

Synthesis of Y_2NiMnO_6 nanoparticles by ethylene glycol sol-gel method

Ming Lei

School of Optics and Electronic Information, Huazhong University of Science and Technology,
Wuhan, Hubei 430074, China

leiming_mb@163.com

Keywords: Y_2NiMnO_6 ; nanoparticles; multiferroics; sol-gel

Abstract. Y_2NiMnO_6 nanoparticles were synthesized via an ethylene glycol sol-gel method. Differential scanning calorimetry, thermogravimetric, X-ray diffraction and environmental scanning electron microscopy were utilized to characterize precursors and derived powders. Single-phase Y_2NiMnO_6 nanoparticles were formed at 800°C for 2h. The analysis suggests that adding ethylene glycol can effectively suppress the formation of metal oxide and promote the formation of Y_2NiMnO_6 . Compared to Polyvinyl alcohol, ethylene glycol is much better for the synthesis of Y_2NiMnO_6 via sol-gel method.

Introduction

Y_2NiMnO_6 with double perovskite structure have attracted much attention due to their unique properties, such as multiferroic, large magnetocapacitance, magnetoresistance and relaxor ferroelectricity [1-4]. Materials with such kinds of properties can be applied to novel devices, including memory and data storage devices [5-10]. Y_2NiMnO_6 can be synthesized via solid state reaction method. In the study of Tang et al., Y_2NiMnO_6 samples were sintered at 1400°C and the dielectric properties were measured [2]. The giant dielectric tunability was found in bulk Y_2NiMnO_6 around room temperature: a 4V/mm direct current electric field was able to suppress permittivity from 5059 to 826 at 10 kHz and the tunability was more than 84% [2]. Such a high tunability means that, this kind of material holds great potential application in the field of microwave tunable devices. Further studies demonstrate that Y_2NiMnO_6 can also be prepared via polyvinyl alcohol (PVA) sol-gel method. In the work of Maiti et al., Y_2NiMnO_6 nanoparticles with the diameter 20nm were synthesized by a sol-gel method [3]. The Y_2NiMnO_6 powder was found single-phase with the calcination temperature 875°C, which is much lower than the sintering temperature in the solid state reaction method. Moreover, the magnetic and dielectric properties of the nanoparticles were measured. The results prove that Y_2NiMnO_6 have the property of multiferroic, which are attracting enormous scientific interest. The strong magnetoelectric coupling of multiferroics is a very desirable property and required for an electric (magnetic) control of magnetic (electric) order parameter [1]. Therefore, the study on how to improve the synthesis of Y_2NiMnO_6 is meaningful.

In this paper, Y_2NiMnO_6 powder was prepared via a sol-gel method with different amount of ethylene glycol (EG). Differential scanning calorimetry, thermogravimetric, X-ray diffraction and environmental scanning electron microscopy were utilized to characterize precursors and derived powders. XRD patterns exhibit that more EG can effectively suppress the formation of metal oxide and promote the formation of Y_2NiMnO_6 . Single-phase Y_2NiMnO_6 nanoparticles were obtained at 800°C for 2h. Compared to PVA, using EG as complexing agent can decrease the synthesis temperature and reduce the amount of complexing agent.

Experimental Procedure

Y_2NiMnO_6 nanoparticles were synthesized by using an EG sol-gel route. The raw chemicals for the synthesis were high purity Y_2O_3 , $MnCO_3$ and $Ni(NO_3)_2 \cdot 6H_2O$. Y_2O_3 , $MnCO_3$ powders were dissolved in nitric acid and mixed with high purity ethylene glycol. The ratios of hydroxyl groups of EG to metal ions (OH/M) are 1.5 and 5.2. After that, stoichiometric $Ni(NO_3)_2 \cdot 6H_2O$ was added to the solution. With continuous heating at 80°C, viscosity of the solution increased and finally became a

colloid and then the colloid was heated at 250°C for 2 h. After expansion and combustion of the colloid, Y_2NiMnO_6 precursors were prepared. Lastly, these precursors were calcined at 500-1000°C for 2 h in air.

Simultaneous differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis (STA449F3, Netzsch, Germany) were used to monitor decomposition and pyrolysis of the precursor at a heating rate of 10°C/min in static air. Crystalline phases were identified by using powder X-ray diffraction with $CuK\alpha$ radiation (Empyrean; PANalytical B.V., Netherlands). Environmental Scanning Electron Microscope (Quanta 200; FEI, Netherlands) was used to observe grain size and the morphology of Y_2NiMnO_6 powder.

Results and Discussion

Fig. 1 shows DSC-TG curves of the Y_2NiMnO_6 precursor (OH/M=5.2). The weight loss between room temperature and 400°C is 27.4%. A strong exothermic peak was observed between 260°C and 410°C in the DSC curve, accompanied by a sharp mass loss of about 20.5% in the TG curve which was caused by the decomposition of nitrates, the carbonization and volatilization of EG and the evolution of gases such as CO_2 . The second small exothermic peak around 870°C, with a small mass loss of 1.3% in the TG curve, is associated with oxidation of residual organics.

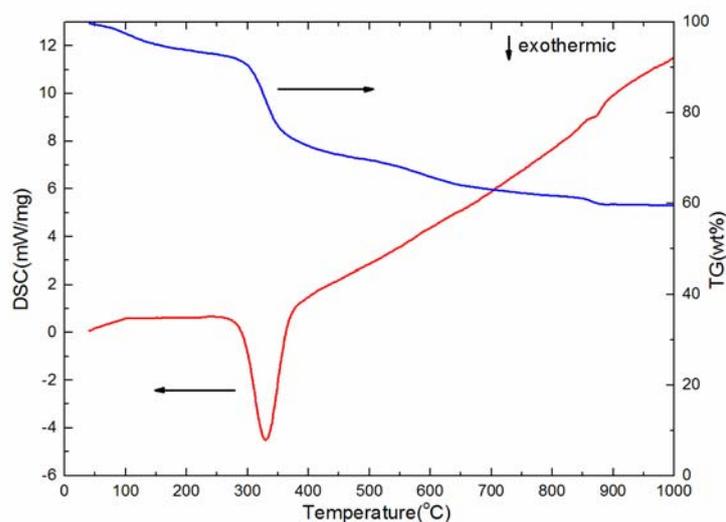


Fig. 1 DSC/TG curves of Y_2NiMnO_6 precursor (OH/M=5.2).

Fig. 2 shows ESEM images of Y_2NiMnO_6 nanoparticles. In Fig. 2a, Y_2NiMnO_6 (OH/M=1.5) were calcined at 900°C for 2h and the diameter of particles is approximately 200nm. While in Fig. 2b, the diameter of Y_2NiMnO_6 nanoparticles (OH/M=5.2), which were prepared at 800°C for 2h, is about 20-50nm. This size is quite close to the Y_2NiMnO_6 nanoparticles in the work of Maiti et al. [3].

Fig. 3 shows the XRD patterns of Y_2NiMnO_6 powder prepared by different OH/M and calcined at various temperatures. In Fig. 3a, we can notice that, from 500°C to 800°C, the peaks of Y_2O_3 and NiO are observed without other phases. When the calcination temperature increases to 900°C, the peaks from Y_2O_3 and NiO disappear, accompanied by the formation of Y_2NiMnO_6 . No other phases are observed at 900°C, so that the single-phase Y_2NiMnO_6 is prepared. In Fig. 3b, the OH/M increases from 1.5 to 5.2. From 500°C to 700°C, the patterns exhibit no change and the powder maintains discrete state. The peaks of Y_2NiMnO_6 first appear at 800°C without other phases, so that the single-phase Y_2NiMnO_6 is prepared at 800°C in this figure. Generally, hydroxyl groups provide a polymeric network to hinder cation mobility allowing local stoichiometry to be maintained and minimizing precipitation of unwanted phases in the sol-gel method [11,12]. So that many metals can be stabilized at the polymer via interactions with hydroxy groups. With adding hydroxy groups, formation of metal oxide becomes harder which is consistent with the XRD patterns. As Fig. 3 shown, more EG can effectively suppress the formation of metal oxide and reduce the synthesis temperature of Y_2NiMnO_6 . In the work of Maiti et al., single phase Y_2NiMnO_6 was obtained at 875°C, while EG

sol-gel method decrease this temperature to 800°C. Reducing calcination temperature is very desirable for the synthesis of compounds. On the other hand, for the same OH/M, the amount of EG needed for the synthesis is less than PVA. Moreover, in our recent work, the effects of increasing PVA content on the synthesis of Y_2NiMnO_6 were analyzed [13]. Though adding PVA content could also promote the formation of Y_2NiMnO_6 , it leads to the generation of $Y(OH)_3$, which still exists at 900°C. While adding EG content did not cause the formation of any impurity phase. All these evidences demonstrate that EG is better than PVA for the synthesis of Y_2NiMnO_6 .

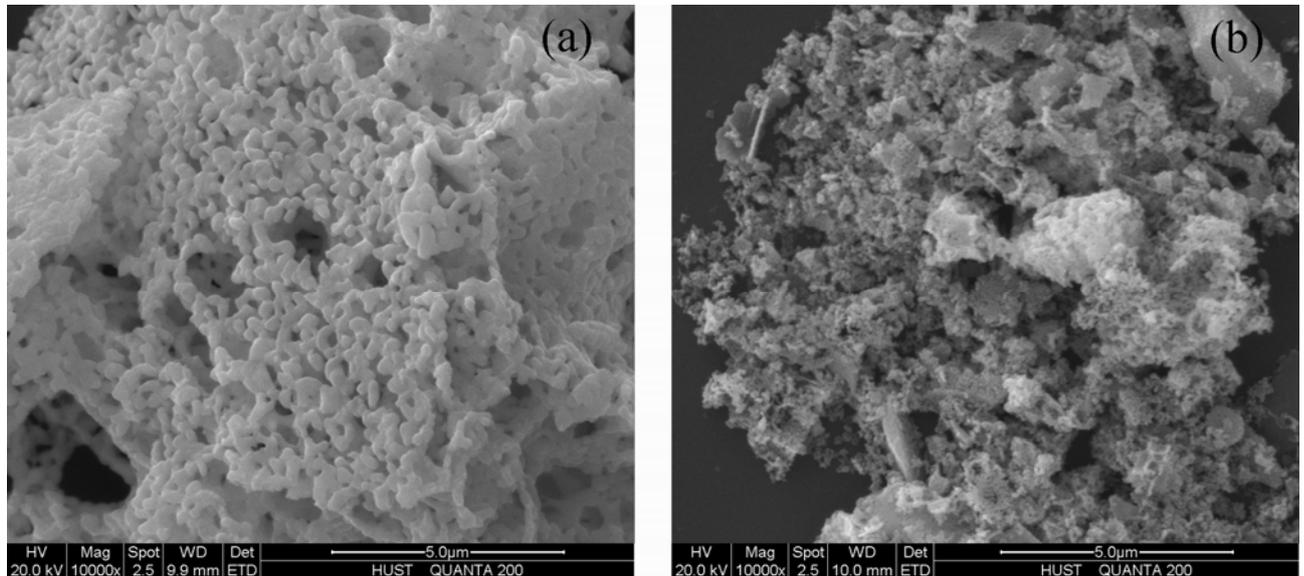


Fig. 2 ESEM micrographs of Y_2NiMnO_6 nanoparticles. (a) Y_2NiMnO_6 precursor (OH/M=1.5) calcined at 900°C, (b) Y_2NiMnO_6 precursor (OH/M=5.2) calcined at 800°C.

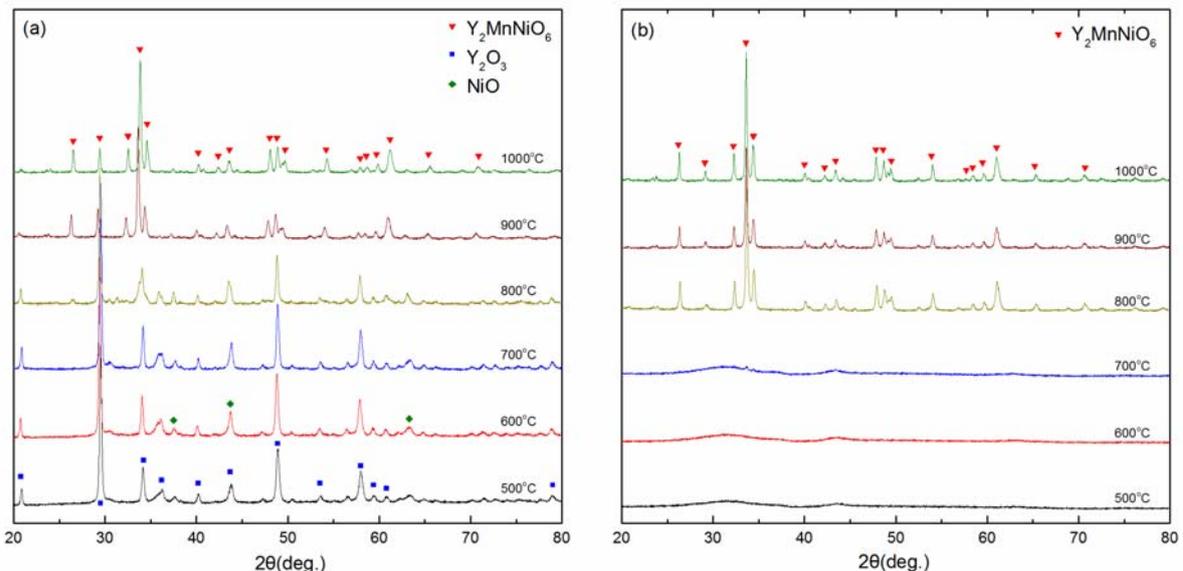


Fig. 3 XRD patterns of Y_2NiMnO_6 precursor calcined at various temperatures for 2 h. (a) OH/M = 1.5, (b) OH/M = 5.2.

Conclusion

Y_2NiMnO_6 nanoparticles were synthesized via an ethylene glycol sol-gel method. Phase pure Y_2NiMnO_6 powders of 20-50nm in diameter were obtained at 800°C for 2 h, without the formation of any intermediate phase. XRD analysis exhibits that more EG can effectively suppress the formation of metal oxide and promote the synthesis of Y_2NiMnO_6 . Compared to PVA, using EG as complexing agent can decrease the synthesis temperature of Y_2NiMnO_6 and reduce the amount of complexing agent. Therefore, EG is preferable to PVA for the synthesis of Y_2NiMnO_6 via sol-gel method.

References

- [1] S. Kumar, G. Giovannetti, J.V.D. Brink and S. Picozzi: Phys. Rev. B Vol. 82 (2010), p. 134429
- [2] M.H. Tang, Y.G. Xiao, B. Jiang, J.W. Hou, J.C. Li and J. He: Appl. Phys. A Vol. 105 (2011), p. 679
- [3] R.P. Maiti, S. Dutta, M. Mukherjee, M.K. Mitra and D. Chakravorty: J. Appl. Phys. Vol. 112 (2012), p. 044311.
- [4] R.B.M. Filho, A.P. Ayala and C.W.A. Paschoal: Appl. Phys. Lett. Vol. 102 (2013), p. 192902
- [5] T. Goto, T. Kimura, G. Lawes, A. Ramirez and Y. Tokura: Phys. Rev. Lett. Vol. 92 (2004), p. 257201
- [6] K.F. Wang, J.M. Liu and Z.F. Ren: Adv. Phys. Vol. 58 (2009), p. 321
- [7] M.P. Singh, K.D. Truong and P. Fourimen: J. Appl. Phys. Vol. 107 (2010), p. 09D917
- [8] C.N. Li, B.X. Liu, Y.Y. He, C. Lv, H. He and Y.B. Xu: J. Alloys Comp. Vol. 590 (2014), p. 541
- [9] S.W. Cheong and M. Mostovoy: Nature Mater. Vol. 6 (2007), p. 13
- [10] R. Ramesh and N.A. Spaldin: Nature Mater. Vol 6 (2007), p. 21
- [11] M.A. Gulgun, M.H. Nguyen and W.M. Kriven: J. Am. Ceram. Soc. Vol. 82 (1999), p. 556
- [12] J.S. Feng, T. Liu, Y.B. Xu, J.Y. Zhao and Y.Y. He: Ceram. Int. Vol. 37 (2011), p.1203
- [13] M. Lei, Z. He, Z.J. Feng and Y.B. Xu: J. Sol-gel Sci. Techn. Vol. 76 (2015), p. 204