مقایسه خصوصیات ساختاری و اپتیکی نانوپودر PZT خالص و آلاییده با آهن تهیه شده به روش سل ژل

زهرا ابراهیم زاده[۱]، محمود مرادی[۱و۲] و اسماعیل پاکیزه[۱]

[۱] بخش فیزیک، دانشکده علوم، دانشگاه شیراز، شیراز

[۲] پژوهشکده نانو تکنولوژی، دانشگاه شیراز، شیراز

چکیده – در این مقاله نانوذرات تیتانیم زیرکونات سرب خالص و آلاییده با آهن به روش سل ژل تهیه شده است. زیروژل در دمای ۷۰۰°*C* کلسینه شده است. ساختار پودر تهیه شده توسط پراش پرتو ایکس(*XRD*) و طیف سنجی تبدیل فوریه مادون قرمز(*FTIR*) مشخصه یابی گردید. نتایج *XRD* نشان می دهد که نانوذرات *PZT* تشکیل ساختار پرووسکایت با فاز تتراگونال می دهند. علاوه بر این یک جابجایی کوچک در الگوهای *XRD* نانوذرات *PZT* دوپ شده آشکار می شود. هم چنین برای داشتن درک بهتر از خصوصیات اپتیکی نانوذرات *PZT* خالص و دوپ شده طیف به دست آمده از *FTIR* تحلیل شده است.

کلید واژه: آلاینده، سل-ژل، نانوپودر، PZT

Comparison of Structural and Optical Properties of Pure and Iron Doped PZT Nanopowders Prepared via Sol-gel Methods

Z. Ebrahimzadeh[1], M. Moradi[1,2], E. Pakizeh[1]

[1] Department of Physics, College of Sciences, Shiraz University, Shiraz, Iran

[2] Institute of Nanotechnology, Shiraz University, Shiraz, Iran

Abstract- *In this paper pure and Fe doped lead zirconate titanate nanoparticles (PZT-NPs) were synthesized using sol-gel method. The xerogel was calcinated at temperature of 700 °C. The structure of the prepared powders is characterized using X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. The XRD results show that the PZT-NPs are formed in perovskite structure with tetragonal phase. In addition, a small shift was detected in XRD patterns of doped PZT-NPs. Also, to have a better understanding of the optical properties of the pure and doped PZT-NPs, the obtained FTIR spectra were analyzed.*

Keywords: Dopant, Sol-gel, Nanopowders, PZT

Comparison of Structural and Optical Properties of Pure and Iron Doped PZT Nanopowders Prepared via Sol-gel Methods

Z. Ebrahimzadeh
Ebrahimzade10@yahoo.com

M. Moradi
moradi@susc.ac.ir

1 Introduction

It is known that the lead zirconate titanate ($Pb(Zr_{1-x}Ti_x)O_3$: PZT) ceramic is a well-known material for various sensors and actuators because of their excellent electrical properties [1]. They can be expressed by the general formula ABO_3 of the perovskite structure, where the A site is occupied by Pb^{2+} and the B site is occupied by Zr^{4+} or Ti^{4+}. The attractive properties of a metal-added PZT system are an interesting topic for investigation. If the dopant type is acceptor then PZT can be named hard PZT, and soft PZT if a donor dopant doped to it. Add each of donor or acceptor dopants cause to the creation of defects in the perovskite structure to maintain lattice electroneutrality. These defects include the creation of vacancies within the lattice. Type of these vacancies depending on the type of dopant (donor or acceptor), are various. The donor dopant induces cationic defects while the acceptor type dopants induce oxygen vacancies[2]. The high electrical properties of PZT ceramic was found for a composition close to the morphotropic phase boundary (MPB). This MPB is located around $PbZrO_3$:$PbTiO_3$ ~ 0.52:0.48 which separates a Ti-rich tetragonal from a Zr-rich rhombohedral phase [3]. Therefore, PZT and modified PZT for electrical applications are designed in vicinity of the MPB. In this paper $Pb(Zr_{0.52}Ti_{0.48})_{1-x}Fe_xO_3$ (PZTF) with x=0.05 and $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) nanopowders were synthesized by chemical sol-gel route. The prepared powders were characterized by XRD, FTIR, UV-vis and FE-SEM.

2 Experimental Method

To prepare the lead zirconate titanate nanoparticles (PZT-NPs) lead (II) nitrate, hydrated zirconium (IV) oxynitrate, titanium (IV) isopropoxide were used as the starting materials. Initially aqueous solution of Pb^{2+}, $Zr^{4+}$and Ti^{4+} were prepared. In sol-gel method the PZT precursor solution was prepared by mixing the aqueous solutions of cations. The resultant gels were dried at 100 °C to form xerogels.The crystalline PZT was obtained after thermal treatment of xerogel at 700 °C. The processes for preparing PZT-NPs doped with Fe (x = 0.05) were the same as pure PZT-NPs, according to $Pb(Zr_{0.52}Ti_{0.48})_{1-x}Fe_xO_3$ compounds, respectively.

3 Results and Discussion

3.1 X-ray Diffraction Analysis

The XRD patterns of the pure and doped PZT compounds are shown in Fig. 1. All the peaks are related to tetragonal phase and prove the formation of the PZT in perovskite structure after calcination process at 700 °C.The crystallite size of the powders are estimated by Scherrer’s equation (1). Where D, K, λ, β and θ are crystallite size, constant proportionality, X-ray wavelength, full width at half maximum and Bragg angle, respectively.

$$D = \frac{K\lambda}{\beta cos\theta} \qquad (1)$$

The crystallite size of the pure and doped PZT is presented in Table 1. A small shift is observed in the doped sample's pattern, in which Ti^{+4} ions are substituted (Ti^{+4} ionic radius = 0.61 Å) by Fe^{3+} (ionic radius = 0.67 Å) comparing to the pure PZT, Fig. 2. Also, it can be seen in the patterns that the intensity of doped sample peaks are less than that for the pure sample. These peak shifts and the intensity changes are attributed to the presence of both uniform and non-uniform strains in the doped compound lattices due to the different ionic radii of the dopants comparing to Ti\Zr ions [4]. For Fe^{3+} the shift is to higher angles.

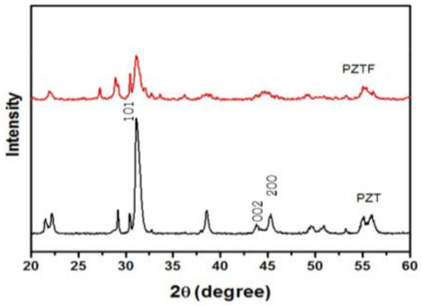

Fig. 1. XRD pattern of pure PZT and Fe doped nanopowders.

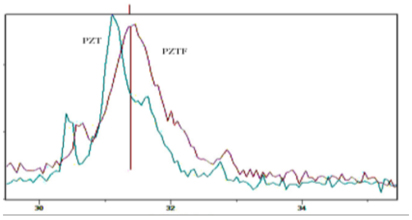

Fig. 2. (1 0 1) crystal surface X-ray diffraction patterns of pure and Fe doped PZT-NPs

3.2 FTIR Characteristics

The transmittance of pure and Fe doped PZT-NPs was investigated by Fourier transform infrared spectroscopy (FTIR) in the range of 400–4000 cm^{-1} and the results are presented in Fig. 3. As expected for perovskite structures, a broad band with minimum transmittance between 580 and 625 cm^{-1} and another one with minimum transmittance in the range of 390–410 cm^{-1} were observed in each spectrum.

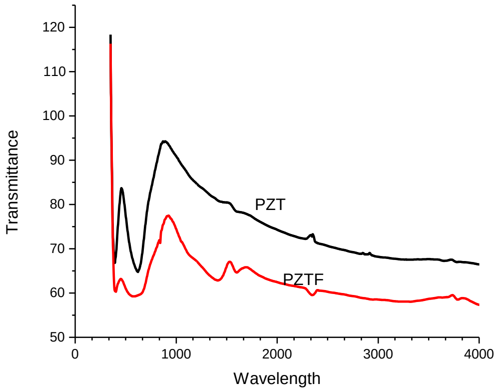

Fig. 3. FTIR pattern of pure PZT and Fe doped PZT calcinated at 700°C.

According to the literature, these two absorption bands are attributed to MO_6 (M = Zr and Ti) stretching and bending in the octahedral normal modes, respectively [5]. The stretching normal vibration occurs at higher frequency, υ_1 and the bending normal vibration at lower frequency, υ_2[6].

Table 1 XRD results for pure PZT and Fe doped PZT

Sample	2θ(degree)	(hkl)	β(radian)	D(nm)	phase	Lattice parameters(Å)
PZT (A)	31.13 43.81 45.2	(101) (002) (200)	0.0042 0.0068 0.0060	33.52	Tetragonal	a=b=4.0061 c=4.1322
PZTF(B)	31.14 44.41 45.05	(101) (002) (200)	0.0051 0.0065 0.0031	27.93	Tetragonal	a=b=4.0242 c=4.0791

The minimum of the transmittance shift occurs by substitution of Ti\Zr with Fe, due to the difference in their ionic radii and weights. There are two other vibration modes (υ_3 and υ_4), which are related to vibrations of Pb–TiO_3/ZrO_3 bonds, but these modes occur below the available experimental frequency range (400–4000 cm^{-1}) used in this experiment and are not seen in the spectra. The results are summarized in Table 2.

Table 2 FTIR results for pure PZT and Fe doped PZT

	PZT	Fe doped PZT
υ_1	620	586
υ_2	392	405

3.3 UV-vis Results

The optical band-gap of the pure and Fe doped PZT-NPs were estimated from UV–vis absorption spectra results which are shown in Fig. 4. The band gaps are obtained by Tauc relation to be 3.23, 3.12 eV, respectively. It was revealed that the optical band gap value of the PZT-NPs decreases when doped with Fe.

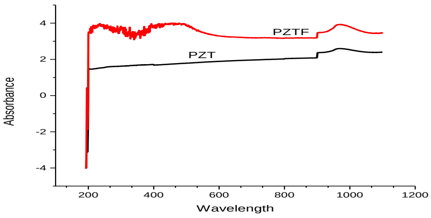

Fig. 4. Absorption spectrum of pure and iron doped PZT-NPs.

3.4 FE-SEM Observations

Morphology of the calcinated at 700°c temperature nanopowders illustrates in Fig. 5.The agglomerated particles have almost spherical shape and their average sizes are about 60-200 nm.

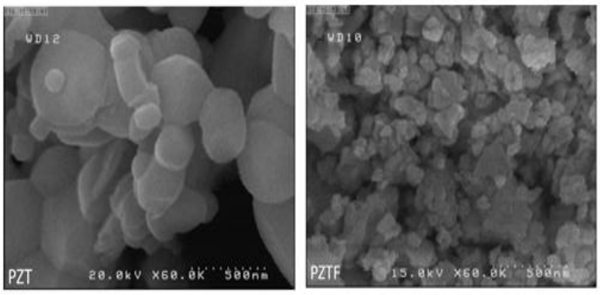

Fig. 4. FE-SEM images of pure PZT and Fe doped nanopowders.

4 Conclusions

Pure and Fe-doped PZT-NPs were successfully prepared by sol-gel method at calcination temperature of 700 °C. The prepared materials were characterized and investigated using XRD, FTIR, FE-SEM. XRD results showed that the PZT-NPs are formed in perovskite structure with good crystallity and the crystalline sizes were found to be 33.52, 27.95 nm for pure and Fe doped PZT-NPs, respectively. The optical properties of the PZT-NPs were investigated by transmittance measurements in the range of 400–4000 cm^{-1} and two bands were observed from the FTIR graphs. The broad band in the transmittance curve is a composition of the υ_1-ZrO_3 and υ_1-TiO_3 stretching normal vibration modes.

References

[1] A. J. Moulson, J. M. Herbert, *Electroceramics: Materials, Properties, Applications*. John Wiley & Sons Ltd, West Sussex, pp. 339, 2003.

[2] S. Puthucheri and P. K. Pandey “Microstructural, Electrical, and Magnetic Properties of Acceptor-Doped Nanostructured Lead Zirconate Titanate, ” *J. Am. Ceram. Soc.*, pp. 3941–3947, 2011.

[3] B. Jaffe and W. R. Cook, *Piezoelectric Ceramics*, Academic Press, New York, pp. 115, 1971 [3] B. Jaffe and W.R. Cook, *Piezoelectric Ceramics*, Academic Press, New York, pp. 115, 1971.

[4] B. D. Cullity and S. R. Stock, *Elements of X-ray Diffraction*, Prentice Hall, Harlow, 2001.

[5] A. K. Zak and W. H. A. Majid, “Effect of solvent on structure and optical properties of PZT nanoparticles prepared by sol–gel method, in infrared region,” *Ceramics International*. Vol. 37, No. 3, pp. 753–758, 2011.

[6] W. G. Spitzer and R. C. Miller, “Far infrared dielectric dispersion in $BaTiO_3$, $SrTiO_3$ and TiO_2,” *Physical Review*.Vol. 126, pp. 1710–1721,1962.