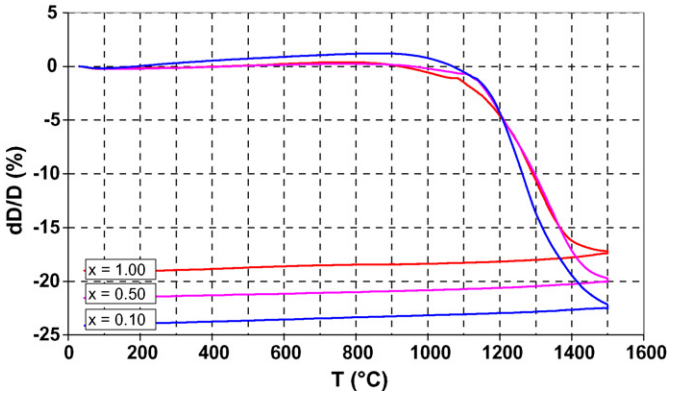

Fig. 1. The TMA analyses of $Mg(Ga,Mn)_2O_4$ samples, up 1500 °C in air atmosphere.

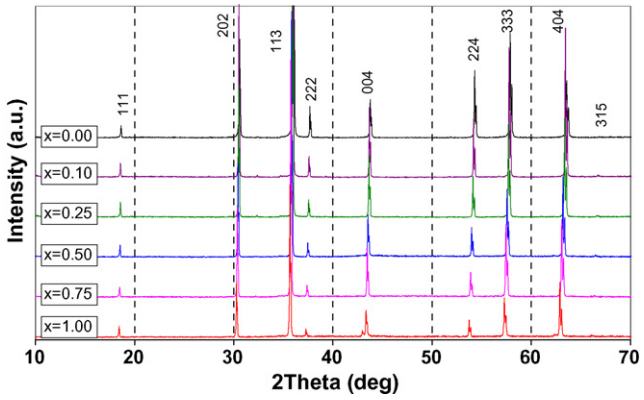

Fig. 2. The XRD patterns for $MgGa_{2-x}Mn_xO_4$ family of compounds.

used during the sintering process. The sintering temperature was determined using the thermo mechanical analyses (TMA) – *Setaram* 92 – and it was chosen as the temperature above which the speed of the shrinkage in the samples decreases (Fig. 1). The samples were heated and cooled in air by 200 °C/h.

For all our analyses the sintered cylindrical pellets were polished on the opposite sides in order to remove a few microns layer of the surface material which may be affected during the sintering process.

The X-ray diffraction (XRD) data have been recorded with a Philips X'Pert diffractometer (Cu Kα radiation). The pellet were analysed in bulk format. The diffraction patterns were treated by profile analysis, based on the Rietveld technique, using the JANA-2000 refinement program.[9]

For electrical measurements the disc shaped samples were painted on both sides with Pt paste. The platinum painted pellets were then fired for 1 h at 1000 °C under air, in order to fix the metallic electrode to the surface of the discs. The thermistor characteristics, resistance versus temperature [$R(T)$], were acquired in the temperature range of room temperature (RT) to 800 °C using a Princeton Applied Research Potentiostat equipment.

The magnetic properties were investigated using a SQUID magnetometer (*QUANTUM DESIGN*) in the temperature range of −268 °C to +77 °C (5–350 K). The measurements were performed in field cooled mode (FC), under a DC magnetic field of 0.1 T.

3. Results and discussion

After studying the shrinkage versus temperature evolution for the MMGO family of compounds we decided to sinter all the samples at 1500 °C in order to achieve the maximum densification for all our samples (Fig. 1).

The XRD studies confirm the structural similarity between all the family members (Fig. 2). The unit cell parameters and the space group are consistent with the $MgGa_2O_4$ spinel type[10] cubic structure ($F_{d\text{-}3m}$-S.G.—No. 227).[11] Small shifts in 2θ caused by the different sizes of the Ga and Mn cations can be remarked ($^{VI}R^{3+}_{Ga} = 0.62$ Å , $^{VI}R^{3+}_{Mn} = 0.65$ Å).[12] Thus, the unit cell parameter, a, evolutes quasi linearly versus substitution level x, increasing from $a = 8.2780(2)$ to 8.3645(3) Å by the increase of manganese content (Fig. 3). This fact confirms the solubility of $MgMn_2O_4$ in $MgGa_2O_4$, the resulting mixture generating solid solutions up to $x = 1$. Nevertheless, at this highest substitution level ($x = 1$), a secondary phase appears (2θ about 43°) which seems to be MgO—unreacted raw material.

Electrical measurements versus temperature were performed on the range of room temperature (RT) to 800 °C. The DC electrical resistance R was measured and the values were used to calculate the material resistivity using the formula

$$R = \frac{\rho l}{S}, \tag{2}$$

where ρ is the resistivity, l and S being the thickness and the side surface of the pellet, respectively.

Thermistor type behaviour, with negative temperature coefficient (NTC), can be clearly remarked for all studied samples (Fig. 4). The value of the resistivity is strongly influenced by the manganese content.

The thermistor constants, β, were calculated using the formula (1) on different thermal ranges:

$$\beta = \frac{\ln R_T - \ln R_{T_O}}{1/T - 1/T_O} \tag{3}$$

We decided to calculate these values for each 100° in order to avoid the effect of nonlinearity of the curves (Fig. 5). $\beta_{100/200}$ denotes the thermistor constant calculated on the thermal range from 100 to 200 °C, etc. On the sensitivity regions we have

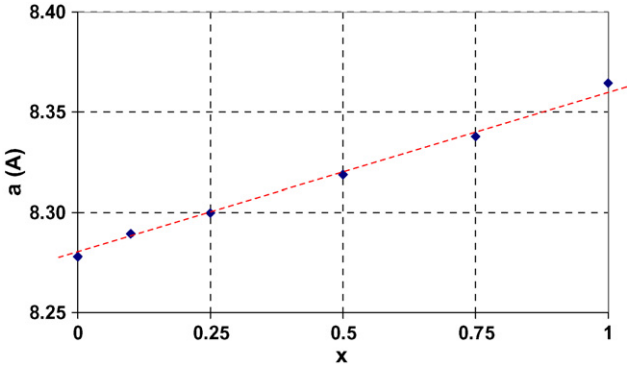

Fig. 3. The lattice parameter, a, evolution vs. Mn content in $MgGa_{2-x}Mn_xO_4$ solid solutions.

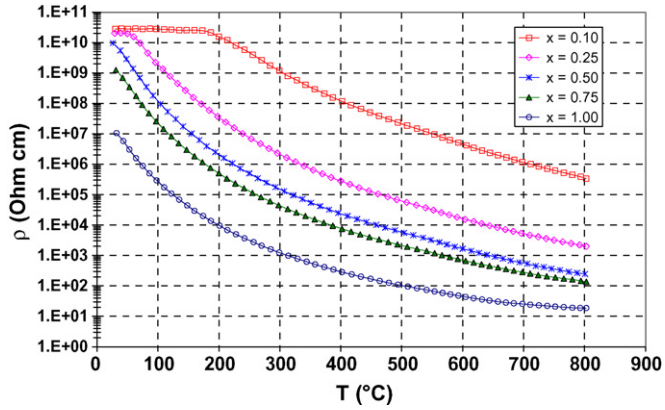

Fig. 4. Resistivity vs. temperature plots for $MgGa_{2-x}Mn_xO_4$ samples at different levels of substitution by manganese.

obtained values of β higher than 5727 °C (6000 K) for a wide range of temperature, making these materials to be extremely promising for thermal detection applications.

From molar magnetic susceptibility, χ_M, versus temperature plots the effective magnetic moments, μ_{eff}, were calculated by fitting the measured data on the paramagnetic region (for temperatures higher than −173 °C (100 K)) using a Curie–Weiss function like:

$$\chi_M = \chi_O + \frac{C}{T - \Theta} \quad (4)$$

where χ_O is the offset due to the sample holder, Θ the Weiss temperature and C is the Curie constant which was approximate with $C \approx 0.1254 \times \mu_{eff}^2$, μ_{eff} being the *total* effective magnetic momentum per nominal formula.

For a better visual comparison we have plotted the measured data and the fitted points of the molar magnetic susceptibility of each sample using the inverse values of this versus temperature (Fig. 6).

The calculated values of the effective magnetic moments and the corresponding Curie molar constants together with the values of the Weiss negative temperatures are shown in Table 1. The negative values of the Weiss constants allow supposing

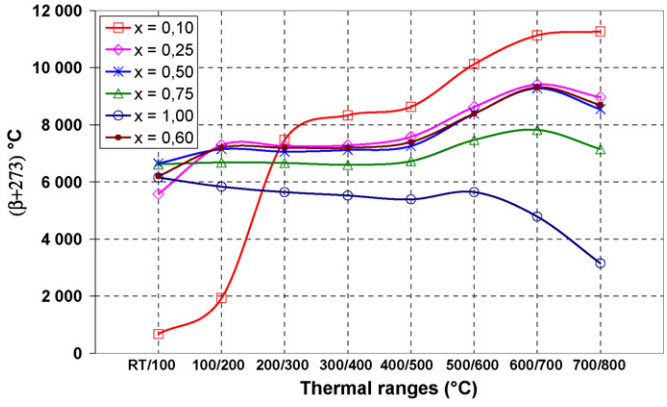

Fig. 5. The evolution of β parameter (the thermistor constant) calculated on different thermal ranges for $MgGa_{2-x}Mn_xO_4$, according to different values of x. RT/100 denotes the thermal range from room temperature to 100 °C, etc.

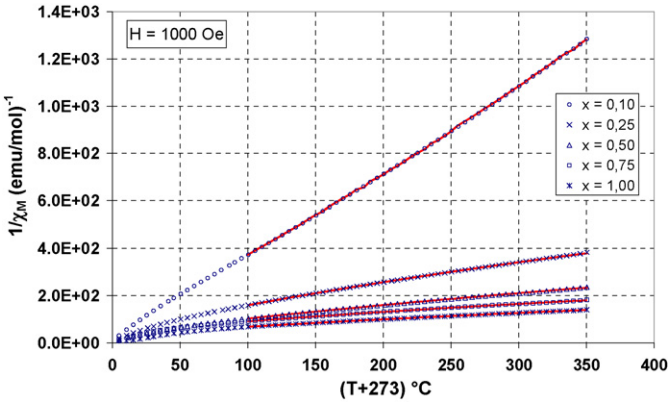

Fig. 6. The reciprocal magnetic molar susceptibility dependence vs. temperature for $MgGa_{2-x}Mn_xO_4$ samples, measured in field cooled mode, under a DC applied field 1000 Oe. The lines above −173 °C (100 K) show the fitted points using χ (T).

Table 1
Some magnetic properties of $MgGa_{2-x}Mn_xO_4$ samples, measured in 1000 Oe DC magnetic field

x	C_M [emu/mol]	μ_{eff} [μ_B] ±0.02	Θ [°C]
0.10	0.34	5.20	−293.0
0.25	0.76	4.92	−308.2
0.50	1.33	4.61	−324.6
0.75	1.67	4.21	−350.6
1.00	2.31	4.29	−352.4

that magnetic ions (manganese) interact at low temperature by exchange mechanisms of antiferromagnetic nature. Regarding the μ_{eff} values one can observe a decreasing tendency with the increase of manganese content, x. For the sample with the lowest Mn content $\mu_{eff} = 5.20\ \mu_B$. This value seems to be close to that corresponding to Mn^{3+} ions ($\mu^{3+}_{eff\,Mn} = 5.9\ \mu_B$) however the presence of Mn^{2+} ions ($\mu^{2+}_{eff\,Mn} = 5.9\ \mu_B$) should be supposed. For the sample with higher content of manganese the μ_{eff} tends to decrease towards the value corresponding to Mn^{4+} ions, suggesting an increase of their proportions. This fact allows supposing the higher the manganese content the higher the Mn^{3+}–Mn^{4+} number of pairs. Thus, magnetic measurements seem to confirm electrical conduction behaviour of this ceramics.

4. Conclusion

NTC type behaviour was revealed for this family of compounds with tunable values of the resistivity for a given temperature by varying the manganese content.

The high values of the thermistor constant, β, on a wide range of temperatures make these compounds very promising for NTC type, high temperature thermistor applications, with tuneable range of sensitivity.

Acknowledgement

Authors would like to thank the *THERMOCOAX* Company for supporting this research project.

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