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Synthesis, characterisation and study of magnetocaloric effects (enhanced and reduced) in manganate perovskites



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ABSTRACT

The effect of the A-site dopant ionic radii on the observed magnetocaloric effect (MCE) exhibited by three different families of manganese-based perovskites was investigated using both induction heating and SQUID magnetometry measurements. The doped perovskites $La_{1-x}Sr_xMnO_3$ (LSMO), $La_{1-x}Ca_xMnO_3$ (LCMO), and $La_{1-x}Ba_xMnO_3$ (LBMO) (x = 0.25, 0.35, 0.4) were prepared using a modified peroxide sol-gel synthesis. This method has not been previously used for the synthesis of LCMO or LBMO. Structural characterisation of the agglomerates of magnetic nanoparticles (MNP) for each material was carried out using SEM, XRD and IR spectroscopy. Magnetic heating was observed for materials with larger A-site dopant radii relative to La^{3+} ; LSMO40 and LBMO40, with average SARs obtained of 51.5 Wg⁻¹_{Mn} and 33.8 Wg⁻¹_{Mn} respectively. However, reduced magnetic heating effects were observed for smaller A-site dopant radii relative to La^{3+} (LCMO). In fact, the calculated Specific Absorption Rate for LCMO40 of 14.72 Wg⁻¹_{Mn} is half that of the blank.

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1. Introduction

Mixed metal oxides with a perovskite-type crystalline structure are of interest in a variety of fields. Investigations have been conducted into areas of application such as fuel cell catalysis [1], superconductors [2], dye-sensitized solar cells (DSSCs) [3], and mediators in hyperthermia treatment for cancer [4]. The physical and chemical properties of these materials depend on their perovskite crystal structure. The ideal metal oxide perovskite structure is of the type ABO₃ with cubic geometry as shown in Fig. 1(b). In this structure, the A site cation (La^{3+}) is larger than the central B site cation (Mn^{3+}) and it occupies the corners of the unit cell. This structure can be modified through the substitution of ions, or doping. By controlling the doping, one can fine tune some physical and chemical properties of the perovskites to target a particular application.

Fig. 1(c) shows the doping of the ABO₃ crystal structure with an A-site cation larger than La^{3+} such as Sr^{2+} in the case of the $La_{1-x}Sr_xMnO_3$ (LSMO) family of perovskites. Their structures have been previously investigated for a variety of compositions [5–8]. In this instance, La^{3+} or Sr^{2+} ions occupy the A-site and either Mn^{3+} or

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Mn⁴⁺ occupies the B-site. As found in a previous work by this group, an increase of the relative weight percentage of the orthorhombic (Pnma) crystalline phase is observed by increasing the strontium dopant in the LSMO synthesised using a modified peroxide sol-gel method [8]. This structural change upon doping can cause a huge variation of the Curie temperature (T_c). For example, increasing the dopant from x = 0.1 to 0.2 increases the T_c from -13 °C to 77 °C [9]. This change in T_c with structure meant that LSMO at a variety of dopant levels exhibited enhanced magnetic heating properties compared with the parent compound [8].

Fig. 1(a) and (c) shows the effect of substituting the A-site cation, La^{3+} (cationic radii of 1.36 Å) with smaller (Ca^{2+}) or larger (Sr^{2+} or Ba^{2+}) cations (cationic radii of 1.34, 1.44 or 1.61 Å respectively) [10] on the structure of the parent perovskite unit cell (1b). As with LSMO, the substitution of a cation for one of differing size (either larger or smaller than La^{3+}) will result in a distortion of the crystal structure. This distortion leads to the alteration of bond angles and bond lengths, which in turn affects the magnetic properties of the material (such as the magnetic susceptibility and magnetocaloric effect).

The magnetic properties of manganates arise from a double exchange mechanism [11]. The strength of the mechanism is determined by two main factors: the oxidation state of manganese and the bond angle formed by the manganese cations and the



Fig. 1. The effect of doping with smaller (a) and larger (c) A-site cations on the ideal structure of pseudo-cubic perovskites of the type ABO₃ (b).

oxygen anion between them. In particular, the double exchange mechanism is most prominent in manganates where the angle is flat and there is maximal overlap of the Mn³⁺-O^{2–}-Mn⁴⁺ bonding dand p- orbitals [11]. The magnetic properties of interest in this work are magnetic susceptibility and magnetocaloric effect (MCE). The origin of the MCE is ultimately associated with the dependence of the magnetic entropy on both temperature and external magnetic field. As a consequence, the magnetic nanoparticles can heat up or cool down in response to a change of the field. By using an alternating magnetic field and tuning its frequency appropriately, one can also exploit a resonance in the (complex) magnetic susceptibility to maximise the heat dissipated during the magnetic process.

When a magnetic field is applied to a ferromagnetic material, three types of dissipative magnetic response are relevant for nanoparticles: Neél rotations, Brownian rotations or hysteresis. Neél rotations are internal rotations where there is realignment of magnetic moments within a particle under the influence of an external magnetic field with respect to the crystal structure. The excess energy absorbed during the realignment is dissipated through an internal friction mechanism. Brownian rotations are external rotations whereby the entire molecule rigidly realigns with the external magnetic field, causing friction between the molecule and the surrounding medium. These first two mechanisms are especially relevant for single-domain nanoparticles. When several magnetic domains are present, the material exhibits the typical 'hysteresis loop' with the energy dissipated in the process proportional to the loop area [12]. The three dissipative response mechanisms of a nanoparticle are associated with an overall positive change of the particle temperature (enhanced magnetocaloric effect). In the right range of temperatures, the heat generated can induce a first order phase transition associated with a change of magnetic (e.g. ferromagnetic to paramagnetic) and crystal structure (e.g. orthorhombic to rhombohedral) [13,14]. In this instance, the latent heat necessary for the phase transition will not be dissipated and the overall temperature will increase to a smaller extent (reduced magnetocaloric effect). This may even manifest as an apparent drop in temperature compared to the blank.

We are particularly interested in developing materials which exhibit a positive MCE with enhanced magnetic heating to develop more effective mediators for magnetic fluid hyperthermia (MFH). MFH is a targeted treatment for cancer whereby a magnetic material in the presence of an alternating magnetic field causes a local temperature increase in the mild hyperthermia range of 41– 46 °C. In the mild hyperthermia range, cancerous tissue will be selectively damaged over healthy tissue. LSMO has already been investigated as a suitable potential mediator for MFH [5–8], but to the knowledge of the authors, little consideration has been given to other perovskite manganates.

In our previous work [8] we identified links between the crystal structure changes (as a result of the dopant concentration on the Asite of LSMO) and the magnetic properties of the resulting nanoparticle clusters. In this work we aim to investigate the effect of the A-site doping radii on the observed MCE of perovskite manganates as a means to improving material design. To this effect, various compositions (x=0.25, 0.35 and 0.4) of the manganate perovskites La_{1-x}Sr_xMnO₃ (LSMO), La_{1-x}Ca_xMnO₃ (LCMO), and La_{1-x}Ba_xMnO₃ (LBMO) were prepared via a modified peroxide sol-gel synthesis [15–17]. This method has not been employed in the synthesis of LCMO or LBMO before. However LSMO has been prepared using this method as described in our previous work [8]. The use of a sol-gel synthesis is advantageous as it not only yields agglomerates of nanoparticles which are more appropriate for *in-vivo* MFH [6], but the variation in crystallite size with this type of synthetic approach will influence the contribution of magnetic hysteresis to the magnetocaloric effect [7]. The structural modifications to the perovskite structure caused by replacing La³⁺ with various dopants (Ca²⁺, Ba²⁺ or Sr²⁺), along with the subsequent effects on the magnetic properties (MCE, magnetic susceptibility and hysteretic losses) of the material are investigated in this work. Alkaline earth metal cations $(Ca^{2+}, Ba^{2+} \text{ or } Sr^{2+})$ were chosen as dopants so as to investigate the effect of cationic radii on the crystal structure, rather than the Mn³⁺/Mn⁴⁺ ratio.

We have chosen to observe the MCE directly from induction heating experiments. The observations are supported by direct magnetic measurements to better represent potential applications. Our approach is also motivated by Phan et al. who highlight the Download English Version:

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