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Ceramics International 39 (2013) 2065–2068

CERAMICS INTERNATIONAL

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High-voltage electrophoretic deposition of preferentially oriented films from multiferroic YMn_2O_5 nanopowders

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Received 19 July 2012; accepted 19 August 2012
Available online 23 August 2012

Abstract

Processing of the YMn_2O_5 powder is very challenging, since it decomposes to $YMnO_3$ and Mn_3O_4 at temperatures close to 1180 °C, while samples consolidation commonly demands high temperatures. The main goal of this work is to investigate a possibility to prepare thick films of YMn_2O_5, since their deposition generally requires significantly lower temperatures. Multiferroic YMn_2O_5 was synthesized by the hydrothermal method from $Y(CH_3COO)_3 \cdot xH_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$ and $KMnO_4$ precursors. XRD, FE-SEM and TEM analysis showed that the obtained powder was monophasic, with orthorhombic crystal structure and columnar particle shape with mean diameter and length of around 20 and 50 nm, respectively. The obtained powder was suspended in isopropyl alcohol with addition of appropriate binder and deflocculant. This suspension was used for electrophoretic deposition of YMn_2O_5 thick films under the high-voltage conditions and electric fields ranging from 250 to 2125 V/cm. The films obtained at 1000 V/cm and higher electric fields showed good adhesion, particle packing, homogeneity and very low porosity. It was shown that the deposition in extremely high electric fields (K_C=2125 V/cm) can influence the crystal orientation of the films, resulting in formation of preferentially oriented films.

Keywords: YMn_2O_5; Multiferroic; Electrophoretic deposition; Oriented films

1. Introduction

Multiferroics are compounds that exhibit both ferroelectric and ferromagnetic properties. These materials have a spontaneous magnetization that can be switched by an applied electric field and a spontaneous electrical polarization that can be switched by an applied magnetic field [1]. There is a very limited number of families of compounds showing multiferroic behavior and one of them is RMn_2O_5 where R is a rare-earth ion (Nd–Lu), bismuth or yttrium [2]. YMn_2O_5 belongs to the orthorhombic space group *Pbam* and shows antiferromagnetic Neel temperature of about $T_N \approx 45$ K, while the ferroelectric Curie temperature is about $T_C \approx 25$–40 K [3,4]. Additional magnetic and ferroelectric transitions were observed at about 18 K and the nature of these transitions is still not well explained [3]. Up to now YMn_2O_5 was synthesized by different methods, such as solid state reaction [5], the Pechini method [3] or hydrothermal synthesis [2]. The morphology of the obtained particles depends on synthesis method and could be almost spherical [6], irregular [3] or most commonly columnar [2]. The further processing of powders is very challenging, since the YMn_2O_5 decomposes to $YMnO_3$ and Mn_3O_4 at temperatures close to 1180 °C [5]. Any attempt to consolidate samples requires high temperatures. Therefore, it is very interesting to investigate a possibility to prepare thick films of YMn_2O_5, since their deposition generally requires significantly lower temperatures. The YMn_2O_5 powders obtained by hydrothermal synthesis are usually in the form of fine nanoparticles which could be an appropriate precursor for homogeneous thick films preparation using, for example, electrophoretic deposition.

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http://dx.doi.org/10.1016/j.ceramint.2012.08.060

The electrophoretic deposition is a simple and convenient technique for deposition of films from suspensions of nanostructured particles [7]. Since the deposition is performed in the presence of electric field it can be also expected that under some optimal conditions of field strength, type of solvent and precursor high quality, dense, homogeneous and in some cases oriented films can be obtained. Although electrophoretic deposition implies the presence of electric field, this field is usually weak to enable preparation of oriented films even in polar materials. This is because the field induced by dipoles of solvent and suspended particles locally neutralizes applied electric field. This means that if one wants to get oriented films it is necessary to apply higher electric fields. However, in this case the deposition rate is too high and also if water is used as the solvent then electrolysis of water occurs [8]. This problem could be solved only if nonpolar organic solvents are used.

The aim of this work is to hydrothermally synthesize YMn_2O_5 nanopowders that could be further used for deposition of high-quality thick films by the electrophoretic deposition method (EPD). It is shown that electrophoretic deposition of suspensions of nanostructured precursors in solvents with low polarity and in the presence of high electric fields can result in homogeneous and dense YMn_2O_5 films with preferential orientation.

2. Experimental

The precursor solution for solvothermal synthesis of YMn_2O_5 was prepared starting from the following chemicals of p.a. quality: $Y(CH_3COO)_3 \cdot xH_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$, and $KMnO_4$. The amount of reagents was not added according to the stoichiometric molar ratios and an excess of yttrium-acetate was used. Starting yttrium and manganese salts were dissolved in 30 ml of distilled water under magnetic stirring at room temperature. The pH of the starting solution was about 5. The synthesis of YMn_2O_5 was performed in a slightly acidic suspension to prevent formation of $Y(OH)_3$.

The solution was solvothermally treated at 280 °C for 6 h. After cooling the suspension was washed with H_2O and centrifuged (10,000 min^{-1}) three times and finally the wet powder was suspended in isopropyl alcohol ($\sim 3.0 \times 10^{-3}$ g/ml) with addition of stearic acid and polyvinyl alcohol (1.5×10^{-4} g/ml and 1.8×10^{-3} g/ml respectively). This suspension was used for electrophoretic deposition. The electrochemical cell and heating elements are placed in the chamber (bottom-stainless steel, cover was made of high-thickness glass). Heating elements are connected with a temperature controller and the chamber could be heated up to 300 °C. Deposition of the films was performed under the following conditions: voltages of 100, 400 and 850 V (which correspond to electric field values of 250 V/cm, 1000 V/cm and 2125 V/cm, respectively), electrode distance of 4 mm, deposition time of 10 min, and planar stainless steel electrodes. After deposition, the almost clear solvent was removed and the deposit was thermally treated at 250 °C for 30 min without turning off the voltage. At the end of heating the voltage was turned off and the chamber was vacuumed to eliminate the traces of organics from the film surface.

The obtained precursor powders and films were characterized using XRD (RIGAKU, Model RINT2000) and FE-SEM (JEOL, Model 7500F) and TEM (JEOL, Model 2010) analysis. For XRD, SEM and TEM analyses hydrothermally synthesized powder was washed and centrifuged three times followed by drying at 150 °C and milling in agate mortar.

3. Results and discussion

The phase composition of hydrothermally synthesized powders was determined by XRD analysis of dried powder (Fig. 1). It is verified that pure orthorhombic YMn_2O_5 was obtained (PDF card number 34-667). As-synthesized powder did not show any preferential orientation. Also, the SEM micrograph (Fig. 2) showed typical columnar particle shape, with mean diameter and length of about 20 and 50 nm, respectively. Columnar morphology was confirmed by TEM analysis which also indicated that crystallites grow along [001] direction, since (001) planes make 90° angle with the growth direction (Fig. 3). It should be emphasized that hydrothermal synthesis of YMn_2O_5 was already performed by Li et al. [2]; however these authors used different precursors and obtained powders of different morphologies.

The suspension of YMn_2O_5 nanoparticles in isopropyl alcohol was of excellent quality, very stable for several days, while particles did not agglomerate. XRD results of deposits obtained at different voltages are shown in Fig. 4. All samples showed the same phase composition as the starting powder, but relative intensity of the peaks was

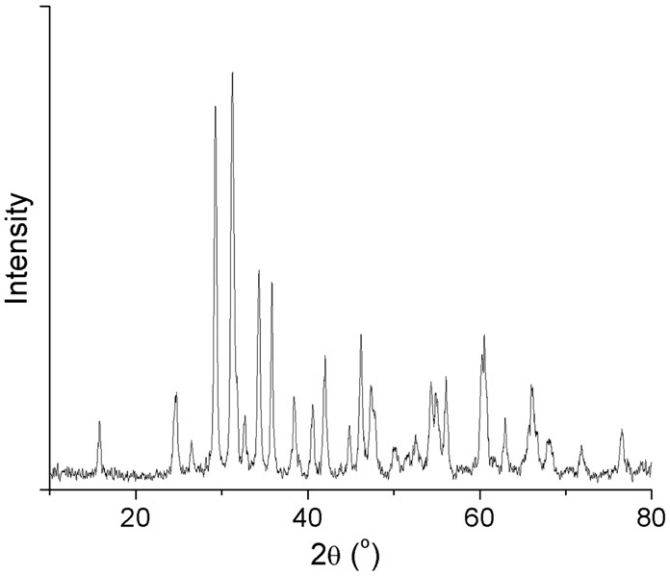

Fig. 1. XRD patterns of the pure YMn_2O_5 obtained by hydrothermal treatment at 280 °C for 6 h.

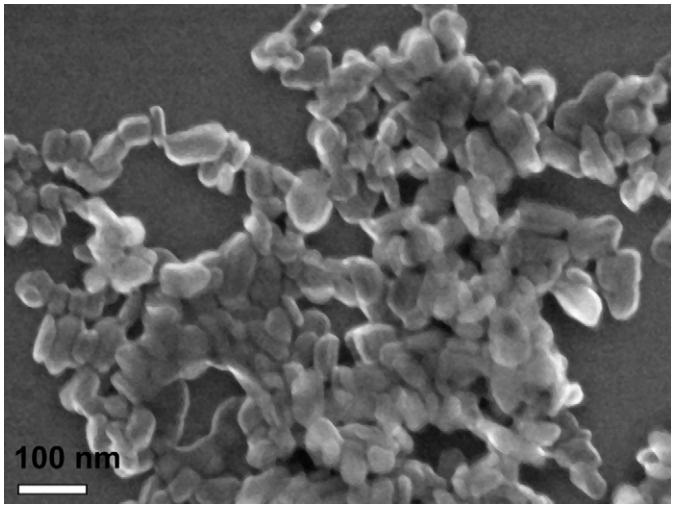

Fig. 2. SEM micrograph of YMn_2O_5 nanopowder.

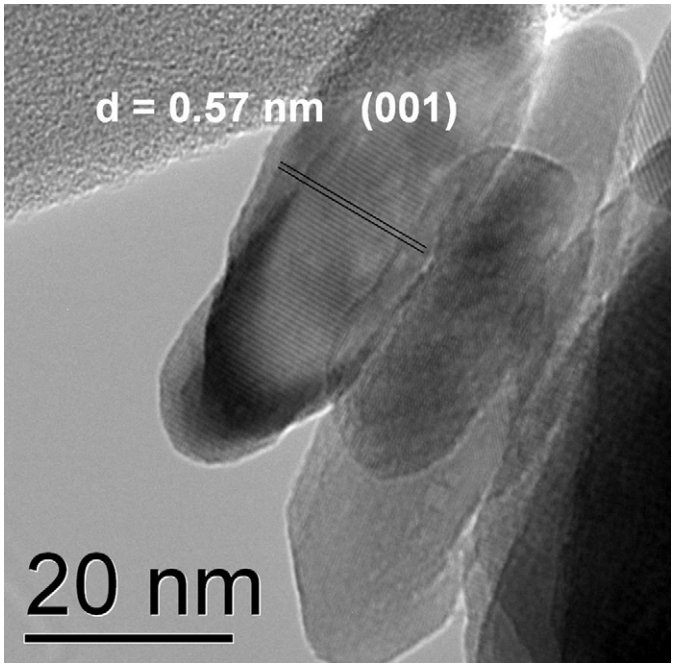

Fig. 3. TEM micrograph of YMn_2O_5 nanopowder, indicating [001] growth direction.

changed. XRD patterns of the samples deposited at 250 V/cm and 1000 V/cm are almost the same and did not show any preferential orientation. As a result of deposition in very high electric field of 2125 V/cm a preferentially oriented crystal structure along [100] direction was obtained (Fig. 4). It is possible to verify that relative intensities of diffraction lines were changed, while some lines almost disappeared. According to our best knowledge up to now there are no reports on preparation of preferentially oriented films prepared by high-voltage EPD. There are several articles about oriented films obtained by EPD in strong external magnetic fields applied in a certain direction (up to 10 T) [9,10] or rotating magnetic field [11,12]. In this work we tried a different

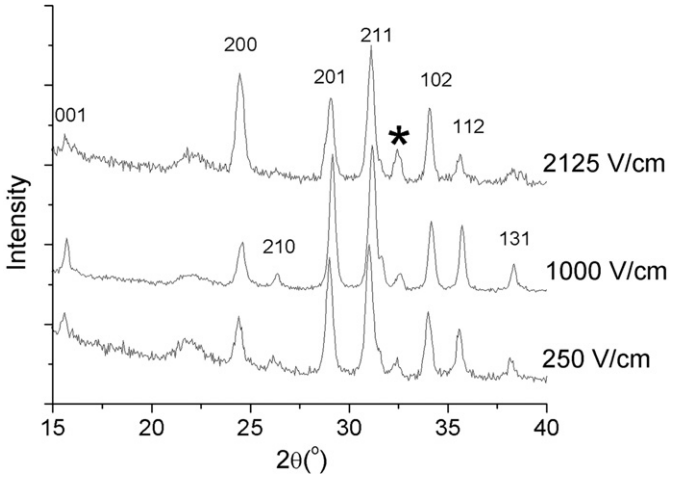

Fig. 4. Comparison of XRD diffractograms of deposits obtained at different voltages (amorphous phase in the interval $2\theta = 21–23^\circ$ is always present when the powder is suspended in isopropyl alcohol; also the peak labeled with * at $2\theta = 32.4^\circ$ is not listed in JCPDF card 34-0667, but some authors label it as (002) plane [6]).

approach, i.e. we applied high voltages to induce preferential orientation, as confirmed through XRD (Fig. 4). According to some authors high-voltage EPD is not recommended since the film quality can be decreased because of suspension turbulence, fast movement of particles and similar problems [8]. Nevertheless, this probably stands for classical micrometer sized particles and commonly used solvents. If one use nanometric particles and solvent with very low dielectric constant then completely different conditions for EPD are necessary. Besides that, the use of different binders and surfactants additionally changes these conditions. Finally, narrow particle size distribution of our powders improves particle deposition. There are only few articles about use of high-voltage EPD but only to produce aligned forests of one-dimensional nanoparticles, i.e. specific microstructures, [13] or to perform selective electrodeposition [14]. The aim of our work was not only to obtain dense and uniform thin films, but also to obtain preferentially oriented films.

Deposited films also show difference in particles packing, film porosity and homogeneity besides different XRD patterns. Micrographs of all deposited films are shown in Fig. 5. The film deposited at 2125 V/cm showed excellent microstructure (Fig. 5a). It was very dense, smooth and homogeneous with mean particle size below 50 nm. The absence of pores is also a confirmation that there was no gas formation during the EPD process. Particles packing and adhesion in films deposited at 250 V/cm are worse than in films deposited at 2125 V/cm. Also, films are rough with not so good contacts between the particles, while porosity is not high although the presence of pores was detected. Better films were obtained at 1000 V/cm in comparison to 250 V/cm. The particles packing is better, but still slightly worse than in films deposited at 2125 V/cm. All films showed similar particle size, since the temperature of

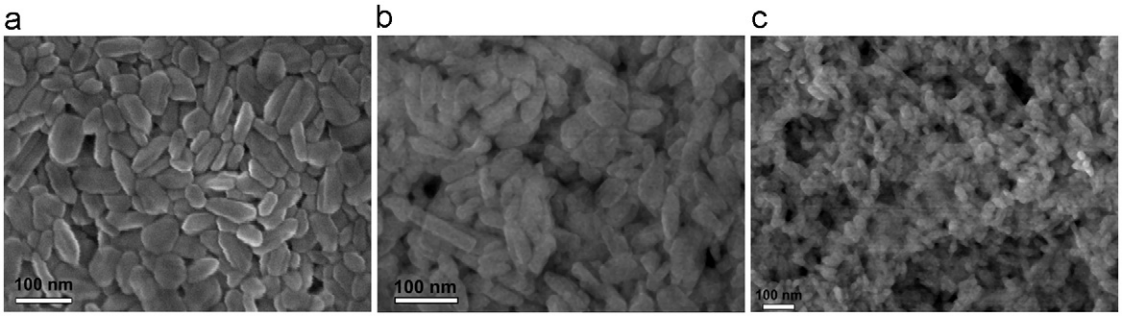

Fig. 5. Plane view of YMn_2O_5 films obtained by EPD at 2125 V/cm (a), 1000 V/cm (b) and 250 V/cm (c).

thermal treatment was too low to promote a significant grain growth.

The obtained results are very encouraging and we will proceed with systematic investigation of possibility to use high voltage EPD technique for deposition of different, for example, polar, non-polar or ferroelectric materials.

4. Conclusions

Multiferroic YMn_2O_5 was successfully synthesized by the hydrothermal method from $Y(CH_3COO)_3 \cdot xH_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$, and $KMnO_4$. According to results of XRD, FE-SEM and TEM analysis the obtained powder was of single phase, with orthorhombic crystal structure and columnar particle shape with mean diameter and length of about 20 and 50 nm, respectively. It was shown that this powder could be used for production of stable suspension in isopropyl alcohol. The equipment for high-voltage EPD was specially constructed to enable heating of the deposit without turning off electrical field, as well as a vacuum system to eliminate adsorbed organic molecules. High-voltage EPD resulted in smooth and dense films of YMn_2O_5 with satisfactory adhesion, especially when high electric field of 2125 V/cm was used. Finally, it was shown that crystal orientation could be changed in extremely high electric fields. Films deposited at 250 V/cm and 1000 V/cm showed XRD patterns in accordance with the relative intensities found in PDF 34-667, while films deposited at 2125 V/cm were preferentially oriented in [100] direction.

Acknowledgment

The authors acknowledge that this work was supported by the Ministry of Education and Science of the Republic of Serbia (Project number III45007) and Fundação de Amparo à Pesquisa do Estado de Saõ Paulo-FAPESP.

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