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Properties of a CaCu_{3-x}Mn_{4+x}O₁₂ system synthesized via a solid-state reaction

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A single-phase CaCu₃Mn₄O₁₂ electroceramic had been prepared via solid state reaction. The preparation conditions have been optimized using a thermogravimetric analysis (TGA) technique. Material formation under the reported conditions have been confirmed by X-ray diffraction (XRD) studies. The results show that the formation of CaCu₃Mn₄O₁₂ started at 600 °C with the presence of secondary phases and was completely formed at 850 °C. Following a similar procedure, then CaCu_{3-x}Mn_{4+x}O₁₂ (where x = 0, 0.1, 0.3, 0.5, 0.7 and 0.9) was sintered at 1090 °C for 24 hours. The microstructure of all CaCu_{3-x}Mn_{4+x}O₁₂ was analysed using field emission scanning electron microscopy (FESEM). The relative density of all samples is higher than 84%. The magnetic hysteresis, (*M*(*H*)) loops, were measured at room temperature which show that the values of saturation magnetization (*M_S*) and remanence (*M_r*) increase, while the coercitivity (*H_C*) decreases with an increase of the relative density of CaCu_{3-x}Mn_{4+x}O₁₂. This behavior proved that CaCu_{3-x}Mn_{4+x}O₁₂ samples are soft magnetic materials. The coercitivity decreases with an increase in the value of x.

Key words: Solid state reaction, Thermal analysis, X-ray diffraction, Microstructure, Soft magnetic.

Introduction

Various physical properties of several manganese perovskite materials have recently been under very active investigation because of the interesting interpay between their magnetic, electronic and structural properties [1-4]. Most of these phenomena are related to magnetic, charge and orbital orderings of interpenetrating sublatices of Mn^{3+} and Mn^{4+} ions in the materials. One of the very interesting classes of perovskite-type manganite materials is one CaCu_{3-x}Mn_{4+x}O₁₂ family. The interest in this group of compounds has grown since the discovery of low-field magnetoresistance in CaCu₃Mn₄O₁₂ [4-9]. CaCu₃Mn₄O₁₂ is also interesting in terms of its fundamental physical properties. The crystal structures, magnetic and electronic properties of the CaCu_{3-x}Mn_{4+x}O₁₂ family compounds for ($0 \le x \le 3$) were also studied by Zeng *et al.* [4].

CaCu₃Mn₄O₁₂ is mainly synthesized via chemical methods such as a co-precipitation technique [4-9]. These chemical methods are very sensitive to the preparation conditions such as stirring speed, time and temperature of the solutions. Complicated procedures have been manipulated with expensive raw materials to obtain precursors. This method is also complex and pressure dependent [4-6]. Therefore, a study following a solid state route with high energy ball milling was applied in this research to reduce the synthesis cost, produce a higher yield which can be done at lower temperature.

To our knowledge, there is no systematic study on the microstructure of the $CaCu_{3-x}Mn_{4+x}O_{12}$ family. Similarly, there is no report published on the magnetic properties (hysteresis loops) of sintered $CaCu_{3-x}Mn_{4+x}O_{12}$. Therefore, it is important to have information about the influence of the sintering conditions on the magnetic properties correlated to the microstructural evolution of the $CaCu_{3-x}Mn_{4+x}O_{12}$ samples.

Materials and Method

Stoichiometric CaCu₃Mn₄O₁₂ was prepared by mixing CaCO₃ (99.9% Aldrich), CuO (99.9% Aldrich) and MnO₂ (99.9%, Merck). A sample from this mixture was subjected to thermogravimetry (TG) and differential thermal analysis (DTA) using a Linseis L80/81 simultaneous thermal analyzer at a heating rate of 10 °C minute⁻¹ in air to determine the possible reaction temperature for the formation of the CaCu₃Mn₄O₁₂ phase. The remaining mixture was calcined from 500 °C to 1000 °C for 12 hours. The phase developments of the calcined powders were examined by XRD using a Bruker D8 Advance with CuK_{α} radiation. The CaCu_{3-x}Mn_{4+x}O₁₂ (where x = 0, 0.1, 0.3, 0.5, 0.7 and 0.9) compositions were prepared with the same technique and calcined at 850 °C for 12 hours. The calcined powders were uniaxially pressed into pellets (13 mm in diameter and 2 mm in thickness) and sintered at 1090 °C for 24 hours. The morphology of the sintered samples was investigated by field emission scanning electron microscopy

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(FESEM) using a Leo Supra 35VP system. Magnetic properties were investigated with a high field vibrating sample magnetometer (VSM) system in an applied field up to 25 kOe at room temperature.

Results and Discussion

A TGA pattern for CaCu₃Mn₄O₁₂ is shown in Fig. 1(a). Major weight losses of the sample occurs at temperatures ~665 and 750 °C (points A and B), respectively. These are attributed to intermediate reaction stages leading to new compound formation [10]. Subsequent heating is accompanied by a progressive weight loss followed by a gradual loss of weight until saturation is attained at a temperature 1000 °C onwards. At this stage, the final compound may have been formed. The observation recorded in the TGA curve is found to be in close agreement with a DTA pattern (Fig. 1(b)). The removal of the water content in the material appears to be an endothermic process as indicated by point C in the DTA pattern. The presence of a small exothermic peak in the DTA pattern at point D (598 °C) is attributed to intermediate reaction steps among the precursor materials leading to the formation of a compound at a stage where weight loss attains a level of saturation. This thermal analysis indicates that a calcination temperature of about 600 °C is suitable for preparing a CaCu₃Mn₄O₁₂ sample



Fig. 1. Thermal analysis pattern of $CaCu_3Mn_4O_{12}$ (a) TGA and (b) DTA.



Fig. 2. XRD patterns from $CaCu_3Mn_4O_{12}$ samples at different calcination temperatures from uncalcined, and 500 °C to 1000 °C ($\Delta = CaCu_3Mn_4O_{12}$, * = MnO₂, # = CaCO₃, • = CuO).

using a solid-state technique.

XRD patterns for an uncalcined sample and samples calcined at 500 °C to 1000 °C, are shown in Fig. 2. The results show that the formation of $CaCu_3Mn_4O_{12}$ begins at 600 °C (as expected based on the thermal analysis). The $CaCu_3Mn_4O_{12}$ was formed completely at 850 °C. The peak positions are in good agreement with the values given in ICDD data (072-0401).

Fig. 3 shows the diffractograms of $CaCu_{3-x}Mn_{4+x}O_{12}$ (where x = 0, 0.1, 0.3, 0.5, 0.7 and 0.9) samples. It is obvious that the trend of the diffraction patterns is shifted to the right hand side which indicates that a there is crystal distortion occurred. Table 1 shows that the values of 2 θ increases with an increase in the x value. A similar trend was also reported by Zeng *et al.* [4] and Przenioslo *et al.* [7-9]. They have reported about the changing of CaCu_{3-x}Mn_{4+x}O₁₂ and CaCu_xMn_{3-x}Mn₄O₁₂ systems from a cubic to a trigonal structure when x = 3 and 0 (i.e. CaMn₇O₁₂).

FESEM micrographs for fractured and thermally etched surfaces of the CaCu_{3-x}Mn_{4+x}O₁₂ samples are shown in Fig. 4. More porosity can be observed in samples with larger x values. The microstructures for samples with x = 0 to 0.3 have less porosity and smaller grains.

The effect of the microstructure on the bulk densities of the sintered $CaCu_{3-x}Mn_{4+x}Mn_4O_{12}$ is obvious i.e. for x = 0, 0.1, 0.3, 0.5, 0.7 and 0.9, the bulk densities were 4.837, 4.841, 4.853, 4.822, 4.757 and 4.744 g/cm³, respectively.



Fig. 3. XRD patterns from $CaCu_{3-x}Mn_{4+x}O_{12}$.

Table 1. XRD pattern from $CaCu_{3\rightarrow x}Mn_{4+x}O_{12}$ (x = 0, 0.1, 0.3, 0.5, 0.7 and 0.9)

CaCu ₃ Mn ₄ O ₁₂		$CaCu_{3-x}Mn_{4+x}O_{12}$						
Intensity (I)	2θ degree	$\mathbf{x} = 0$	x = 0.1	x = 0.3	x = 0.5	x = 0.7	x = 0.9	
100%	35.04	35.55	35.49	35.59	35.67	35.79	35.87	
100%	62.82	62.91	62.98	63.05	63.35	63.52	63.59	
60%	30.21	29.92	30.25	30.30	30.33	30.51	30.59	
60%	39.35	38.81	38.90	38.93	38.95	39.11	39.18	
60%	43.25	43.69	43.77	43.79	43.84	43.88	43.93	
60%	46.91	47.41	46.46	47.52	46.71	46.91	48.08	
10%	53.66	53.23	53.28	53.31	54.02	54.20	54.28	
10%	59.86	59.85	59.94	60.08	60.15	60.71	61.13	



Fig. 4. Field emission scanning electron micrographs of $CaCu_{3-x}Mn_{4+x}O_{12}$ sintered at 1090 °C. (a) x = 0, (b) x = 0.1, (c) x = 0.3, (d) x = 0.5, (e) x = 0.7, (f) x = 0.9.

Therefore, their relative density (theoretical density for $CaCu_3Mn_4O_{12}$ is 5.620 g/cm³) reduces from 86.1% to 84.4%.

The room temperature hysteresis loops (M(H)) for CaCu_{3-x}Mn_{4+x}O₁₂ samples are shown in Fig. 5. The graphs indicate that the values of saturation magnetization (M_s) and remanence (M_r) increase, while the coercitivity (H_c) decreases with the density of CaCu_{3-x}Mn_{4+x}O₁₂. The trend of these magnetic properties follows the changes of their respective microstructure and density as can be seen from Fig. 6 and Table 2. An increasing tendency of these magnetic parameters with densification (or porosity reduction), is clearly noted. These results can be understood when the pores in the grains are considered to act as pinning sites of domain walls, which disturb domain wall movements thus causing a demagnetizing field effect. Moreover, densification leads to a larger number of atoms contributing to the magnetic moment per unit volume [11].

The variations of coercitivity with the final relative density are presented in Fig. 6. It is obvious that for the $CaCu_{3-x}Mn_{4+x}O_{12}$ samples with x = 0, 0.1 and 0.3, their coercitivity decreases with an increase in the relative density. However for x = 0.5, 0.7 and 0.9, their coercitivity increases with increasing relative density. These results show that H_C is independent of the relative density. This relationship between coercitivity and density is in agreement with the research done by Igarashi and Okazaki [11]. They analyzed the porosity and grain size effects on the magnetic properties of NiZn ferrites. They also studied samples with high porosities (2-40%) and verified an independence of coercitivity with density and remanence with grain size. They examined groups of specimens with controlled porosities and grain sizes, which allowed them to discuss separately the effects of each parameter on the magnetic properties.

Conclusion

The present study reports the result of an investigation on the microstructure and magnetic properties of $CaCu_{3-x}Mn_{4+x}O_{12}$ (where x = 0.1, 0.3, 0.5, 0.7 and 0.9) compounds which



Fig. 5. Room temperature hysteresis loops from $CaCu_{3-x}Mn_{4+x}O_{12}$ ceramics with (a) x = 0, (b) x = 0.1, (c) x = 0.3, (d) x = 0.5, (e) x = 0.7, and (f) x = 0.9.



Fig. 6. Relationship between coercitivity (H_C) and relative density with different x values.

were synthesized via a solid state technique. DTA/TGA analyses show that a single-phase CaCu₃Mn₄O₁₂ can be formed above 600 °C, which was further confirmed by

 Table 2. Summary of magnetic properties for CCMO samples obtained at +25 kOe

x value	Ms	M _r	H _c	Relative density
	(emu/g)	$(emu/g)(10^{-2})$	(kOe)	(%)
0	0.760	1.46	0.277	86.11
0.1	0.747	1.36	0.274	86.17
0.3	0.502	1.29	0.244	86.38
0.5	0.680	1.33	0.259	85.83
0.7	0.667	1.67	0.267	84.67
0.9	0.823	1.18	0.273	84.43

XRD diffraction. XRD showed the diffraction pattern was shifted to the right hand side which showed distortion in their crystal structures. The results show that $CaCu_3Mn_4O_{12}$ is a soft magnetic material which has high values of saturation magnetization, low remanence and a coercitivity field. An increasing tendency for the saturation and remanent magnetization with the final relative density was observed.

This result was attributed to the reduction in the demagnetizing fields in the grains, besides an increase in the number of dipoles per unit volume. The observed coercitivity variations could be related to the microstructural evolution of the samples. It remains constant for samples with the values of saturation magnetization (M_s) and remanence (M_r) increasing, while the coercitivity (H_c) decreases with density.

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