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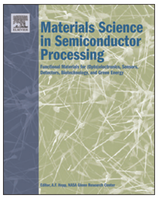

Pure and zirconium-doped manganese(II,III) oxide: Investigations on structural and conduction-related properties within the Lattice Compatibility Theory scope

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ABSTRACT

Manganese(II,III) oxide Mn_3O_4 thin films have been deposited on glass substrates using a simple spray pyrolysis method. Zirconium doping protocol was applied in order to verify some recently claimed enhancements of hausmannite physical properties. Gradual doping was achieved with ratio [Zr]/[Mn]=1%, 2% and 3% in addition to pure Mn_3O_4. Beyond classical characterization techniques, effects of Zr-doping were studied in reference to the expected use in rechargeable batteries and sensing devices. Moreover, additional opto-thermal investigation and analyses of the Lattice Compatibility Theory led to a founded understanding to the dynamics of Zirconium ion incorporation inside Mn_3O_4 host matrices.

1. Introduction

In the last decades, much attention has been paid to the investigation of spin canting structures of Manganese(II,III) oxide Mn_3O_4. It was commonly known that Mn_3O_4 stable phase is mainly tetragonal, with alternative octahedral and tetrahedral positions of Mn^{3+} and Mn^{2+} ions, respectively [1-5]. Recently, a particular attention has been paid to Hausmannite Mn_3O_4 utilization within high-rate lithium-ion batteries [6], supercapacitors [7] and UV sensors [8]. Thin films of this binary oxide have been synthesized via several methods such as SILAR route [9]. CBD method [10] and MOCVD [11]. Much earlier, synthesis methods were rather sophisticated, like sol–gel processing of manganese alkoxides [12] and $Mn(OH)_2$ aqueous suspensions controlled oxidation [13,14]. Some recent works outlined a non-expensive method: that of spray pyrolysis [10–13].

Mn_3O_4-like compounds have been found recently to have also potential for UV detection. Other studies have revealed the activity of this compound in oxidative coupling reactions of some saturated and aromatic hydrocarbons [14,15].

We present here a detailed investigation of the thermal properties of hausmannite. Zr-doping dependence of opto-thermal properties as well as the intriguing phenomena of irregular doping-related incorporation of Zirconium within host Mn_3O_4 lattices are also discussed. This may be of great interest in some heat transfer and optoelectronic applications as well as in sensitivity tests as mentioned above.

2. Experiment and characterization techniques

Pure Mn_3O_4 Manganese(II,III) oxide thin films have been first fabricated by spraying a mixed precursor solution onto a glass substrate. The substrate temperature was fixed at 350 °C using a bulk heater along with a digital temperature controller. The nozzle-to-substrate plane distance was fixed, as reported previously by Boubaker et al. [16], at the optimal value of 27 cm. Filtered compressed nitrogen air was used as gas carrier. The as-grown thin films were labeled as (MN,0).

Consecutively, and under similar experimental conditions, Zirconium-doped Mn_3O_4:Zr thin films solution have been fabricated by adding hydrated Zirconium chlorine hexahydrate ($ZrCl_2(6H_2O)$, 99.9% purity) to the precursor solution while maintaining acidity level [20–23]. In the different elaborated samples, the 1–3%. In order to obtain the respective samples (Zr,1), (Zr,2) and (Zr,3). The total deposition time was maintained at 20 min. After deposition, the coated substrates were allowed to cool down

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naturally to room temperature.

In the following stage, opto-thermal investigations have been applied to the pure and doped as-grown samples. These investigations were based on the “Mirage Effect” protocol [17–20], which is detailed later, and yielded interesting values of thermal conductivity and diffusivity. Finally, optical measurements, in the UV-Visible range were carried out using a Schimadzu UV 3100 double-beam spectrophotometer, within a (300–1800 nm) wavelength range. The obtained data enabled analyses in terms of the optothermal expansivity ψ_{AB}. These analyses presented a plausible attempt for evaluating the enhancement of the suitability of the doped material for PVT application.

3. Results and discussion

3.1. “Mirage Effect” investigation and thermal parameters evaluation

“Mirage Effect” method is based on the fact that when a target is heated by a distant source (Fig. 1), and when a determined fluid separates source from target, the incident energy flow induces a temperature gradient inside the bulk fluid [18, 19]. In the particular case of a modulated light beam of intensity $I = I_0\,(1 + \cos \omega t)$, the generated thermal propagates into the sample and in the surrounding fluid inducing a pulsed temperature gradient. This gradient leads to a refractive index gradient in the fluid. A laser probe beam crossing the fluid will undergo a deflection. The theoretical model [19–22] is built on the resolution of the one dimension z-dependent heat equation in the different media, fluid, sample and backing by assuming the continuity of the temperature and the heat flow at the different interfaces (Fig. 2a and b). This model yields a complex expression of the photo-thermal deflection $\Psi(z, t)$ as a function of the thermal conductivity K_i, the thermal diffusivity D_i of the targeted material.

Precedent studies [21,22] demonstrated that the variations of amplitude and phase of the photo-thermal deflection signal, which are measured by a synchronous detector, are efficient guide for determining thermal conductivity and diffusivity.

Plots of the amplitude and the phase of the photo-thermal deflection $\Psi(z, t)$ versus chopping frequency square root are performed in (Fig. 2a and b) for the pure and Mn_3O_4 thin films (MN,0) and doped samples (Zr,1), (Zr,2) and (Zr,3) Fig. 3.

For each sample, thermal conductivity K_i, and thermal diffusivity D_i are determined through evaluation of curves slopes and extreme points coordinates along with identification regarding theoretical fittings with thermal conductivity profiles, as detailed elsewhere by Gherouel et al. [23], Boubaker [24,25] and Saadallah et al. [26]. The obtained values are gathered in Table 1.

First, a good agreement between thermal conductivity and thermal diffusivity results has been recorded. In fact, according to the universal equation

$$D = \frac{K}{\rho c} \qquad (1)$$

where c is specific heat capacity and ρ is density, for constant values of these two last parameters (which is an acceptable presumption since doping ratio is weak), must vary proportionally, which was the case in the actual study.

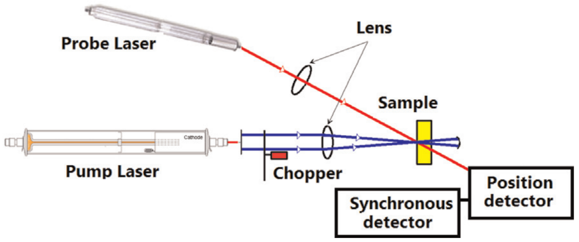

Fig. 1. Mirage Effect synoptic scheme.

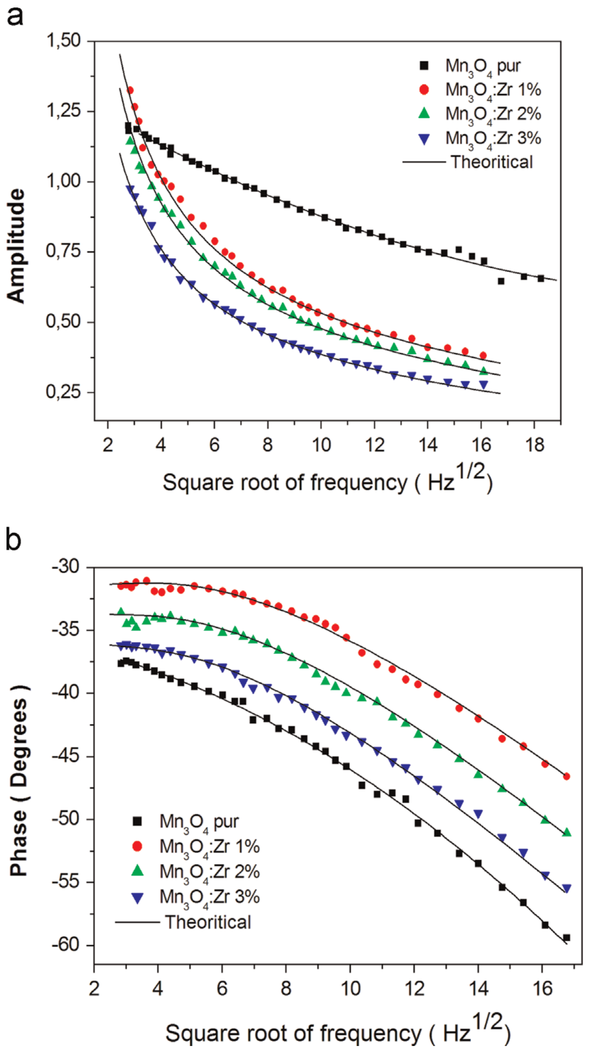

Fig. 2. (a) Normalized amplitude of the photo-thermal deflection signal for pure and doped Mn_3O_4 films. (b) Phase of the photo-thermal deflection signal for pure and doped Mn_3O_4 films.

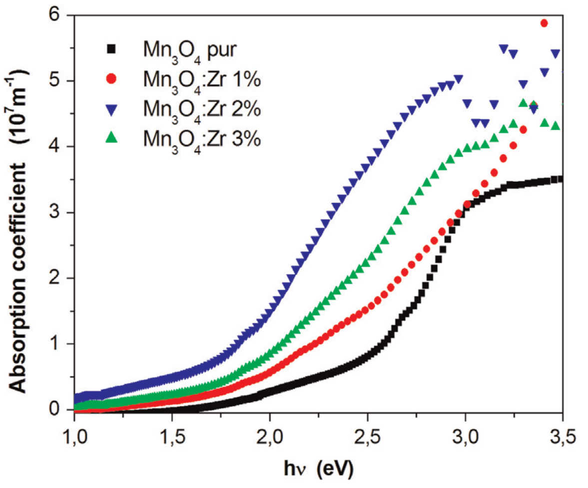

Fig. 3. Absorption coefficient values for pure and doped Mn_3O_4 films.