Microwave synthesis of magnetoresistive La$_{0.7}$Ba$_{0.3}$MnO$_3$ using inorganic precursors

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We report here the use of inorganic precursors as good microwave absorbers, by virtue of its polarity and high dielectric constant, to synthesize high temperature stable rare earth manganite, La$_{0.7}$Ba$_{0.3}$MnO$_3$. Compared to other wet chemical methods, the oxides prepared by microwave assisted route give fine particle oxides (<30 nm) with effective BET surface area of ~25 m^2/g. Two factors contribute to the rapid synthesis of these high temperature phases. Firstly, the dielectric constant of the precursors employed increases the microwave power loss in the material and this leads to a local heating effect. Secondly decomposition of these precursors, lead to formation of finely divided oxides often accompanied by an exothermic reaction which provides the needed energy to effect the formation of the product. This method offers a new approach to employ inorganic precursors as starting materials to realize fast and effective reaction in microwave assisted material synthesis.
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1. Introduction

Emerging trends in material synthesis indicate that rapid synthetic routes are becoming increasingly important to realize new compositions and meta-stable phases and materials with distinct particulate properties [1]. Conventional solid state method is a diffusion controlled process involving counter diffusion of the cations through the product layer. This diffusion process is controlled by an energy barrier and can be represented as $D = D_0 e^{-\Delta G\#/RT}$. To overcome this energy barrier a relatively high thermal energy (>1000°C) is normally required, which however leads to long processing time and chemical inhomogeneity in the desired sample. This kinetic and thermodynamic barrier encountered can thus be overcome by initiating *in-situ* exothermic reactions often achieved through wet chemical means [2]. Among various *wet* and *non-wet chemical* routes reported so far, use of combustion reaction and microwave synthesis to realize high temperature phases has been noted respectively. The range of oxides that can be prepared includes, oxides of different crystal symmetry, carbides and nitrides [3–6]. Although many reports are available on the use of the microwave energy to increase the rate of the solid state reactions by orders of magnitude compared to the conventional solid state route, there are no reports to prepare these high temperature phases using wet starting materials as precursors. Mingos and co-workers [7] have observed that, not all the simple transition metal oxides which are employed as starting materials could couple effectively with electromagnetic radiation. Key to this process is the microwave absorbing power of the starting materials. The microwave coupling with materials largely depend on factors such as Ohmic losses and dipolar loss of the material [8]. However, when metal oxides having low dielectric constants are employed as precursors, the absorption of microwave can be enhanced using some known microwave absorbers such as carbon etc. [9]. Alternatively, use of wet chemical precursors can enhance microwave absorption. The advantage in employing wet precursors is two fold. Firstly, they are polar and they can easily couple with the electric vector of the electromagnetic radiation. Secondly, on decomposition they yield very fine metal oxides which react to form single phase products in a very short time. The formation of component oxides occur as a transient phase, as a result, the final oxide product is realized in very less time. We show in this paper, the use of microwave synthesis and the importance on the choice of the starting material which can largely affect the particulate properties of the final oxide product. We highlight here the synthesis of rare earth ortho-manganites using salts of metal nitrates as precursors.

The electromagnetic field polarizes dipolar substances such as metal nitrates which induces dipole in the molecule. As a result increased rotation sets in which causes internal heating of the substance due to frictional effects. This internal heating is proportional to the dielectric constant of the material, ϵ_r, where

$$P = 2\Pi f \epsilon_0 \epsilon_r' \tan \delta |E|^2 \tag{1}$$

Where P is the microwave power absorbed by the material, f is the frequency of the microwave, ϵ_0 is the permitivity in space, ϵ_r' is the relative dielectric constant of the material, E is the electric field. It is this factor ϵ_r' (in Equation 1) which determines the power absorbed and is directly correlated to the dielectric constant of the interacting material. It is observed that strongly polar compounds such as water, alcohols and ketones whose dielectric constant, ϵ_r' is 78.5, 30–40, 15–20 respectively, are heated up most rapidly [10]. Metal nitrates ($\epsilon_r' = 18$–25) absorb microwave radiation effectively which results in internal heating and decomposition to release heat energy which is utilized by the transient metal oxide mixture to form stable oxide phase.

2. Experimental

As a typical example, we outline below the synthetic aspects involved in the preparation of $La_{0.7}Ba_{0.3}MnO_3$. Stoichiometric amounts of $La(NO_3)_3 \cdot 9H_2O$, $Ba(NO_3)_2$, $Mn(NO_3)_2 \cdot 6H_2O$, all with purity >99.9% were taken and ground in an agate mortar. The homogenous mixture was dissolved in de-ionized water to obtain a homogenous precursor solution. The solution thus formed by the mixing of the metal nitrates and de-ionized water was transferred into a 300 ml capacity Pyrex (with $\epsilon = 4.65$) dish, which was introduced into the microwave oven with an output power of 800 Watt and frequency 2.45 GHz. The solution on exposure to radiation, boils with evolution of oxides of nitrogen, $(NO)_x$. On complete evaporation it ignites with an appearance of a flame, resulting in formation of the product. This process is instantaneous and the product is achieved in less than five minutes. X-ray powder diffraction pattern was recorded using Rich-Seifert 3000 TT X-ray diffractometer and the lattice constants were calculated using slow 2θ scan. The resistivity of the sample was measured using the standard four probe method with a temperature range 20–300 K using liquid He–cryostat. The temperature dependence of the magnetization of the sample was measured in a field of 0.5 Tesla using a vibrating sample magnetometer from 300–400 K with fabricated heating arrangement. The morphology of the as-prepared powder and the sintered sample was studied using a JEOL JSM-840A Scanning Electron Microscope. The size and shape of the product was observed by Transmission Electron Microscope (TEM). Effective surface area was measured by BET method using a surface area analyzer employing N_2 as the adsorbate.

3. Results & discussion
3.1. Mechanism of microwave interaction
The interaction of microwave radiation with metal salts in solution phase depends on the relative dielectric constant (ϵ_r') of the reaction mixture, polarity of the solvent and the applicator. Hydrated water molecules act as a solvent enhancing the microwave power loss of the metal nitrates in two ways. Firstly,

water has a high dielectric constant ($\epsilon_r' = 78.4$). Secondly, it increases the polarity of the metal nitrates, allowing strong microwave coupling. As a consequence an internal heating results which leads to the formation of metal oxides as a transient phase, which cannot be isolated. Heat of formation of these finely divided oxides is negative, and therefore the reaction is exothermic. However, during the formation of finely divided oxides, an exothermic reaction occurs. The enthalpy of formation and dielectric constant of the corresponding metal oxides in transient phase are La_2O_3 (−428.7 kcal/mole, 27), BaO (−151.6 kcal/mole, 34) and MnO_2 (−124.29 kcal/mole, $\sim10^4$) respectively [11]. The coupling of the microwave radiation is due to the substantial dielectric constant of these metal oxides, MnO_2 (formed as a transient phase) in particular, has high dielectric constant value, which enhances the microwave coupling in the transient phase. Hence, both microwave coupling and enthalpy of formation of component metal oxides eventually contribute to the thermodynamic requirement of the final phase formation. The local temperature decreases the activation energy which leads to an increase in the reaction rate.

3.2. Characterization details
The XRD pattern of $La_{0.7}Ba_{0.3}MnO_3$ shows a pseudo-cubic symmetry (space group Fm3m) as is shown in Fig. 1. The lattice constant (7.8310 Å $\pm$ 0.002 Å) of the product formed by microwave method is identical with the sample prepared by conventional solid state method. No detectable impurity peak is observed in the X-ray diffraction pattern. The particle size of the product prepared by microwave method is in *nano* range (<30 nm), calculated from XRD using Debye-Scherrer equation and this has been confirmed from TEM. The effective surface area of the powders is 25 m^2/g, which is substantially large. The smaller particle size results out of rapid reaction rates and due to the evolution of gaseous products which scavenges out the local heat. The morphology of the particles were studied by SEM and TEM techniques. SEM morphology (Fig. 2a) shows a cluster type agglomerate of the as-prepared powder. The
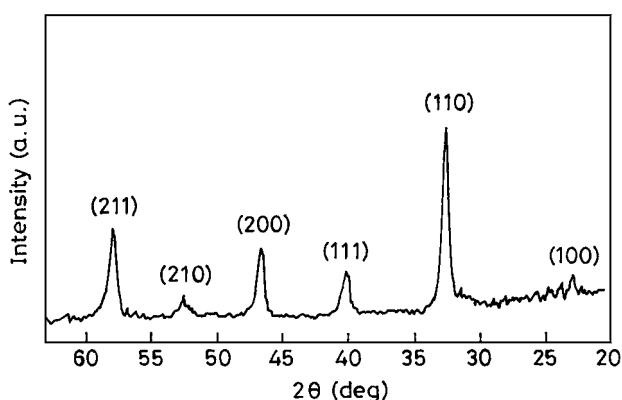

Figure 1 The X-ray diffraction pattern of polycrystalline $La_{0.7}Ba_{0.3}MnO_3$ sample prepared by microwave method. The broadening of the x-ray peaks reflect the fine particle nature of the product. The particle size calculated from the broadening is below 50 nm.
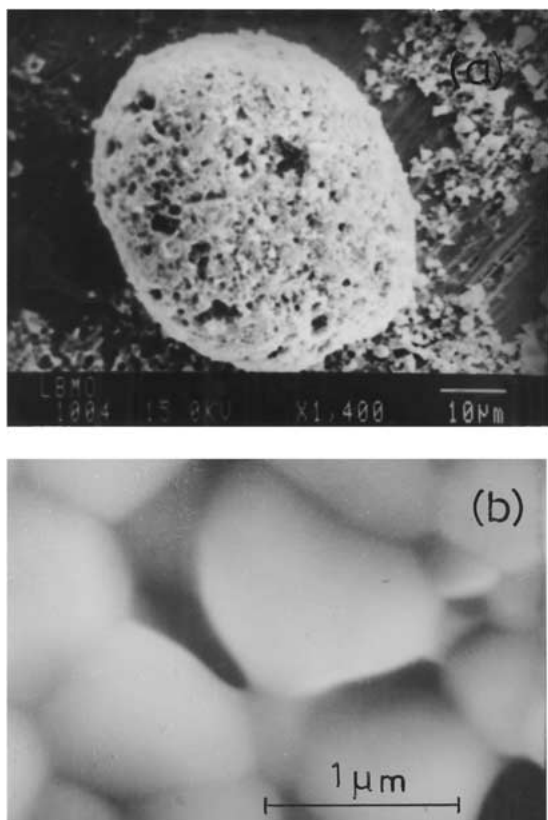
Figure 2 (a) The SEM micrograph of the as-prepared powder shows agglomeration due to very high reactivity of the crystallites. (b) SEM micrograph shows dense compact of the sintered pellet, sintered at 1050°C, for 6 hours, with 90% of the theoretical density.
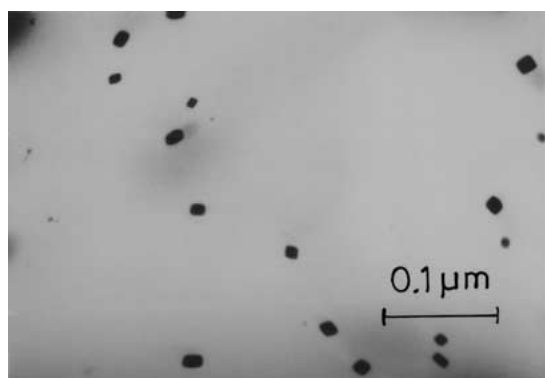

Figure 3 The TEM picture of the LBMO sample prepared by microwave method shows uniform size and shape, often desired for dense compacts. The average particle size measured is below 30 nm.

tendency to form such agglomerates reflects the surface energy of the crystallites. Shown in Fig. 2b is the SEM micrograph of the sintered pellet of the $La_{0.7}Ba_{0.3}MnO_3$ powder sintered at 1050°C for 6 hours. A dense compact with 90% of the theoretical density is achieved due to highly reactive powders. The TEM micrograph shows platelets of LBMO powder with nearly uniform size and shape (see Fig. 3). The significance of microwave synthesized powder is further highlighted in the transport and magnetic properties. Shown in Fig. 4 is a plot of resistance and magnetization versus temperature. It is indeed gratifying to note that the sintered compacts show excellent agreement between the metal-insulator transition (T_p) and magnetic transition
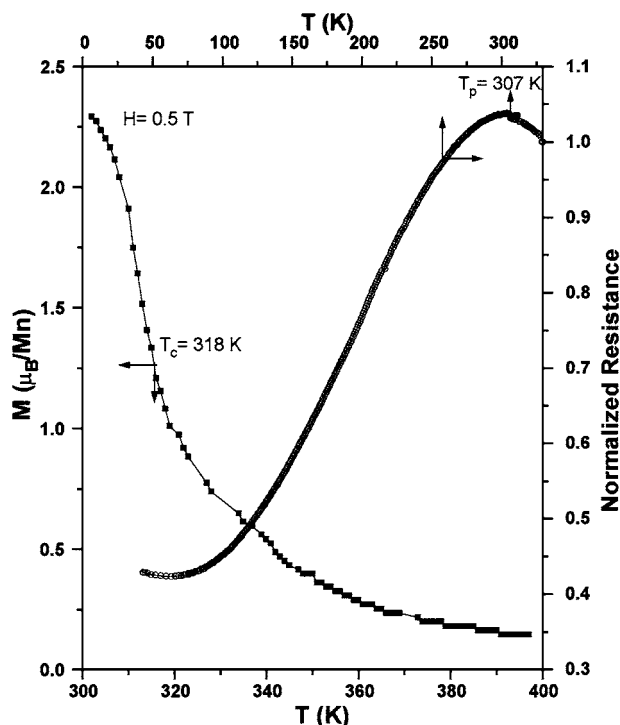

Figure 4 Shows a plot of magnetization and normalized resistance for the $La_{0.7}Ba_{0.3}MnO_3$ as a function of temperature. An excellent agreement between Curie temperature and metal-insulator transition is observed for the powder sintered at 1000°C.

temperature (T_c) which is critical for observing colossal magnetoresistive behavior. However in polycrystalline samples, a more frequently encountered problem is that of grain boundary effect in sintered compacts. The effect of grain size on the transition temperature has been highlighted by several authors (Mahendiran *et al.* [12]. Verelst *et al.* [13], Ju *et al.* [14]). It is generally agreed that while considering manganites with same Mn^{+4} content, main disparity in M-I transition seems to emerge from the difference in grain size. Smaller the grain size, more the mismatch in T_c and T_p, often the T_p values shifted to low temperature regime. Therefore the need for finely reactive powders which favor dense sintered compacts are desired. The microwave synthesized powders offer such characteristics, aiding solid state reactivity and chemical homogeneity, which is exemplified by the same transition temperature observed for both T_c and T_p.

4. Summary
In summary, we observe that the metal nitrates act as excellent microwave absorbers by virtue of their polarity, thereby leading to the formation of high-temperature phases. Few factors underline the use of this approach for realizing high temperature phase. Firstly, effective microwave coupling, and secondly the enthalpy of formation realized by the component oxides which permit the reaction to proceed instantaneously. A good agreement between the ferro-para magnetic transition and metal-insulator transition highlights the novelty of the powders prepared by this method. This method of preparation is simple and effective compared to the conventional methods with regard to saving both energy

and time. This approach can be extended to other transition metal oxides.

Acknowledgements

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