SYNTHESIS OF HEXAGONAL $YMnO_3$ NANOPARTICLES BY SOL-GEL ROUTE AND THEIR CHARACTERIZATION

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Abstract: *Hexagonal yttrium manganese oxide (h-$YMnO_3$) nanoparticles were prepared by a modified citrate sol-gel process at a lower heating temperature (200°C-230°C) followed by grinding and calcination. The structure and morphology of the synthesized nanoparticles were studied using an X-ray diffraction (XRD) technique and scanning electron microscope (SEM). $YMnO_3$ nanoparticles with a uniform micro structure were observed in SEM images. The XRD analysis showed that the prepared precursor powder was well crystallized. The elemental compositional analysis using energy-dispersive X-ray analysis (EDX) confirmed the elemental base composition of pure yttrium, manganese, and oxygen.*

Keywords: *Hexagonal, $YMnO_3$, Nanoparticles, Citrate sol-gel Process, X-ray Diffraction*

1. INTRODUCTION

Hexagonal and rare-earth manganite, yttrium manganese oxide (h-$YMnO_3$) is an interesting class of type-I multiferroic material, which attracted a great deal of research interest due to its outstanding properties [1-3]. Multiferroics are the materials that possess both ferroelectricity and ferromagnetism in the same phase [3-5]. $YMnO_3$ has a single spontaneous polarization axis and does not contain any volatile elements such as Pb and Bi [2]. $YMnO_3$ can be crystallized in either orthorhombic phase or hexagonal perovskite phase crystal structure depending on ionic radius size of Y [5, 6]. The orthorhombic $YMnO_3$ (o-$YMnO_3$), with space group Pbnm/ Pnma, exhibits ferroelectric transition temperature (T_C ~ 30K) and a low anti-ferromagnetic transition temperature (T_N ~ 42K) [5, 7]. Whereas the hexagonal $YMnO_3$ (h-$YMnO_3$), with space group $P6_3cm$ exhibits high ferroelectric transition temperature (Tc ~ 900K) and a low anti-ferromagnetic transition temperature (TN ~ 70K) [3, 8-10]. The h-$YMnO_3$ is also a pyroelectric material, which produces a temperature dependent spontaneous electric polarization response [1, 11, 12]. Because of these exclusive properties of h-$YMnO_3$, it became an ideal candidate for potential applications in the preparation of metal/ ferroelectric/ insulator/ semiconductor field effect transistors (MFISFET) [13, 14], nonvolatile ferroelectric random access memories, magneto electric sensors [2, 3, 15, 16], magnetic data storage and actuators [4]. The h-$YMnO_3$ is also exhibited high catalytic activity for oxidation of carbon monoxide and pronounces photocatalytic activity for decomposition of methyl red under ultraviolet and visible light irradiation [2]. There is a work showing the new application of h-$YMnO_3$ as a high near-infrared (NIR) reflective inorganic pigment and it can be well served as colored "cool colorant" [16]. There is also a work proving that h-$YMnO_3$ nanoparticles suitable for sensing devices for detecting H_2S gas [17].

In the past several years, studies on h-$YMnO_3$ ceramics [8-10, 18-20], h-$YMnO_3$ nanoparticles [2,5,17], h-$YMnO_3$ nanorods [4], h-$YMnO_3$ thin films [13-15, 21-25] have been carried out. In major part of the earlier reports synthesis of h-$YMnO_3$ was done by using solid-state reaction method [10,19-21,26], some studies followed the sol-gel process (Pechini method) [3,14,17,18,27] and some other studies followed polyacrylamide gel route [2,16], glycine-nitrate process [28], spark plasma sintering (SPS) [8], hydro thermal synthesis [4,5], thermolysis [29]. However, solid-

state reaction method requires high calcination temperature (~1100°C to 1400 °C), long milling and calcination time (~30-35hours) [19,20], but sol-gel synthesis process is somewhat easy in preparation and requires less calcination temperature.

In the present work, a modified citrate sol-gel route followed by grinding and calcination was used to prepare h-$YMnO_3$ nanoparticles. The crystal structure and micro structural characteristics were evaluated for the prepared nanoparticles.

2. EXPERIMENTAL WORK

The h-$YMnO_3$ nanoparticles were synthesized using a modified citrate sol-gel method. Stoichiometric amounts of yttrium oxide Y_2O_3 99.9% (0.02 mol), manganese acetate tetra hydrate $Mn(CH_3COO)_2$ (0.02 mol), citric acid monohydrate $C_6H_8O_7.H_2O$ (0.04 mol) were dissolved in a minimum amount of deionized water and 0.02 mol nitric acid HNO_3 was also added to the solution. This solution was stirred at room temperature for two hours. Then ammonia solution about 25% was added to the above-stirred solution until a pH value of 7 was reached. Ethylene glycol 98% $C_2H_6O_2$ (0.04 mol) (which is a polymerization agent) and a catalytic amount of C-TAB (which is a structure directing agent) were added to the solution and then stirred for half an hour at room temperature. The resulting solution was heated on a hot plate along with stirring, continuously until the solution was evaporated and decomposed into a black carbonaceous precursor. The entire process of converting liquid solution into solid mass took 12 to 14 hours depending upon the amount of de-ionized water taken to make the solution. The evaporation of solution took place between temperatures 180°C to 220°C. The obtained precursor was cooled to room temperature, ground in a mortar for half an hour and then calcined for 2 hours at 700°C to 1100 °C (700°C, 800°C, 900°C, 1000°C and 1100°C) in a muffle furnace to obtain pure hexagonal $YMnO_3$ nanoparticles.

The crystalline nature and phase identification of synthesized particles were done by an X-ray powder Diffraction (XRD) performed in an X-ray diffractometer (Rigaku, Miniflex 300/600) with Cu Kα radiation and with scan range 10°-80° (2θ). The microstructure and the elements present in the prepared particles were studied with SEM-Carl

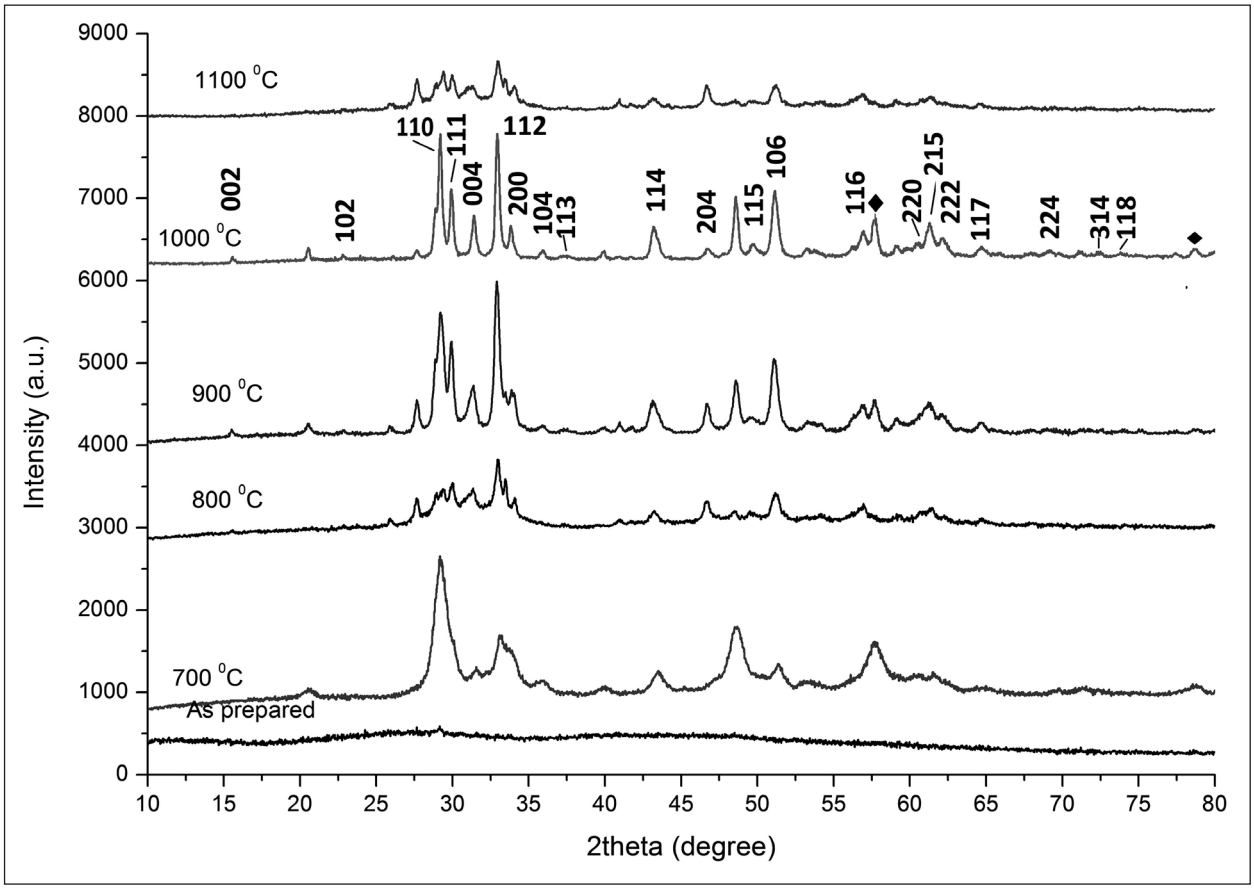

Fig 1. XRD Patterns of as-Prepared Particles and the Particles Calcined at 700°C, 800°C, 900°C, 1000°C and 1100°C

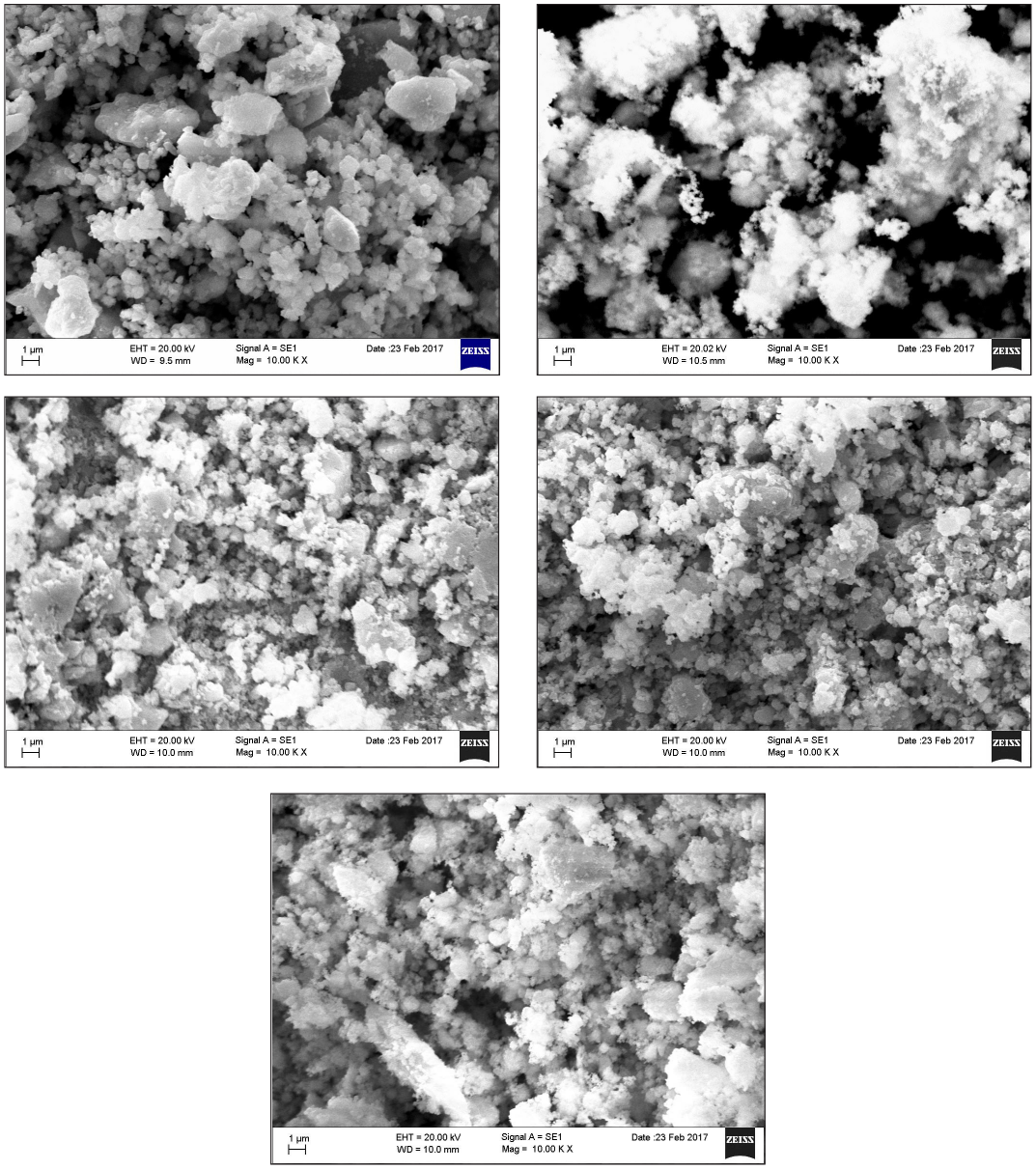

Fig 2. SEM images of the Particles Calcined at 700°C, 800°C, 900°C, 1000°C and 1100°C

Zeiss (Model: EVOMA15) with EDS-Oxford Instruments (Inca PENTAFET X3).

3. RESULTS AND DISCUSSION

The crystallinity and phase purity of the prepared particles and the particles calcined at 700°C to 1100 °c were examined via X-ray diffraction and shown in Fig.1. It shows that the crystallinity of the particles started at 700°C calcination temperature itself; in addition, the particles are well crystallized at 900°C as well as at 1000°C. Most of the diffraction peaks of particles calcined at 900°C and 1000°C are indexed with the hexagonal phase $YMnO_3$ (space group: $P6_3cm$, JCPDS 25-1079) and the two small peaks (denoted by black diamond symbol) are identified as Orthorhombic in phase. The intense and sharp diffraction peaks of the particles (calcined at 900°C as well as at 1000°C) indicate the better crystallinity and pure hexagonal phase of $YMnO_3$. The average particle size of synthesized $YMnO_3$ particles (calcined at 900°C and 1000°C) are determined from XRD data using well known Scherrer's formula $D= K\lambda/\beta\cos\theta$. Where D is the mean size of the crystal (nm), K is crystallite shape factor a good approximation is 0.89, λ is the wavelength of X-rays whose value is 0.15406nm (JCPDS 25-1079), β is the full width half maximum (FWHM) (in radians) (from XRD data using origin software) at predominant peak and θ is Bragg's angle (in degrees) of predominant peak [3, 16].

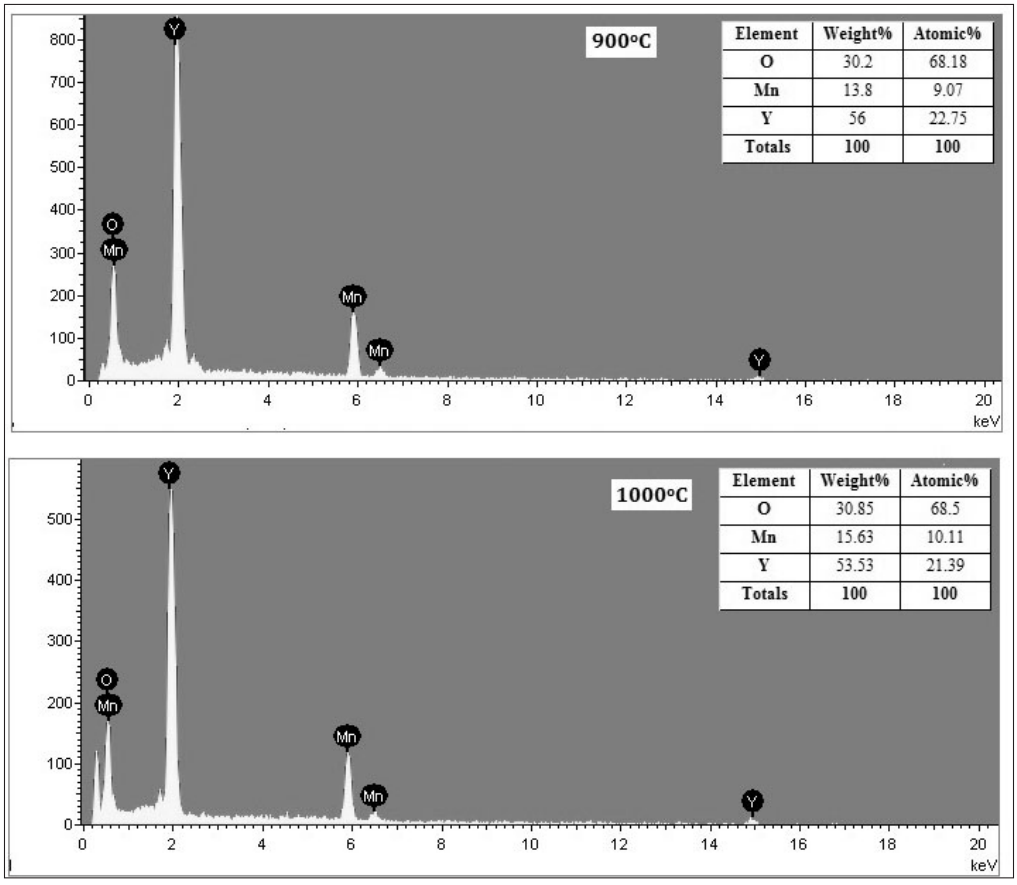

Fig 3. EDS Results of the Particles Calcined at 900°C and 1000°C

The average particle size of the synthesized $YMnO_3$ particles calcined at 900°C with the predominant peak (112) is 21nm and for particles calcined at 1000°C with the predominant peak (110 or 112) is 28nm which confirms the formation of h-$YMnO_3$ nanoparticles. The lattice parameters of synthesized $YMnO_3$ particles calcined at 900°C are a = b = 6.150 °A & c = 11.41 °A and for particles calcined at 1000°C are a = b = 6.036 °A and c = 11.28 °A (from XRD results) which are closest to the standard values a = b = 6.136 °A and c = 11.4 °A (JCPDS 25-1079).

The surface morphology of synthesized $YMnO_3$ particles was studied by SEM and the SEM images of $YMnO_3$ particles (calcined at 700°C to 1100°C) with '1μ' magnification were shown in Fig.2. The SEM images reveal that some of the particles combined with each other leaving some space as pores and also it shows that particles are approximately uniform and nano level in size. The Fig.3 shows the EDS spectrum of $YMnO_3$ particles calcined at 900°C, 1000°C. The elements observed in the spectrum are yttrium, manganese, and oxygen only and no other elements were detected. The atomic % of each element was as shown in the Fig.3.

4. CONCLUSION

The h-$YMnO_3$ nanoparticles were successfully synthesized by using a modified citrate method followed by grinding and calcination. By this synthesis process, h-$YMnO_3$ nanoparticles were obtained at 900°C and 1000°C calcination temperatures. The XRD analysis proves the formation of a well-crystallized hexagonal phase of $YMnO_3$ and also particles are in the nano level. SEM images prove that $YMnO_3$ particles are approximately in the nano level and uniform. The EDS spectrum diagrams show that no other elements are present in the synthesized sample.

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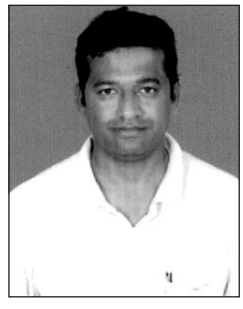

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