www.amlett.com, www.amlett.org, DOI: 10.5185/amlett.2013.fdm.06

Synthesis of $(Ag_{0.5}Fe_{0.5})TiO_3$ nanocrystalline powder using stearic acid gel method

Sandeep Kumar[1], L. K. Sahay[1], Anal K. Jha[2], K. Prasad[3*]

[1]*University Department of Chemistry, T.M. Bhagalpur University, Bhagalpur 812007, India*
[2]*Aryabhatta Centre for Nanoscience and Nanotechnology, Aryabhatta Knowledge University, Patna 800005, India*
[3]*University Department of Physics, T.M. Bhagalpur University, Bhagalpur 812007, India*

[*]Corresponding author. E-mail: k.prasad65@gmail.com

Received: 06 January 2013, Revised: 12 March 2013 and Accepted: 17 March 2013

ABSTRACT

A low-cost, green and reproducible stearic acid assisted synthesis of nanocrystalline powder of $(Ag_{0.5}Fe_{0.5})TiO_3$ (n-AFT) is reported. X-ray, FTIR, energy dispersive X-ray and transmission electron microscopy analyses are performed to ascertain the formation of n-AFT. Rietveld refinement of X-ray data indicated the formation of a single-phase monoclinic structure. Individual nanoparticles almost spherical in shape having the sizes of 5-14 nm are found. The mechanism of nanotransformation for the soft-chemical synthesis of n-AFT has been explained using nucleation and growth theory. UV-visible study revealed the surface plasmon resonance at 318 nm. Dielectric study revealed a low value of dielectric constant (= 177) and dielectric loss (= 0.013) at 1 kHz. Magnetic studies have been carried out using vibration sample magnetometer, which indicated the possibility of magnetoelectric coupling. Copyright © 2014 VBRI press.

Keywords: Green synthesis; stearic acid gel method; $(Ag_{0.5}Fe_{0.5})TiO_3$; nanoparticle; dielectric properties.

Sandeep Kumar was born on Feb. 02, 1981. He obtained his B.Sc. (Hons.) in Chemistry from Magadh University, Bodh Gaya and M.Sc. (Chemistry) degree in 2004 from University of Delhi, Delhi, India. Presently, he is carrying out his research work leading to the Ph.D. degree at University Department of Chemistry, T.M. Bhagalpur University, Bhagalpur under the joint supervision of Prof. L.K. Sahay and Dr. K. Prasad.

L. K. Sahay, M.Sc., Ph.D. was Associate Professor in the University Department of Chemistry, Tilkamanjhi Bhagalpur University, Bhagalpur, India and retired in 2010. He has successfully supervised four Ph.D. students and two more are pursuing their works for the same. He has a dozen of research articles to his credit. His current research interest includes the natural product chemistry and soft-chemical synthesis of advanced materials.

Anal K. Jha, M.Sc., M. Phil., M.Tech., Ph.D. is working as Establishment cum Scientific Officer in Aryabhatta Centre for Nanoscience and Nanotechnology, Aryabhatta Knowledge University, Patna, India He is on lien from T.M. Bhagalpur University, Bhagalpur. He has published more than 40 papers in reputed scientific journals and book chapters on Nanotechnology. His current research activities are concerned with the Natural Product Chemistry and Biologically assisted synthesis of different nanomaterials. He is an active referee of various international journals. He has presented papers in many national/international conferences and delivered invited lectures.

K. Prasad, M.Sc., PGDCA, M.Tech., Ph.D. is Associate Professor in University Department of Physics, T.M. Bhagalpur University, Bhagalpur, India. He also served SLIET, Longowal (Punjab) and Central University of Jharkhand, Ranchi, India. His current research interests include synthesis and characterizations of eco-friendly friendly ferroelectric/piezoelectric ceramics and ceramic-polymer composites and advanced nanomaterials. He has authored/co-authored over 150 publications including a book, three book chapters and three XRD-reference data in ICDD. He has presented papers at major national and international conferences and delivered invited lectures. Dr. Prasad has successfully guided six Ph.D. students. He is an active referee of various international journals.

Introduction

Materials belonging to the perovskite ABO_3–type structure have attracted widespread scientific and technological interest over the past few decades [**1, 2**]. Lead-bearing compounds such as - $PbTiO_3$, $Pb(Zr,Ti)O_3$, $Pb(Mg_{1/3}Nb_{2/3})O_3$, *etc.* are widely used for capacitor, pyroelectric and piezoelectric applications. The searches for alternative environment friendly lead-free materials, for such applications have become the focal theme of present day's research [**3-9**]. Among them sodium bismuth titanate,

$(Na_{0.5}Bi_{0.5})TiO_3$ is considered to be an excellent candidate as a key material of lead-free piezoelectric ceramic, which shows strong ferroelectric properties. Recent works on the identical compound $(Ag_{0.5}Bi_{0.5})TiO_3$ also showed excellent electrical properties [**10, 11**]. During the past few years, several investigations have been made to study the electrical properties of $(Ag_{0.5}Bi_{0.5})TiO_3$–based solid solutions for their possible applications in electronic devices [**12-15**]. One such materials in this series is perovskite $(Ag_{0.5}Fe_{0.5})TiO_3$. The material is mechanically tough and lead-free, ensure environment-friendly applications. Also, it is expected that this compound may show magnetoelectric effect due to the iron-content.

An extensive literature survey indicated that no attempt, to the authors' knowledge, has so far been made to study the nanocrystalline powder of $(Ag_{0.5}Fe_{0.5})TiO_3$. Accordingly, the present work reports the structural (X-ray and its Rietveld analysis), transmission electron microscopy, Fourier transformed infrared, UV-Vis, dielectric, and magnetic studies of nanocrystalline $(Ag_{0.5}Fe_{0.5})TiO_3$ (abbreviated hereafter n-AFT). Also the mechanism of nanotransformation for the soft-chemical synthesis of n-AFT has been explained using nucleation and growth theory.

Experimental

Synthesis of nanocrystalline $(Ag_{0.5}Fe_{0.5})TiO_3$ powder

A stearic acid gel method was used to prepare $(Ag_{0.5}Fe_{0.5})TiO_3$ powder. Steric acid was dissolved into deionized water and the value of the pH of the solution was adjusted to 7–9 by adding the appropriate amount of ammonia solution. Titanium (IV) n-Butoxide (Across, USA) was to this solution which was vigorously stirred and heated at about 70ºC for 1 h on a hot plate. This solution was then added with aqueous solutions of $AgNO_3$ (Merck, Germany) (40%) and $Fe(NO_3)_3$ (Across, USA) (50%) and stirred at 80ºC for 2 h. Further, the precursor solution was dehydrated at 100ºC to form a sol. Subsequent heating at a higher temperature of 160ºC yielded a gel. The gel initially started to swell and filled the beaker producing a foamy precursor. The gel was pulverized and then heated at 300ºC for 2 h in air to get carbonaceous mass. Finally carbonaceous mass were calcined at 700ºC for 5 h. Completion of the reaction and formation of the desired compound were checked by X-ray diffraction technique. The as-calcined powder was compacted into thin (~1.5 mm) cylindrical disks with an applied uniaxial pressure of 650 MPa. The pellets were then sintered in air atmosphere at 750^{o}C for 3 h in alumina crucible.

Characterization

X-ray diffraction (XRD) data of n-AFT were obtained using an X-ray diffractometer (XPERT-PRO, PW3050/60) with CuK_α radiation (λ = 1.5406Å) between the angles 20° and 80°. Full Prof 2012 software was used to find the dimensions of unit cell, *hkl* values and space group using the TREOR program. TEM micrographs and energy dispersive X-ray (EDX) pattern were obtained using High resolution Bruker transmission electron microscope. The Fourier Transformed Infrared (FTIR) spectrum of n-AFT was collected in the transmission mode using an Alpha-T Bruker FTIR spectrophotometer in the range of 400-4000 cm^{-1}. The absorption spectrum was obtained by a computer interfaced UV-visible spectrophotometer (DR 5000, Hach, Germany). A sintered pellet was polished and electroded with air-drying silver paste (SPI supplier, USA) to measure the electrical properties. Dielectric measurement was carried out using a computer-interfaced LCR Hi-Tester (HIOKI 3532-50, Japan). Magnetization behavior was studied by Vibrating sample magnetometer (PAR-155).

Results and discussion

Rietveld refinement of the XRD data of n-AFT was carried out, selecting the space group $P2/m$. The XRD (observed, calculated and difference XRD profiles) pattern of n-AFT synthesized using stearic acid gel method is presented in **Fig. 1**. It can be seen that the profiles for observed and calculated one are perfectly matching (χ^2 = 0.887). The profile fitting procedure adopted was minimizing the χ^2 function. The XRD analyses indicated that n-AFT has a monoclinic unit cell. The crystal data and refinement factors of n-AFT obtained from XRD data are depicted in **Table 1**. Further, the XRD patterns showed the presence of broad peaks which may be due the nanosizing effect in n-AFT.

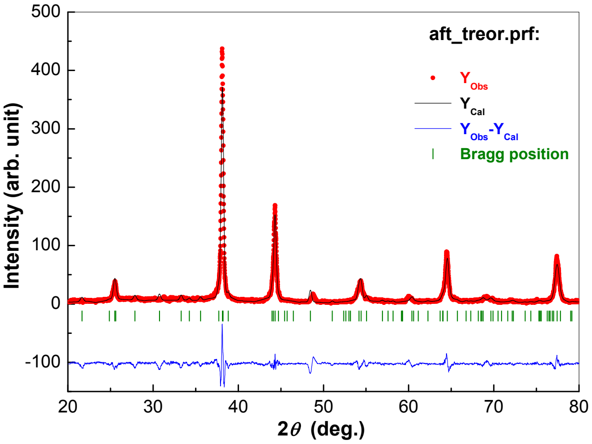

Fig. 1. Rietveld refined XRD pattern of nanocrystalline powder of $(Ag_{0.5}Fe_{0.5})TiO_3$ in space group $P2/m$. Symbols represent observed data points and solid lines their Rietveld fit.

Fig. 2 shows the EDX pattern and TEM image (inset) of n-AFT. All the peaks in the EDX pattern have perfectly assigned to the elements present in $(Ag_{0.5}Fe_{0.5})TiO_3$. This clearly indicated the successful synthesis and purity of chemical composition of n-AFT. The TEM micrographs clearly illustrate individual nanoparticles which are almost spherical in shape having the sizes between 5-14 nm. The difference in size may possibly be due to the agglomeration of individual nanoparticles. This clearly indicates the formation of nanocrystalline AFT. Present nanotransformation mechanism could be understood using the nucleation and growth theory to form a spherical particle. According to which the overall free energy change (ΔG) must be overcome. ΔG is the indicative of sum of the free energy due to the formation of a new volume and the free energy due to the new surface created:

$$\Delta G = -\tfrac{4}{V}\pi r^3 k_B T \ln(S) + 4\pi r^2 \gamma$$

where V, r, k_B, S and γ are the molecular volume of the prepared species, radius of the nucleus, Boltzmann constant, saturation ratio and surface free energy per unit surface area, respectively. It follows from equation that a decrease in γ or an increase in S is helpful in the formation of nanoparticles (n-AFT, in this case). In the present soft-chemical method, the interactions of steric acid with Ag^+, Fe^{3+} and Ti^{4+} ions in stoichiometric ratio made it possible to lower down the surface energy. Therefore, the effect of such soft-chemical ambiance could have made the reaction to occur more easily.

Table 1. The crystal data and refinement factors of nanocrystalline $(Ag_{0.5}Fe_{0.5})TiO_3$ powder obtained from X-ray powder diffraction data.

Crystallographic data		**Description of parameters:**
Formula	$(A_{0.5}Fe_{0.5})TiO_3$	R_p (profile factor) = $100[\Sigma\lvert y_i\text{-}y_{ic}\rvert/\Sigma\lvert y_i\rvert]$, where y_i is the observed intensity and y_{ic} is the calculated intensity at the i^{th} step.
Crystal System	Monoclinic	
Space group (No.)	$P2/m$ (10)	
a (Å)	6.9548	
b (Å)	3.1982	R_{wp} (weighted profile factor) = $100[\Sigma\omega_i\lvert y_i\text{-}y_{ic}\rvert^2/\Sigma\omega_i(y_i)^2]^{1/2}$, where and is variance of the observation.
c (Å)	4.1034	
β (°)	91.5840	
V (Å^3)	91.2368	R_{exp} (expected weighted profile factor) = $100[(n\text{-}p)/\Sigma\omega_i(y_i)^2]^{1/2}$, where n and p are the number of profile points and refined parameters, respectively.
Data collection	24.0	
Temperature (°C)	1.5406	
Wavelength [CuK_α] (Å)	Graphite	
Monochromator	$35 \leq 2\theta \leq 80$	R_B (Bragg factor) = $100[\Sigma\lvert I_{obs}\text{-}I_{calc}\rvert/\Sigma\lvert I_{obs}\rvert]$, where I_{obs} is the observed integrated intensity and I_{calc} is the calculated integrated intensity.
Measuring range (°)	0.02	
Step (°2θ)	30	
Integration time (s)	FULLPROF	
Rietveld data	Polynomial 5-order	R_F (crystallographic R_F factor) = $100[\Sigma\lvert F_{obs}\text{-}F_{calc}\rvert/\Sigma\lvert F_{obs}\rvert]$, where F is the structure factor, $F = \sqrt{(I/L)}$, where L is Lorentz polarization factor.
Program	Pseudo-Voigt	
Function for background level	32.3	
Function for peak shape	40.8	
R_p	43.3	$\chi^2 = \Sigma\omega_i(y_i\text{-}y_{ic})^2$.
R_{wp}	2.57	d (Durbin–Watson statistics) = $\Sigma\{[\omega_i(y_i\text{-}y_{ic})\text{-}\omega_{i\text{-}1}(y_{i\text{-}1}\text{-}y_{ic\text{-}1})]^2\}/\Sigma[\omega_i(y_i\text{-}y_{ic})]^2$.
R_{exp}	1.17	
R_B	0.887	
R_F	0.0739	Q_D = expected d.
χ^2	1.9223	S (goodness of fit) = (R_{wp}/R_{exp}).
d	0.9423	
Q_D		
S		

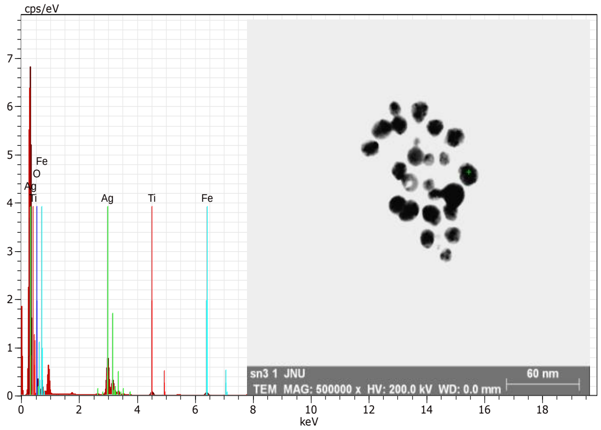

Fig. 2. EDX spectrum and TEM image (inset) of nanocrystalline $(Ag_{0.5}Fe_{0.5})TiO_3$ powder.

FTIR analysis was used to characterize the synthesized n-AFT (**Fig. 3**). The FTIR spectrum exhibits a prominent fundamental absorption band at 520 cm^{-1}, which is due to Ti–O vibration. The peaks around 873 cm^{-1} and 650 cm^{-1} are attributed to stretching metal-oxygen bond. Multiple peaks (A-O absorption bands) in the frequency region 900-1640 cm^{-1} are due to the presence of Ag-O and Fe-O vibrations. Further, a broad and strong peak can easily be seen around 3435 cm^{-1} which are due to free water molecules (H_2O bands) and strong stretching (antisymmetric and symmetric) modes of the OH group. No other band appeared in the FTIR spectrum clearly revealed the formation of $(Ag_{0.5}Fe_{0.5})TiO_3$ after calcination at 700ºC.

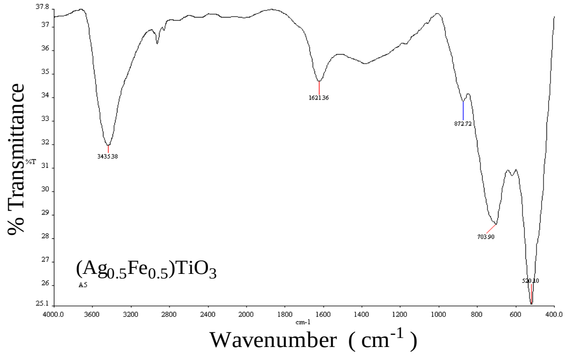

Fig. 3. FTIR spectrum of nanocrystalline $(Ag_{0.5}Fe_{0.5})TiO_3$ powder.

Fig. 4 shows the UV-vis spectrum recorded for n-AFT. The surface plasmon resonance was observed at 318 nm. Also, the plasmon bands are broadened with an absorption tail in the longer wavelengths, which may be due to the size distribution of the particles. This supports the distribution of particle sizes observed in TEM micrograph (inset **Fig. 2**).

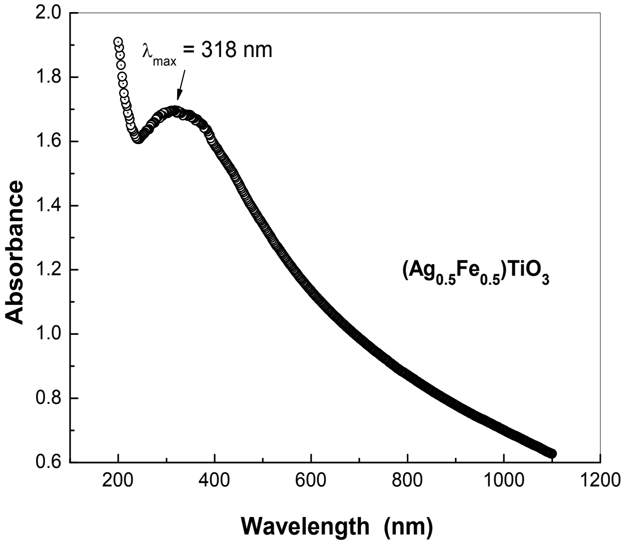

Fig. 4. UV-vis spectrum of nanocrystalline $(Ag_{0.5}Fe_{0.5})TiO_3$ powder.

Fig. 5 shows the variation of dielectric constant (ε) and loss tangent (tanδ) with temperature at 1 kHz. It is observed that both ε and tanδ increases with increment in temperature in the investigated temperature range. The room temperature values of ε and tanδ are, respectively, found to be 177 and 0.013 at 1 kHz. Since the observation was made for only in a limited range of temperature dielectric anomaly could not be observed as similar material {*e.g.* $(Ag_{0.5}Bi_{0.5})TiO_3$} has high phase transition temperature (~800 K) [**7**]. It can also be noted that the value of tanδ are of the order of 10^{-2} in the working temperature range (up to 100°C). The low tanδ of this kind can be advantageous when improved detectivity (pyroelectric applications) is required.

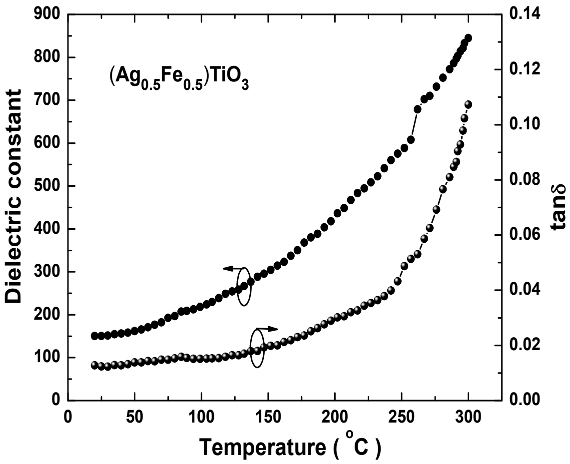

Fig. 5. Temperature dependence of dielectric constant and loss tangent of $(Ag_{0.5}Fe_{0.5})TiO_3$ ceramic pellet at 1 kHz.

Fig. 6 depicts the magnetization versus an applied field (M-H) for n-AFT at room temperature. It is observed that M-H curve is very slim and is not completely saturated till the applied field of 10 kOe, indicating thereby the size of the particles are very small (nanosizing effect). This may be due to the less number of Fe-Fe pairs, giving low value of coercive field (H_C = 533.1 Oe) and negligible retentivity (M_R = 0.016 emu/g). The saturation magnetization (M_S = 0.046 emu/g) is likewise small. This study clearly indicates that there is a possibility of magneto-electric coupling, suggesting electric ordering controlling magnetic properties at the microscopic scale.

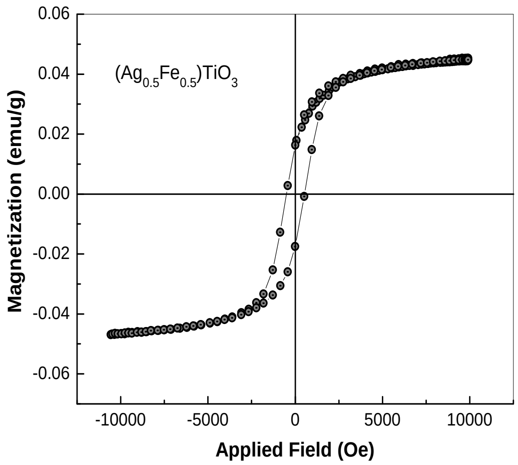

Fig. 6. Magnetization curve of nanocrystalline $(Ag_{0.5}Fe_{0.5})TiO_3$ powder at room temperature.

Conclusion

The present soft-chemical method is truly a green cost-effective approach, capable of producing nanocrystalline $(Ag_{0.5}Fe_{0.5})TiO_3$ powder. AFT was found to have a perovskite-type monoclinic structure with the particle sizes of 5-14 nm. EDX and FTIR studies confirmed the formation of pure AFT. UV-vis study exhibited the surface plasmon resonance at 318 nm. Dielectric study revealed a low value of dielectric constant (= 177) and dielectric loss (= 0.013) at 1 kHz. Magnetic study indicated the possibility of magneto-electric coupling.

Acknowledgements

Authors gratefully acknowledge Dr. G.S. Saini, Advanced Research Instrumentation Centre, Jawaharlal Nehru University, New Delhi for providing the EDX pattern and TEM image and Dr. K. AmarNath, HEG Ltd., Bhopal, India for arranging the XRD data.

References:

1. Rödel, J.; Jo, W.; Seifert, K.T.P.; Anton, E.-M.; Granzow, T.; Damjanovic, D. *J. Am. Ceram. Soc*. **2009**, *92*, 1153.
   DOI: 10.1111/j.1551-2916.2009.03061.x
2. Eichel, R.-A.; Kungl, H. Funct. Mater. Lett. **2010**, *3*, 1.
   DOI: 10.1142/S179360471000097X
3. Takenaka, T.; Nagata, H. *J. Euro. Ceram. Soc*. **2005**, *25*, 2693.
   DOI: 10.1016/j.jeurceramsoc.2005.03.125
4. Hao, J.; Wang, X.; Chen, R.; Li, L. *Mater. Chem. Phys*. **2005**, *90*, 282.
   DOI: 10.1016/j.matchemphys.2004.05.019
5. Shrout, T.R.; Zhang, S.J. *J. Electroceram.*, **2007**, *19*, 111.
   DOI: 10.1007/s10832-007-9047-0
6. Prasad, K.; Lily, Kumari, K.; Chandra, K.P.; Yadav, K.L.; Sen S. *Appl. Phys. A: Mater. Sci. Process.* **2007**, *88*, 377.
   DOI: 10.1007/s00339-007-3989-6
7. Kumari, K.; Prasad, A.; Prasad, K. *J. Mater. Sci. Technol.* **2011**, *27*, 213.
   DOI: 10.1016/S1005-0302(11)60051-0
8. Roy, A.K.; Singh, A.; Kumari, K.; AmarNath, K.; Prasad, A.; Prasad, K. *ISRN Ceram*. vol. 2012, Article ID 854831, 10 pages.
   DOI: 10.5402/2012/854831
9. Sahoo, S.; Pradhan, D.K.; Choudhary, R.N.P.; Mathur, B.K. *Adv. Mat. Lett*. **2012**, *3*, 97.
   DOI: 10.5185/amlett.2011.4250
10. Inaguma, Y.; Katsumata, T.; Wang, R.; Kobashi, K.; Itoh, M.; Shan, Y.-J.; Nakamura, T. *Ferroelectr.* **2001**, *264*, 127.
    DOI: 10.1080/00150190108008558
11. Park, J.-H.; Woodward, P.M.; Parise, J.B.; Reeder, R.J.; Lubomirsky, I.; Stafsudd, O. *Chem. Mater*. **1999**, *11*, 177.
    DOI: 10.1021/cm9806533
12. Wu, L.; Xiao, D.; Zhou, F.; Teng Y.; Li, Y. *J. Alloys Comp.* **2011**, *509*, 466.
    DOI: 10.1016/j.jallcom.2010.09.062
13. Liao, Y.; Xiao, D.; Lin, D. *Appl. Phys. A: Mater. Sci. Process. 2008*, *90*, 165.
    DOI: 10.1007/s00339-007-4246-8
14. Lu, Y.; Li, Y.; Wang, D.; Wang, T.; Yin, Q. *J. Electroceram.* **2008**, *21*, 309.
    DOI: 10.1007/s10832-007-9145-z
15. Raevskii, I.P.; Reznichenko L.A.; Malitskaya, M.A. *Techn. Phys. Lett*. **2000**, *26*, 93.
    DOI: 10.1134/1.1262752