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Combustion synthesis of sodium-substituted lanthanum manganites

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The sodium-substituted lanthanum manganites $La_{1-x}Na_xMnO_3$ ($x = 0.0$–0.4) were synthesised in air by self-propagating high-temperature synthesis using only solid oxidizers.

Sodium-doped lanthanum manganites have been extensively studied due to their colossal magnetoresistance (CMR) effect near the Curie temperature.[1,2] Conventional methods to prepare these materials involve repeated heating and milling operations at 1300–1500 K with mixtures of La_2O_3, Na_2CO_3 and MnO_2($MnCO_3$).[3,4] It has also been obtained by sol-gel (Pechini method) and propellant synthesis,[5] as well as by the thermal decomposition of appropriate metal salt precursors.[1] Pure and alkaline-earth-substituted lanthanum manganites have been synthesised by self-propagating high-temperature synthesis (SHS) in air using different types of solid oxidizers.[6,7] These combustion syntheses involve a rapid reaction of the starting green mixture in the combustion wave – with the product being formed directly in the reaction in a matter of seconds. Here we report the SHS of the sodium-substituted lanthanum manganites $La_{1-x}Na_xMnO_3$ ($0 \le x \le 0.4$). The effect of internal solid oxidizers was explored. The reaction pathway was investigated using thermogravimetry and differential thermal analysis (TGA/DTA), as well as by a very sensitive thermal imaging method. This method is based on the continuous registration of the whole combustion process by using a highly sensitive IR camera and software of the MIKRON Instrument (M9100 Pyrovision Series – Imaging Pyrometer).[6]

Combustion processes were carried out in air with mechanically pre-ground mixtures of La_2O_3, Na_2O_2, Mn and $NaClO_4$. All the reagents were combined in stoichiometric quantities according to the reaction:

$$(1-x)La_2O_3 + xNa_2O_2 + 2Mn \rightarrow 2La_{1-x}Na_xMnO_3 \qquad (1)$$

$$(1-x)La_2O_3 + xNa_2O_2 + 2Mn + jNaClO_4 \rightarrow 2La_{1-x}Na_xMnO_3 + jNaCl \qquad (2)$$

$x = 0, 0.05, 0.1, 0.2, 0.3, 0.4$

j values were adjusted to the oxygen stoichiometry

The SHS reaction is driven by the exothermic oxidation of manganese metal. Sodium peroxide and perchlorate are the internal oxidizing agents in the reaction. Lanthanum oxide acts as a heat sink. This starting material (~1–2 g) was pressed isostatically with a pressure of 1 *t* into pellets with a diameter of 13 mm and a thickness of 2 mm. A REKROW RK-2060 Micro Torch (UK) special device was used to ignite the pellets from the lateral surface. This promoted an orange-yellow pro-

Table 1 Lattice parameters, specific surface area d/m^2 g^{-1}, Curie points T_C, Na contents (wt%) and room temperature magnetic susceptibility χ/cm^3 g^{-1} for pure and sodium-substituted lanthanum manganites $La_{1-x}Na_xMnO_3$ produced by SHS. The magnetic parameters were recorded in an external field of 10 kOe.

Compound	Unit cell parameters				T_C/K	χ/10^{-5} cm^3 g^{-1}	d/m^2 g^{-1}	$Na_{green\ mixture}/Na_{final\ products}$ (wt%)
	a/Å (±0.004)	b/Å (±0.004)	c/Å (±0.004)	α/°				
$LaMnO_3$	5.537	5.737	7.687		176	3.35	4.7	—
$La_{0.95}Na_{0.05}MnO_3$	6.561			92.99	153	5.92	0.8	0.49/0.45
$La_{0.90}Na_{0.10}MnO_3$	6.558			92.82	218	6.22	0.7	1.00/0.96
$La_{0.80}Na_{0.20}MnO_3$	6.555			92.93	263	6.49	0.7	2.10/2.02
$La_{0.70}Na_{0.30}MnO_3$[a]	6.552			92.66	283	6.77	1.1	3.33/3.19
$La_{0.60}Na_{0.40}MnO_3$[a]	6.549			92.72	286	12.78	0.8	4.70/4.49

[a] Main phase.

pagation wave, which traveled at ~1.0 mm s^{-1} and T_{comb} = = 1350–1400 K. The reaction products were ground and, in case of reaction (2), triturated with water to remove the traces of sodium chloride. All of the final powder products were analysed by X-ray powder diffraction, Raman spectroscopy, vibrating sample magnetometry (VSM) and scanning electron microscopy/energy dispersive analysis by X-rays (SEM/EDAX). The phase formation reactions were studied step-by-step by TGA/DTA on a SETARAM TAG24S24 instrument (France). Alkaline metal contents were also determined by AAS-3 absorption spectrometer (Germany) at λ = 589.0 nm by spraying the sample solution in $AgNO_3$ to the air–acetylene flame.

Rare-earth manganites, which contain only trivalent metals, are very attractive systems for the investigation of isovalent and non-isovalent substitutions. In particular, the replacement of lanthanum by sodium or other alkali metal and its effect on the structural, magnetic and other properties have been reported. X-ray powder diffraction data showed the single-phase orthorhombic perovskite structure were produced in the SHS reaction for pure lanthanum manganite ($LaMnO_3$) (Table 1). The diffraction patterns indexed well and agreed with published data for conventionally prepared materials. X-ray diffraction data showed that single phase orthorhombic manganites were produced for $x = 0$ while a low degree of alkaline substitution in $La_{1-x}Na_xMnO_3$ ($x = 0.05$) leads to a lattice transformation from orthorhombic to rhombohedral. The unit cell volume decreased with sodium substitution. This is related to a partial non-isovalent substitution of La^{3+} (ionic radius of 0.106 nm) from the rare-earth sites of the perovskite-type structure by Na^+ (ionic radius of 0.092 nm). The substitution of sodium in the structure partially oxidizes the manganese to Mn^{4+} to maintain a charge balance.

The specific surface area of undoped SHS lanthanum manganite is 4.7 m^2 g^{-1}; much higher than the sodium doped materials (0.7–1.1 m^2 g^{-1}). The EDAX spot analysis of the washed products showed the expected Na:La:Mn ratios and notably no chlorine. FT-IR spectra for a pure material ($LaMnO_3$) in the range of 400–4000 cm^{-1} show two main intense absorption bands at ~640 and ~570 cm^{-1}. These two bands in the range of 1000–400 cm^{-1} shift strongly for substituted materials. For Na-substituted materials even for low Na concentrations a strong shift of these two bands: for $LaMnO_3$, 640 and 575 cm^{-1}; for $La_{0.95}Na_{0.05}MnO_3$, 580 and 510 cm^{-1}. It may be explained in terms of the modification of exchange interaction between the Mn atoms with non-isovalent substitution of lanthanum by sodium. With an increase in x in this system, the amount of Mn^{4+} increases to ensure valency compensation. The ν_{Mn-O} shifts are occurring due to deformation in the structure of Mn–O polyhedrons. Positions of two last bonds are practically unchanged until $x = 0.4$.

Pure rare-earth manganites, as well as ferrites and chromites (RMO_3, R = rare-earth, M = Fe, Cr, Mn), constitute a family of Dzyaloshinsky – interaction antiferromagnetics, which exhibit an unusual variety of magnetic properties. Magnetic susceptibility χ (cm^3 g^{-1}) of non-doped $LaMnO_3$ was found to be 3.35×10^{-5} due to the presence of only Mn^{3+}–O–Mn^{3+} antiferromagnetic exchange interactions. As can be seen in Table 1, increasing sodium substitution leads to a reduction in the magnetic susceptibility and specific surface area. The reduction in magnetic susceptibility is caused by the presence of (La,Na)–O interactions in the structure of final product together with the Mn–O–Mn and Mn–O interactions due to substitution of Na for La. The ferromagnetic-paramagnetic transition occurred for all the compounds and the metal-insulator transition temperature T_C (K) increases with Na concentration x due to a greater number holes in the structure. However, the shape of the transition curve clearly indicates the presence of a second phase in the structure with $x \geq 0.2$. The highest T_C value for SHS-prepared substituted lanthanum manganites has been achieved for $La_{0.6}Sr_{0.4}MnO_3$. The Curie point for this compound was 375 K, which is much higher than room temperature. Note that the results for SHS samples are mainly in agreement with the results for the conventionally prepared materials, especially for the concentration x = 0–0.15.

(x – T_C/K): 0.07 – 220 K; 0.10 – 278 K;
0.13 – 292 K; 0.17 – > T_{room} (ref. 3)
(x – T_C/K): 0.05 – 273 K; 0.10 – 283 K;
0.125 – 294 K; 0.15 – 297 K; 0.2 – > T_{room} (ref. 8)
(x – T_C/K): 0 – 150 K; 0.05 – 235 K; 0.10 – 290 K; 0.11 – T_{room} (ref. 10)

Malavashi *et al.* noted that T_C is very sensitive to the oxygen content of sodium-doped manganites. In dependence from the $La_{1-x}Na_xMnO_3$ oxygen content it may be tens degrees of difference between T_C values for the same sodium concentration. For example, at $x = 0.05$ and $3 - y = 2.99 - 3.078$, the T_C value may be changed from 107 to 157 K. At $x = 0.13$ and $3 - y =$ $= 2.96 - 3.00$, T_C value is in the limits from 265 to 305 K. Probably, in the SHS made samples the same situation taking place when the oxygen index of final products is slightly different from stoichiometric.

The reaction mechanism was probed by extensive TGA/DTA measurements of individual components and mixtures from room temperature to 1300 K and a heating velocity of 10 K min^{-1}. Analysis of manganese metal fuel source shows that it starts to oxidise in air at ~500 K and shows a wide oxidation peak with double maximum heat evolution at 750 and 830 K. This is attributed to Mn metal powder particle size non-uniformity. This oxidation corresponds to a weight increase by 13.7% and is incomplete. The addition of sodium perchlorate to Mn metal leads to a single sharp oxidation process at 760 K. The weight increase in this case is 17.0%, which corresponds to virtually complete oxidation. In the presence of lanthanum(III) oxide, the oxidation of manganese metal begins at 830 K. Pure lanthanum manganite formation during the heating-cooling process was not completed without a solid oxidizer. The addition of internal solid oxidizers such as sodium perchlorate ($NaClO_4$) or sodium peroxide (Na_2O_2) considerably modifies the whole combustion process. In case of Na_2O_2 at low temperature $T \leq 423$ K weight decreased by ~ 2% due to water desorbtion from the La_2O_3 and Na_2O_2 powders. It is necessary to note that with x increasing (system 1) from 0.1 to 0.4, the temperature characteristics of metal oxidation and final product formation changed dramatically. An increase in x leads to a reduction of the melting and decomposing temperatures of the initial and intermediate compounds. At the same time, all the characteristic thermal peculiarities of the process were retained. In the range $423 \leq T \leq 523$ K a correlation of the oxidation process (DTA curve) and mass decrease by 0.5–1.0% (TG curve) took place. The DTA maxima were at $T = 543$ ($x = 0.1$) and 533 K ($x = 0.5$). The presence of Mn in the reaction system leads to intensive Na_2O_2 decomposition and a mass reduction of 5%. Endothermic maxima on the DTA curve took place at 653 ($x = 0.1$) and 606 K ($x = 0.5$). With T increasing the intensive Mn oxidation and final product formation took place. This complex process has three characteristic temperature maxima at 683, 773 and 863 K for $x = 0.1$ and 658, 713 and 793 K for $x = 0.5$. Final product formation occurred at 1035 K (TG curve) for non-doped samples. For sodium-substituted compounds this temperature increased with x. For $x = 0.1$ the maximum temperature value increased to 1100 K and for $x = 0.5$ to 1195 K.

SHS offered a new route to alkaline-substituted lanthanum manganite $La_{1-x}Na_xMnO_3$. The reaction is promoted by the oxidation of Mn metal from atmospheric and internal solid oxidizers. The products from the SHS process show physical properties comparable to the conventionally produced materials.

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