

A multiferroic behavior of TbMnO₃ nanorods prepared by microwave-assisted chemical route

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Abstract TbMnO₃ rods-like morphology were prepared by the microwave-assisted chemical route. The samples were synthesized at different microwave heating conditions. We synthesized nanorods of size 100 nm in diameter and length in several micrometers. SEM and TEM confirmed the morphology and size of the samples. Orthorhombic phase was indexed from XRD data. The temperature profile of the magnetization (*M*) at *H* = 50 Oe indicates well defined feature around 8 K for almost all samples. Temperature dependence of dielectric constant demonstrates an upward rise in dielectric constant start near 50 K and continues up to 23 K and lowering near 10 K. Magnetization and dielectric constant (ϵ) was observed to be strongly influenced by microwave power level used for synthesis of the samples.

Keywords Multiferroic · TbMnO₃ nanorods · Microwave assisted chemical route · Microwave synthesis

Introduction

Recently multiferroic materials have been extensively studied because of their significance in basic research and in potential application using magneto-electric effects. In multiferroic systems, magnetic and ferroelectric orders co-exist and are cross correlated (Cheong and Mostovoy 2007; Kimura et al. 2003). These materials exhibit interplay

between lattice distortion and electric and magnetic ordering. They have great possibilities for application in multifunctional devices. These applications are specially based on the control of magnetic state by electric fields and ferroelectric state by magnetic fields. These type of materials are called magnetoelectric, a subclass of multiferroics (Hur et al. 2004). The revival of interest in magnetoelectric materials was initiated by the theoretical investigation of Hill (2000) and by the recent discoveries of new mechanisms of ferroelectricity in perovskite TbMnO₃, hexagonal YMnO₃, RMn₂O₅, and Ni₃V₂O₈ (Lawes et al. 2005). Efforts have been devoted to find new multiferroic materials or to investigating multiferroic properties in known oxides, such as BiCrO₃ (Niitaka et al. 2004; Baettig et al. 2005), BiMnO₃ (Montanari et al. 2005a, b), BiFeO₃ (Wang et al. 2006; Baettig et al. 2005), BiCoO₃ (Belik et al. 2006a), BiScO₃ (Belik et al. 2006b) and double perovskite Bi₂MnNiO₆ (Azuma et al. 2005). Recently, multiferroic effects have been found in some rare earth manganates. Perovskite rare-earth manganites RMnO₃ (*R* = Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, etc.) are representative examples of multiferroic materials. Kimura et al. (2003). have explored TbMnO₃ to observed giant magneto-capacitance and magneto-electric.

Recently, synthesis of low-dimensional nanomaterials with well controlled size, morphology, and chemical composition has attracted considerable research interest due to their distinctive geometries, novel physical and chemical properties, which make them to be potential application in modern electronics and photonics. With this motivation, in the present work, we report the synthesis of TbMnO₃ in rods like morphology at nano-scale by microwave assisted soft chemical route. According to our knowledge, this is the first efforts to synthesize multiferroics perovskite in rods like morphology by microwave-assisted method. The effect of microwave synthesis

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conditions (i.e., microwave power, corresponding temperature, and irradiation time, etc.) on magnetic and electric properties are studied in view point of multiferroic.

Experimental

The starting materials used in the present work included terbium trichloride hexahydrate $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$, manganese dichloride tetrahydrate $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and sodium hydroxide NaOH. All chemicals were GR grade procured from Sigma-Aldrich and used without further purifications. TbMnO_3 nano-rods, were prepared using stoichiometric (1:1) amount of 0.05 M solutions of $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, mixed in 500 ml flask and vigorously stirred for 2 h. This solution of the mixed salts was then drop wise added to 0.05 M solution of NaOH with vigorous stirring leading to a dark brown solution. The flask containing the solution was placed in microwave synthesis assembly having a chamber of 360 mm \times 210 mm \times 430 mm dimensions with a 2.45 GHz frequency multimode source reflexor. Maximum deliverable power output was 700 W. Samples were prepared for different microwave synthesis conditions by varying the scale of microwave power level from 120 to 650 W and irradiation time 15 min to 65 min. The reaction product in the form of colloidal particles was filtered and dried in vacuum. The final black product was collected for characterization.

Characterization

The phase composition of as prepared powder samples was detected by X-ray powder diffraction (D8 Advanced Bruker instrument with $\text{Cu K}\alpha$ radiation (1.54 Å) at a scanning rate of 1° min^{-1} . The morphology of the sample was observed using JEOL JSM-6360A scanning electron microscope (SEM). The TbMnO_3 powder was spin-coated on to silicon substrate and a thin coating of platinum was sputter-deposited on this film in order to avoid any charging propel due to high energy electron bombardment during SEM. The transmission electron microscopy (TEM) was carried out using a Technai 20 G². Temperature profile of the magnetization of the samples was measured by ADE-Digital measurements system model vibrating sample magnetometer. Dielectric measurements were carried out by 4192 A impedance analyzer.

Result and discussion

Figure 1 shows the XRD pattern of TbMnO_3 sample prepared at microwave power 550 W for 15 min exposure

time. All the diffraction peaks are well matched with the (JCPDS 72-0379) orthorhombic structure of TbMnO_3 (space group *pbnm*) with unit cell constant of $a = 5.378 \text{ \AA}$, $b = 5.893 \text{ \AA}$, $c = 7.399 \text{ \AA}$. The average crystallite size calculated using Scherrer formula for these particles is found to be about $90 \pm 10 \text{ nm}$. The morphology of the samples was examined by SEM and TEM as shown in Fig. 2 a, (b), respectively. TEM and SEM image exhibits a rod like morphology of TbMnO_3 particles with average size 100 nm and length in micrometer. Almost same morphology was obtained for all the samples with change in scale of dimensions of the rods.

The field cooled temperature dependence of DC magnetization of TbMnO_3 bulk in a field of 50 Oe is shown in Fig. 3 for all samples. Above 50 K, there is almost no difference between the curves of all the samples. The anomaly in the magnetization is observed near $\sim 8 \text{ K}$, corresponding to the magnetic ordering of Tb^{3+} moments. The transitions around 40 K and 27 K observed in single crystalline TbMnO_3 and is attributed to the sine wave ordering of Mn^{3+} moments and lock-in transition, respectively don't appear to be strong in the rods-like morphology. There is possibility that the sine wave ordering of Mn^{3+} is localized due to nano-dimensions of the rods. The rods-like morphology develop intrinsic strain gradient which is responsible for softening of lock-in transition. Since these both transition are related to longer length scale. Although, the magnetization anomaly is observed at almost same temperature in all the samples, decrease trend in magnetization is detected for samples synthesized at increasing microwave power level. The samples proceed at higher microwave power level gives rise to an increase in radial dimension of the rod. This could be attributed to an Ostwald ripening process. Such a process of widening of the rods is quite possible since there is no capping agent used to cap their boundaries. This widening results in change in impact factor (diameter/length) of rods, which

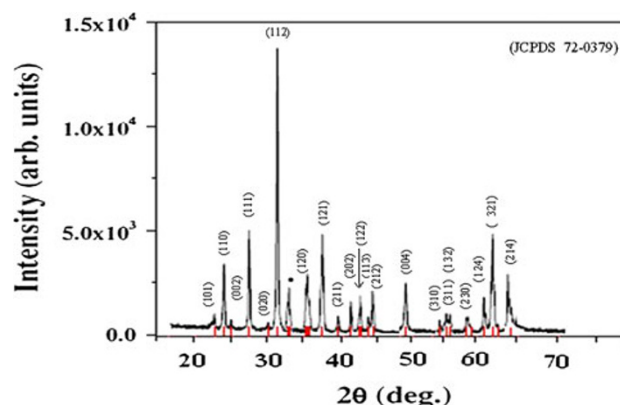


Fig. 1 XRD of TbMnO_3 prepared at microwave power 550 W for 15 min exposure time

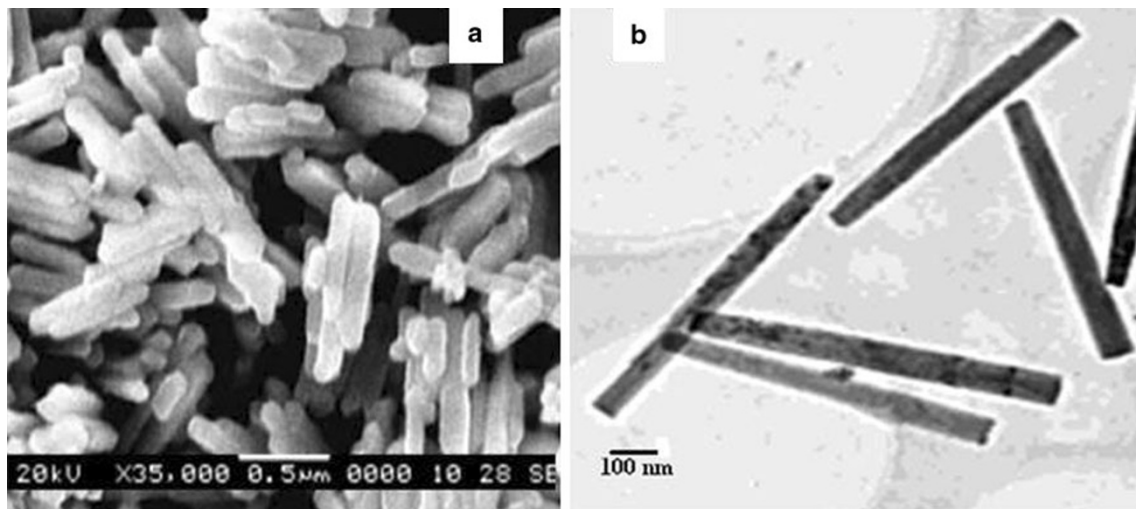


Fig. 2 **a** SEM, **b** TEM of TbMnO_3 prepared at microwave power 550 W for 15 min exposure time

causes change in magnetic ordering of Tb^{3+} ions on the surface layer to core. The widening of rods gives rise to the decrease in surface layer attributes to low magnetic ordering of Tb^{3+} ions on the surface. This results out the decrease in magnetization with increasing microwave synthesis power level.

Temperature dependence of dielectric constant (ϵ) at $H = 10$ Oe and frequency 10 kHz is shown in Fig. 4. The temperature profile of dielectric constant exhibits that below 50 K, $\epsilon(t)$ began to increase rapidly and passes through a maximum at vicinity of ~ 15 K. The dielectric feature occurs at almost the same temperature at which the magnetic transition observed. It implies that the multiferroic behavior is retained in the rods-like morphology. Enhancement of ϵ is up to 9–15% for the samples synthesis at microwave power level from 450 to 650 W. The microwave power level is found to be diameter manipulative parameter of the TbMnO_3 rods.

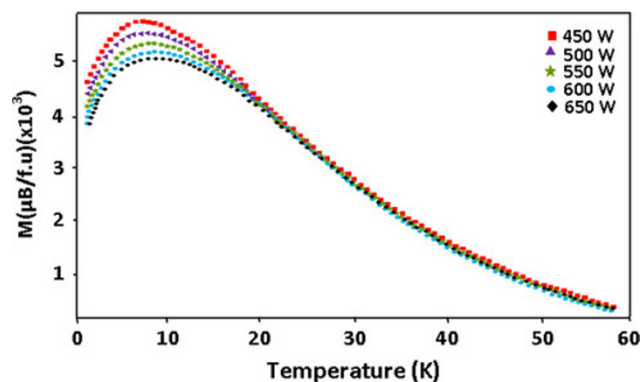


Fig. 3 Temperature dependent magnetization of the TbMnO_3 nanorods synthesized at different microwave power for exposure time 15 min

The influence of size on ϵ is understood as; at nanoscale dimension has large surface-to-volume ratio raised number of surface atoms compare to core. The termination of lattice periodicity on the surface leads to reduction in the coordination number of surface atoms. It attributes to surface bond contraction and thus the band gap expansion. The energy band gap is correlated to dielectric constant by relation $\Delta\chi/\chi = -2(\Delta E_g/E_g)$ (Tsu and Babic 1994), where, ΔE_g change in band gap energy, E_g original energy, $\Delta\chi$ change in static polarization, χ actual static polarization. It clearly indicates that decrease in size of particles increases band gap expansion and thus decreases dielectric constant.

In the present work observed trends of increase of dielectric constant with increasing microwave synthesis power level (from 450 to 650 W) can be explained as: the sample synthesis at increasing power level widen the

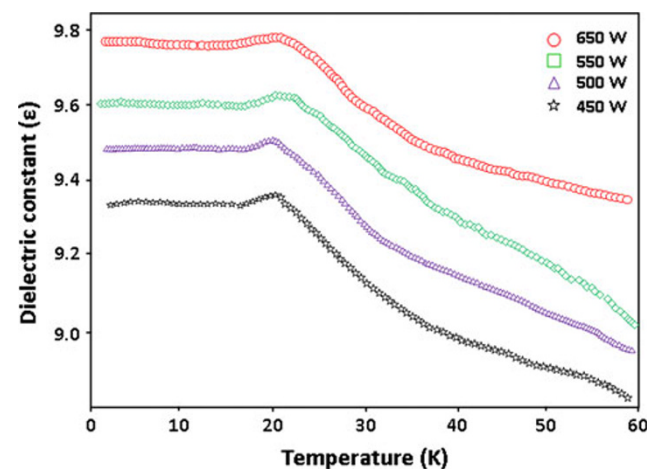


Fig. 4 Temperature dependent dielectric constant of the TbMnO_3 nanorods synthesized at different microwave power for exposure time 15 min

diameter of rods and reduces the surface-to-volume ratio. Thus, the band gap expansion is decreasing and dielectric constant is increasing with increasing power level in accordance with band gap correlation with dielectric constant.

The magnetization and dielectric constant TbMnO_3 nanorods are observed to be strongly influenced by microwave power used for the synthesis of the samples. In the microwave-assisted synthesis, molecular level dielectric heating is key factor of processing of reaction. The size and the morphology of the product depend on rate of crystal nucleation and growth. Microwave heating maintain uniformity of temperature in the reaction by avoiding thermal gradient, which generally occur in the reaction process by conventional way of heating. Uniform thermal conditions during the reaction keep control on rate of crystal nucleation and growth. It indicates that the size and morphology of the product can be manipulated by controlling microwave thermal conditions. The microwave thermal condition is decided by microwave power. In the present work, it is observed that the products synthesized by different microwave power level have same morphology (rod-like). Microwave power has not any significant influence on the morphology. The size of the rods gets affected by variation of microwave power. The increase in size with microwave power is responsible for enhancement of magnetization and dielectric constant of the samples.

Conclusion

Nanorods of TbMnO_3 were synthesized by microwave-assisted soft chemical route for different microwave power and exposure time. Temperature of solution was observed to be increasing with microwave power at initial stages of exposure time around 15 min by microwave-assisted processing of the reaction. For constant time and with increasing power, temperature is closely monitored to steeply rising. All samples were indexed to the orthorhombic structure from the XRD data. SEM and TEM confirmed nanorods of diameter 100 nm. Magnetization value was observed to be decreasing and dielectric value was observed to be increasing with increasing microwave power used for the synthesis of the TbMnO_3 samples. The simple technique using a multimode microwave source may prove to be a potential tool for growing similar nanostructures of other Perovskite oxide.

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