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# In situ synthesis of multiferroic $YMnO_3$ ceramics by SPS and their characterization

Yan Ma, Yong Jun Wu, Xiang Ming Chen *, Ji Peng Cheng, Yi Qi Lin

*Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China*

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**Abstract**

Dense $YMnO_3$ multiferroic ceramics were prepared by a novel technique of in situ SPS (spark plasma sintering) combined with annealing, and both the dielectric and magnetic characterizations were conducted. Compared with the conventional ceramic process, the synthesis process was greatly simplified, and dense $YMnO_3$ ceramics with uniform microstructures were achieved at a relatively low temperature in very short time. Dielectric characteristics of dense $YMnO_3$ ceramics were well evaluated over broad temperature and frequency ranges. An obvious dielectric relaxation was observed in the low temperature range and a dielectric step was detected in the higher temperature range. Systemic magnetism studies of the present $YMnO_3$ ceramics indicated a weak ferromagnetic characteristic in the temperature lower than the antiferromagnetic transition temperature ($T_N$).


*Keywords:* A. Sintering; C. Dielectric properties; C. Magnetic properties; $YMnO_3$ ceramics

## 1. Introduction

In the past few years, multiferroic materials have attracted the increasing scientific and technological interest because of their unusual properties. Ferroelectricity and magnetic properties coexistence with in this class of materials, and the two order can strongly coupled, which makes it has potential applications in memory and logic device [1,2]. As a member of this rare class multiferroics, hexagonal $RMnO_3$ (R = Ho, Er, Tm, Yb, Lu, Sc and Y) has attracted much scientific attention. These materials are known as low-temperature ferroelectromagnets and have potential use for application such as volatile ferroelectricity memory because of their fairly high ferroelectric transition temperature [3–7].

$YMnO_3$ is one of the most intensively studied hexagonal manganates. It belongs to the space group of $P6_3cm$, with a high ferroelectric transition temperature ($T_C \sim 900$ K) and a low antiferromagnetic transition temperature ($T_N \sim 70$ K) [8–14]. Recent studies have revealed that, there is a coupling between the ferroelectric and antiferromagnetic order in $YMnO_3$, and direct and strong coupling evidences have also been detected [7,10,15]. However, in the previous studies, $YMnO_3$ ceramics were mainly prepared by conventional solid state reaction [10–14]. In such synthesis route, high sintering temperature and long calcining and sintering time were required to get qualified ceramics dense enough for electric characterization. During the sample preparation, intermediate grindings were also needed to eliminate the secondary phases. So the preparation cycles were very long and much complex, and therefore searching for a rapid and simple synthesis method is necessary. In addition, only a few studies are about the dielectric behaviors of $YMnO_3$ ceramics, and the dielectric relaxations of $YMnO_3$ ceramics in wide frequency ranges and temperature range around room temperature have not been well investigated.

In recent years, spark plasma sintering (SPS) has been widely used as a rapid preparation method to prepare composites and ceramics [16–21]. It is a newly developed sintering technology that makes use of microscopic electrical discharges between particles under pressure and allows for quick densification. In addition, a relatively low sintering temperature and a short sintering time are the most attractive features.

In the present work, an in situ SPS technique combined with annealing is used to prepare multiferroic $YMnO_3$ ceramics, and this synthesis approach has not been used in previous work on

* Corresponding author. Tel.: +86 571 87952112; fax: +86 571 87952112.
*E-mail address:* xmchen59@zju.edu.cn (X.M. Chen).

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$YMnO_3$. The dielectric characteristics of $YMnO_3$ are evaluated over broad temperature (123–573 K) and frequency (10 Hz–1 MHz) ranges to determine the dielectric behavior, and the magnetic properties are also investigated together with the microstructures.

## 2. Experimental

The raw materials were analytical-grade $Y_2O_3$ (99.99%, Shanghai Yuelong New Materials Co. Ltd., Shanghai, China) and $Mn_2O_3$ (98%, Johnson Matthey Company, MA). Stoichiometric amounts of oxide compounds were carefully weighted and mixed thoroughly and ground in anhydrous alcohol for 3 h to get homogeneous mixture. After the mixture were dried, some of them were put into a graphite die and sintered at 1000 °C for 5 min in a vacuum of 6 Pa with an SPS apparatus (SPS-1050, SPS SYNTEX Inc., Kanagawa, Japan). During the period of heating and soaking, a pressure of 30 MPa was applied to the sample. The heating rate was 100 °C/min from room temperature to 900 °C, 40 °C/min from 900 to 980 °C and 20 °C/min from 980 to 1000 °C. All the in situ synthesized samples by SPS were polished and then annealed at 1200 °C for 1 h in air to ensure their homogeneity.

Density of $YMnO_3$ ceramics after annealing was measured by the Archimedes method. The crystalline phases of the as-sintered and annealed $YMnO_3$ ceramics were characterized by X-ray diffraction (D/MAX 2550/PC, Rigaku, Tokyo, Japan) using Cu Kα radiation. The microstructures were evaluated on the polished surfaces of $YMnO_3$ ceramics after annealing with a field emission scanning electron microscopy (S-4800, Hitachi, Tokyo, Japan). The polished surfaces were thermally etched at 1175 °C for 1 h before observation. Both the dielectric and magnetic characterizations were conducted for $YMnO_3$ ceramics after annealing. The dielectric characteristics were measured with a broadband dielectric spectrometer (Turnkey Concept 50, Novocontrol Technologies, Germany) in a broader range of temperature (123–573 K) and frequency (10–1,000,000 Hz), where the silver paste was adopted as the electrodes. The magnetic properties were evaluated by the Quantum Design Polyfunctional Physical Property Measurement System (PPMS-9, Quantum Design, TN).

## 3. Results and discussions

Fig. 1 shows the sintering behavior of the $YMnO_3$ ceramics in situ synthesized by spark plasma sintering. A very small thermal expansion is observed when the temperature increases from room temperature to 330 °C, and then a relatively large thermal expansion takes place until approximately 640 °C. The shrinkage initiates at about 800 °C, and it increases rapidly when the temperature increases up to 960 °C. Subsequently, almost no shrinkage is observed until the soaking period, suggesting that the densification almost completes at temperature below 1000 °C. After the sample was sintered at 1000 °C for 30 s, it begins to expanse. It should be noted that the densification temperature of in situ SPS synthesis is about 300–525 °C lower than that of the conventional solid state sintering

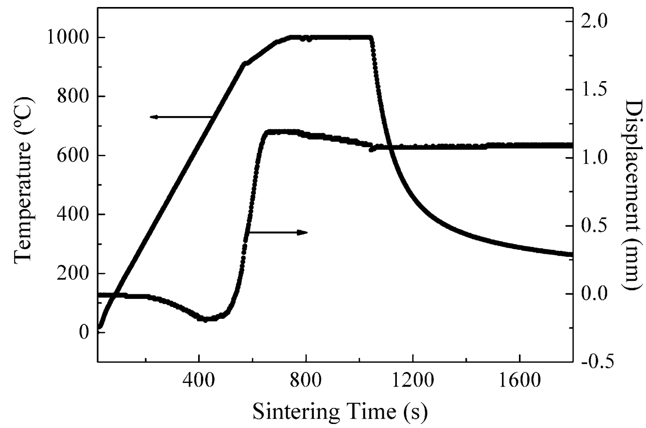


Fig. 1. Shrinkage curve and sample's temperature as a function of sintering time in the process of in situ spark plasma sintering of $YMnO_3$ ceramics.

method used in the previous studies [10–14]. This should be attributed to the microscopic electric discharge between particles and the application of mechanical pressure during the SPS. These two merits of SPS play important roles in lowering sintering temperature and shortening sintering time. During the initial period of SPS, the microscopic electric discharges between particles are said to clean the surfaces of particles from the absorbed species and activate the surfaces. The cleaned and activated surfaces enhance the diffusion, promote transfer of material, and densify the sample. One the other hand, the application of mechanical pressure aids in removing pores and enhancing the diffusion during the SPS.

Fig. 2(a) shows the XRD pattern of dense samples in situ synthesized ceramics by spark plasma sintering at 1000 °C for 5 min. The hexagonal $YMnO_3$ is synthesized as the major phase, and a small amount of secondary phases ($Y_2O_3$ and MnO) is also detected. However, after the subsequent annealing at a high temperature of 1200 °C for a short time of 1 h, the secondary phases are almost removed. As shown in Fig. 2(b), dense $YMnO_3$ ceramics with a single hexagonal phase in space group $P6_3cm$ is obtained after annealing. Compared with the conventional solid synthesis route used in previous studies, the

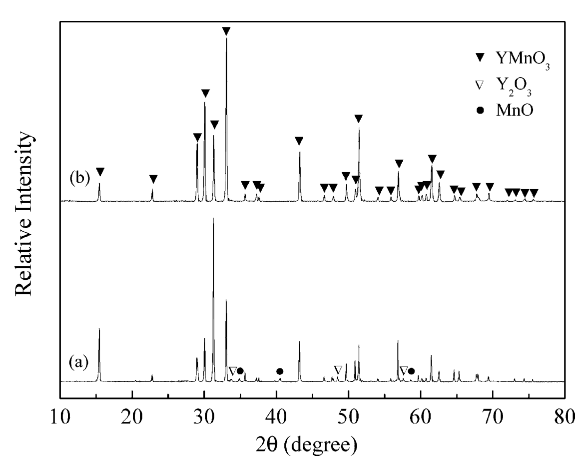


Fig. 2. XRD patterns of $YMnO_3$ ceramics (a) in situ synthesized by spark plasma sintering at 1000 °C for 5 min; (b) subsequently annealed at 1200 °C in air for 1 h.

present synthesis method incorporate the reaction synthesis with the densification process, so the prepare cycle is greatly simplified. Moreover, this in situ SPS synthesis combined with subsequent annealing has rarely been reported to prepare multiferroic ceramics before.

The density of the as-prepared sample is above 94% of the theoretical density according to the measuring results of the Archimedes method. Fig. 3 shows the SEM micrograph on the thermally etched surfaces of $YMnO_3$ ceramics sintered by SPS combined with subsequent annealing. The dense ceramics are well crystallized with the fine grain size. Small amount of crack was observed in the thermally etched surfaces, and this phenomenon is common in $YMnO_3$-based ceramics [12,13].

Fig. 4 shows the temperature dependence of dielectric properties for $YMnO_3$ ceramics at different frequencies (10 Hz–1 MHz). An obvious dielectric relaxation is observed at the temperature range from 160 to 300 K, and a peak in the $\tan\delta$-$T$ curve is observed, which shifts toward higher temperature with increasing frequency. A dielectric constant step ($\varepsilon' \sim 500$) is detected on the $\varepsilon'$-$T$ curve in the medium temperature range (300–420 K), and it is weakened at high frequencies. In the higher temperature range, the dielectric constant increases rapidly and the corresponding abnormity in the $\tan\delta$-$T$ curve is also detected. In the whole testing temperature range, strong frequency dispersion is indicated.

In order to get a deep insight into the low temperature dielectric relaxation, the frequency dependence of the $\tan\delta$ peak temperature has been studied. As shown in Fig. 5, the variation relation obeys the Arrhenius law,

$$f = f_0 \exp\left(\frac{-E_a}{kT}\right),$$

where $f_0$ is the preexponential term, $E_a$ is the activation energy, and $k$ is Boltzmanns constant. The fitting parameters are obtained as $E_a = 0.45$ eV and $f_0 = 8.67 \times 10^{12}$ Hz. Therefore, the low temperature dielectric relaxation in $YMnO_3$ ceramics is a thermally activated process.

Fig. 6(a) shows the temperature dependence of ZFC and FC magnetic susceptibility for the as-prepared $YMnO_3$ ceramics in a field of 0.1 T. The divergence of the ZFC and FC susceptibility is observed below 69 K, the antiferromagnetic transition temperature ($T_N$) of $YMnO_3$. In addition, below $T_N$, ZFC magnetization reaches a maximum value at around 40 K and decreases at the lower temperatures. On the other hand, the FC magnetization undergoes an abrupt increase tending toward a saturated value, suggesting weak ferromagnetic effect. Similar to the previous results for $ScMnO_3$ [5], the second abnormity below $T_N$ of $YMnO_3$ corresponds to a spin

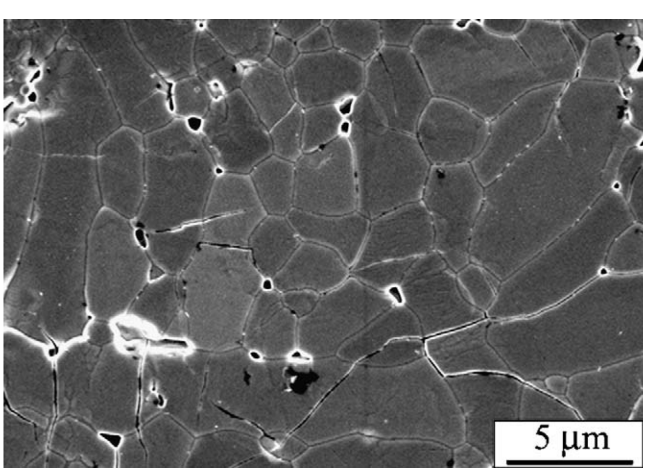


Fig. 3. SEM micrographs on the polished and thermally etched surfaces of $YMnO_3$ ceramics after annealing.

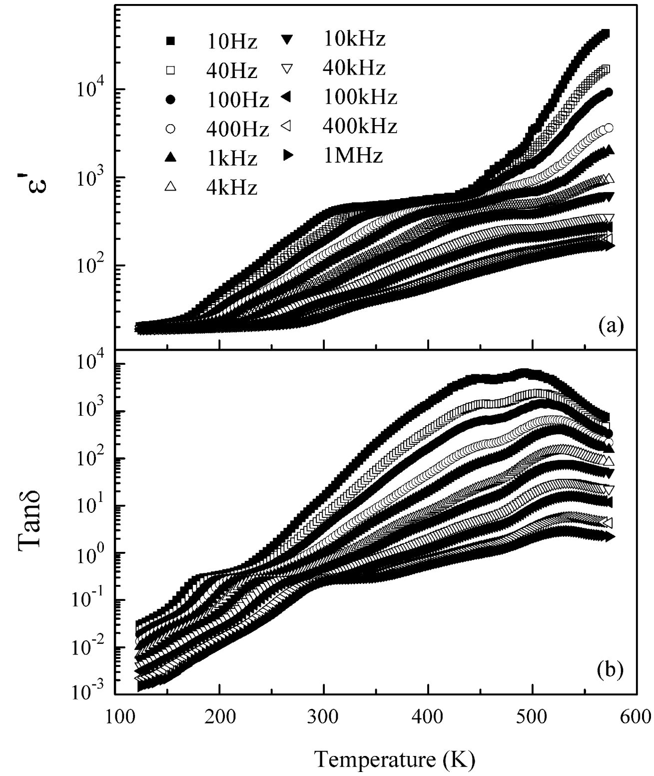


Fig. 4. Temperature dependence of (a) real dielectric permittivity $\varepsilon'$ and (b) dielectric loss $\tan\delta$ of $YMnO_3$ ceramics at different frequencies between 10 Hz and 1 MHz.

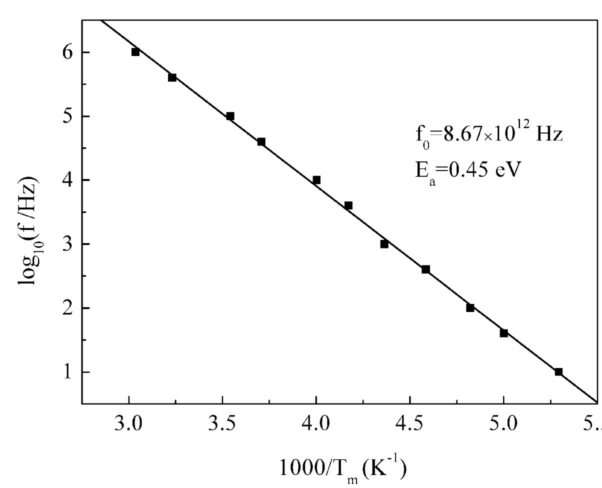


Fig. 5. Frequency dependence of $\tan\delta$ peak temperature for low temperature dielectric relaxation in $YMnO_3$ ceramics. Symbols are experimental points and solid line is Arrhenius fitting.

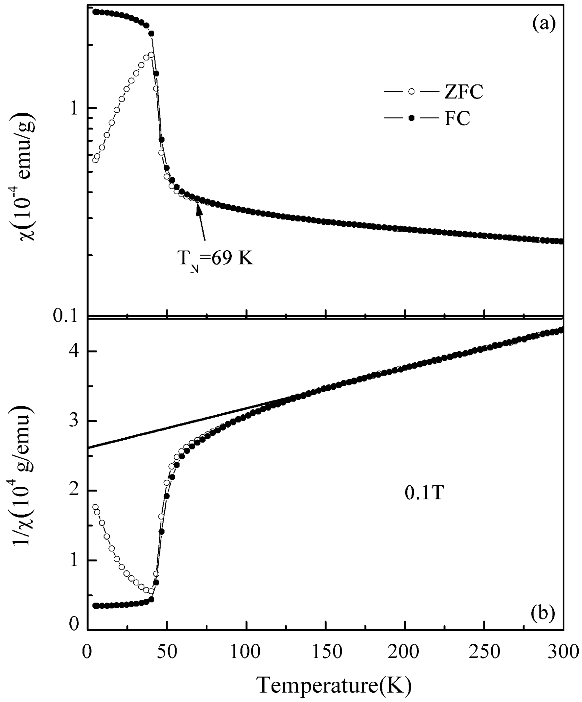


Fig. 6. (a) Temperature dependence of ZFC and FC magnetic susceptibility of $YMnO_3$ ceramics in a field of 0.1 T. (b) The inverse susceptibility vs temperature. The solid line is the high-$T$ Curie–Weiss fit.

reorientation, revealing a transition to another magnetic phase. The reciprocal ZF and ZFC magnetic susceptibility as a function of temperature is shown in Fig. 6(b). The reciprocal susceptibility has a linear dependence above 142 K. The data is fitted by Curies–Weiss law, and the Curies–Weiss ($\theta_P$) is found to be −465.19 K. This confirms the antiferromagnetic coupling between Mn ions and the antiferromagnetic nature is attributed to the super exchange interaction between the Mn sites.

Fig. 7 shows the M–H hysteresis loops of $YMnO_3$ ceramics at different temperatures. Above 40 K, no magnetic hysteresis loops are detected in the magnetic-ordered temperature range, suggesting the antiferromagnetic nature of $YMnO_3$. In addition, an obvious magnetic hysteresis loop is observed at 25 K, with remnant magnetization ($M_r$) of 0.24 emu/g and a coercive field

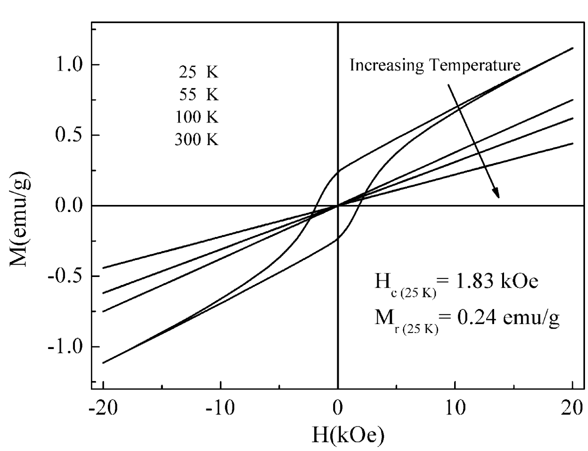


Fig. 7. M–H hysteresis loops of $YMnO_3$ ceramics at different temperatures.

($H_c$) of 1.83 kOe. It indicates a weak ferromagnetic characteristic, in good agreement with the susceptibility measurement results. This differs from the previous magnetism studies of $YMnO_3$, which showed that spontaneous magnetization and hysteresis phenomenon all vanish below $T_N$ [5]. This difference is very interesting, and further investigation is needed for details.

## 4. Conclusions

$YMnO_3$ multiferroic ceramics were successfully prepared in situ by SPS (Spark Plasma Sintering) followed by annealing. Compared with conventional ceramics synthesis route, the synthesis process was greatly simplified, and dense $YMnO_3$ ceramics with uniform microstructures were achieved in a very short time at relatively low temperature. An obvious dielectric relaxation was observed in the low temperature range and a dielectric step was detected in the higher temperature range. The low temperature dielectric relaxation in $YMnO_3$ ceramics is a thermally activated process. Systemic magnetism studies of the present $YMnO_3$ ceramics indicated a weak ferromagnetic characteristic in the temperature lower than the antiferromagnetic transition temperature ($T_N$).

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## References

[1] Y.-H. Chu, L.W. Martin, M.B. Holcomb, M. Gajek, S.-J. Han, Q. He, N. Balke, C.-H. Yang, D. Lee, W. Hu, Q. Zhan, P.-L. Yang, A. Fraile-Rodriguez, A. Scholl, S.X. Wang, R. Ramesh, Electric-field control of local ferromagnetism using a magnetoelectric multiferroic, Nat. Mater. 7 (2008) 478–482.

[2] R. Ramesh, N.A. Spaldin, Multiferroic: progress and prospects in thin films, Nat. Mater. 6 (2007) 21–29.

[3] J. Hemberger, F. Schrettle, A. Pimenov, P. Lunkenheimer, V.Yu. Ivanov, A.A. Mukhin, A.M. Balbashov, A. Loidl, Multiferroic phases of $Eu_{1-x}Y_xMnO_3$, Phys. Rev. B 75 (2007) 035118.

[4] T. Katsufuji, S. Mori, M. Masaki, Y. Moritomo, N. Yamamoto, H. Takagi, Dielectric and magnetic anomalies and spin frustration in hexagonal $RMnO_3$ (R = Y, Yb, and Lu), Phys. Rev. B 64 (2001) 104419.

[5] A. Munoz, J.A. Alonso, M.J. Martinez-Lope, M.T. Casais, J.L. Martinez, M.T. Fernandez-Diaz, Magnetic structure of hexagonal $RMnO_3$ (R = Y, Sc): thermal evolution from neutron powder diffraction data, Phys. Rev. B 62 (2000) 9498–9510.

[6] Y. Aikawa, T. Katsufuji, T. Arima, K. Kato, Effect of Mn trimerization on the magnetic and dielectric properties of hexagonal $YMnO_3$, Phys. Rev. B 71 (2005) 184418.

[7] S. Lee, A. Pirogov, J.H. Han, J.-G. Park, A. Hoshikawa, T. Kamiyama, Direct observation of a coupling between spin, lattice and electric dipole moment in multiferroic $YMnO_3$, Phys. Rev. B 71 (2005) 180413 (R).

[8] U. Adem, A.A. Nugroho, A. Meetsma, T.T.M. Palstra, Ferroelectric displacements in multiferroic Y(Mn, Ga)$O_3$, Phys. Rev. B 75 (2007) 014108.

[9] B.B. Van Aken, T.T.M. Palstra, A. Filippetti, N.A. Spaldin, The origin of ferroelectricity in magnetoelectric $YMnO_3$, Nat. Mater. 3 (2004) 164–170.

[10] Z.J. Huang, Y. Cao, Y.Y. Sun, Y.Y. Xue, C.W. Chu, Coupling between the ferroelectric and antiferromagnetic orders in $YMnO_3$, Phys. Rev. B 56 (1997) 2623–2626.

[11] D.G. Tomuta, S. Ramakrishnan, G.J. Nieuwenhuys, J.A. Mydosh, The magnetic susceptibility, specific heat and dielectric constant of hexagonal $YMnO_3$, $LuMnO_3$, and $ScMnO_3$, J. Phy.: Condens. Matter. 13 (2001) 4543–4552.

[12] C. Moure, J.F. Fernandez, M. Villegas, P. Duran, Non-ohmic behaviour and switching phenomena in $YMnO_3$-based ceramic materials, J. Eur. Ceram. Soc. 19 (1999) 131–137.

[13] G. Lescano, F.M. Figueiredo, F.M.B. Marques, J. Schmidt, Synthesis and electrical conductivity of $Y_{1-x}Mn_{1-y}O_{3-\delta}$, J. Eur. Ceram. Soc. 21 (2001) 2037–2040.

[14] M.C. Sekhar, N.V. Prasad, Dielectric, impedance, magnetic and magnetoelectric measurements on $YMnO_3$, Ferroelectrics 345 (2006) 45–57.

[15] M. Fiebig, Th. Lottermoser, D. Fröhlich, A.V. Goltsev, R.V. Pisarev, Observation of coupled magnetic and electric domains, Nature 419 (2002) 818–820.

[16] X.T. Wang, N.P. Padture, H. Tanaka, Contact-damage-resistant ceramic/single-wall carbon nanotubes and ceramics/graphite composites, Nat. Mater. 3 (2004) 539–544.

[17] T. Isobe, K. Daimon, T. Sato, T. Matsubara, Y. Hikichi, T. Ota, Spark plasma sintering technique for reaction sintering of $Al_2O_3$/Ni nanocomposite and its mechanical properties, Ceram. Int. 34 (2008) 213–217.

[18] T. Takeuchi, M. Tabuchi, H. Kageyama, Y. Suyama, Preparation of dense $BaTiO_3$ ceramics with submicrometer grains by spark plasma sintering, J. Am. Ceram. Soc. 82 (1999) 939–943.

[19] Y. Gao, Y.J. Wu, X.M. Chen, J.P. Cheng, Y.Q. Lin, Y. Ma, Dense $YMn_2O_5$ ceramics prepared by spark plasma sintering, J. Am. Ceram. Soc. 91 (2008) 3728–3730.

[20] Y.F. Zhang, J.X. Zhang, Q.M. Lu, Synthesis of highly textured $Ca_3Co_4O_9$ ceramics by spark plasma sintering, Ceram. Int. 33 (2007) 1305–1308.

[21] Y. Shimojo, R. Wang, Y.J. Shan, H. Izui, M. Taya, Dielectric characters of $0.7Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.3PbTiO_3$ ceramics fabricated at ultra-low temperature by the spark-plasma-sintering method, Ceram. Int. 34 (2008) 1449–1452.