روش کرامرز کرونیگ برای محاسبه ثابت های اپتیکی نانولوله های PZT تولید شده با روش سل ژل غشایی با نسبت جهتی بالا

محمود مرادی[۱،۲] و اسماعیل پاکیزه[۱]
[۱]بخش فیزیک، دانشکده علوم، دانشگاه شیراز، شیراز
[۲]پژوهشکده نانو تکنولوژی، دانشگاه شیراز، شیراز

چکیده – در این مقاله نانوله های *$Pb(Zr_xTi_{1-x})O_3$ (PZT)* با ترکیب دو روش سل ژل و نهشت چرخشی تولید شدند. در این روش محلول حاصل از فرایند سل ژل در غشاهایی که از آنودایز کردن آلومینیوم تهیه شدند نفوذ می کنند. نسبت جهتی (طول به قطر) برای این نانولوله های *PZT* حدود ۷۰۰ بدست آمد. مبنای این روش تکرار فرایند پر کردن-خشک کردن-پرکردن حفره ها می باشد. پروسه تولید در ای روش بسیار سریع می باشد، زیرا زمان لازم تا رسیدن به مرحله کلسینه کردن تنها یک ساعت بود و در مقایسه با مقالات پیشین بسیار کمتر می باشد. تصاویر *FE-SEM* نشان داد که نانولوله های *PZT* با موفقیت تولید شدند. پیوندهای اکسید فلزی نظیر ZrO_6 و TiO_6 توسط آنالیز *FTIR* تایید شدند. همچنین ثابت های اپتیکی نظیر ضریب شکست، ضریب خاموشی، قسمت های حقیقی و موهومی تابع دی الکتریک و مدهای فنونی عرضی و طولی با استفاده از روابط کرامرز-کرونیگ و داده های *FTIR* محاسبه شدند.

کلید واژه- سل ژل، کرامرز-کرونیگ، AAO، PZT.

Kramers-Kronig method for the determination of optical constant of PZT nanotubes synthesized by sol-gel membrane process with high aspect ratio

M. Moradi[a,b], E. Pakizeh[a,1]

[a] Department of Physics, College of Sciences, Shiraz University, 71946-84795 Shiraz, Iran

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

Abstract- We report a template-directed growth of $Pb(Zr_xTi_{1-x})O_3$ (PZT) nanotubes in conjunction with sol-gel process and spin coating technique. This method employs the spin-coating of a sol–gel solution into an anodic aluminum oxide membrane (SSAM). The aspect-ratios of the PZT nanotubes were about ***700***. The method is based on repeated pores filling by precursor solution. The filling-pyrolys-filling process was repeated several times. The process of fabrication was fast in our research because the required time until calcination step was ***1*** hour and very low in comparison with pervious work. Field emission scanning electron microscope (FE-SEM) images show that PZT nanotube is successfully synthesized. The metal oxide bands like ZrO_6 and TiO_6 of the final PZT nanotubes were confirmed by FTIR analysis. The optical constants such as refractive index, extinction coefficient, real and imaginary part of dielectric function were determined from the FTIR spectra using Kramers-Kronig transformation (KKT) method.

Keywords: PZT, sol gel, Kramers-Kronig, AAO.

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M. Moradi
moradi@susc.ac.ir

E. Pakizeh
esmaeil_pakizeh@yahoo.com

1 Introduction

In recent years, there has been an increased interest in studies of perovskite nanostructure. In the perovskite oxides with the chemical formula ABO_3, the large A cation is coordinated to twelve anions to form the AO_{12} cluster, with the B cation occupying a six-coordinate site of the BO_6 cluster which forms a network of corner-sharing BO_6 octahedra. Tilting these octahedra leads to deviations from the ideal cubic symmetry [1]. Among large number of different perovskite materials, the lead zirconate titanate $Pb(Zr_{1-x}Ti_x)O_3$ due to their piezoelectric, dielectric, mechanical, optical, electro-mechanical, and electro-optical properties are an important class of ferroelectric materials. A few studies on the optical properties of PZT nanotubes have been reported. In the infrared region the electromagnetic field of the photons is strongly coupled to the polarization field of the vibrating ions and optical phonons can be created [2]. The Kramers-Kronig transform is a numerical method for obtaining the optical constants and the dielectric response curves from FTIR spectra [3]. In the present work we prepared the $PbZr_{0.52}T_{0.48}O_3$ nanotube. The optical properties of PZT nanotubes such as refractive index (n), extinction coefficient (k), real (ε_1) and imaginary (ε_2) parts of dielectric function and frequency of transverse optical phonon mode (ω_{TO}) and longitudinal optical phonon mode frequency (ω_{LO}) were studied from the FTIR spectra using kramers-kronig method. The PZT nanotubes were characterized by FE-SEM images.

2 Experimental

Firstly, the cleaned and dried AAO membrane (Figure 1) is placed on a custom mad Teflon support. Secondary the PZT solution is dropped on AAO template and spin coated at the condition of 3000 rpm for 2 min. then the excess sol on template surface was wiped off using a cotton swab dipped in tow-methoxyethanol. In order to the PZT solution transformed in to an amorphous oxide layer the template was heated from room temperature to 300 °C in air. Then for obtained the PZT nanotube with desired wall thickness the process was repeated several times. Finally the AAO membrane for crystallization of PZT nanotubes heated at 650° C for 1h with heating rate of 5° C/min. A schematic illustration of experiment process of PZT nanotubes is illustrated in Figure2.

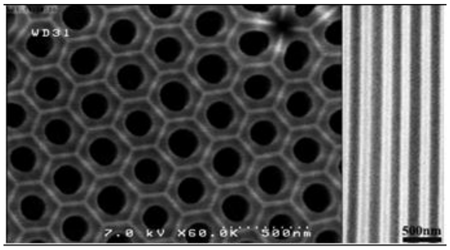

Figure 1: FE-SEM images of a typical AAO membrane fabricated by the two-step anodization

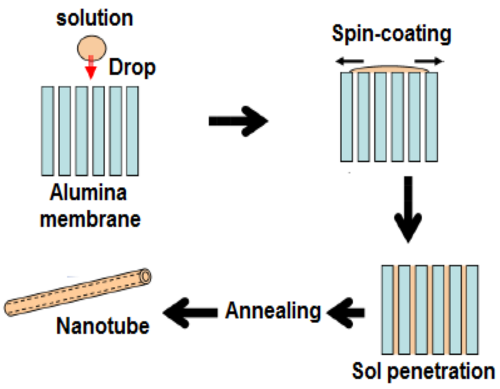

Figure 2: Schematic diagram of the synthesis process of PZT nanotubes [4]

3 Result and discussion

3.2 FE-SEM observation

Figure 3 illustrates the FE-SEM image of PZT nanotube. The obtained PZT nanotubes have length about of 50–60 µm. Figs. 3(b), 3(c) and 3(d) shows higher magnification FE-SEM images of a portion in Fig. 3(a). The inset picture in fig 3(d) clearly show that tube-like nanostructures of PZT with wall thickness 35 nm, pore diameter about 60-70 nm and outer diameter 130 nm are formed inside the porous alumina membrane (PAM).

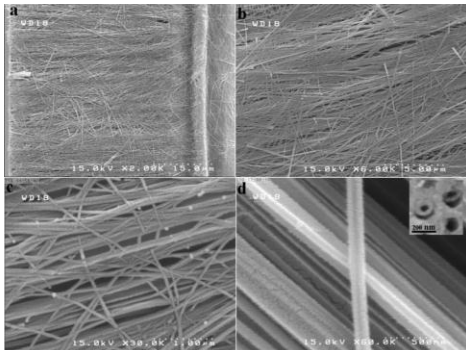

Figure 3:FE-SEM images of PZT nanotube.

3.2 FTIR characteristics

FTIR spectroscopy was used to investigate the vibration spectrum in the range of 400–4000 cm^{-1}. Figure 4 shows the transmission spectra as a function of wavenumber for PZT. In the PZT nanotube with tetragonal-rhombohedral phases three A(TO) modes which labeled A(1TO), A(2TO) and A(3TO) happened in 400-800 cm^{-1}. However the sample is found to exhibit a broad peak 719.466 cm^{-1} and is attributed to the metal oxygen bonds. This result indicated that the perovskite phase was formed at this sample. These bonds are associated to the extensional vibrations of the perovskite BO_6 octahedron.

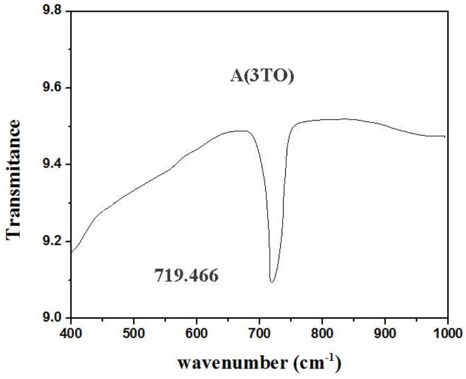

Figure 4: FTIR spectra of PZT nanotubes

3.3 Optical constant

It is prominent from Fresnel equation that, in every solid material, the complex reflectance is given as

$$r = \sqrt{R(\omega)}e^{i\varphi(\omega)}$$
(۱)

Where r, R(ω) and φ(ω) is the reflection coefficient, reflectance and the phase change between the incident and reflected signals for a particular wave number respectively. The φ(ω) can be derived from Kramers-Kronig (K–K) dispersion relation as [5]:

$$\varphi(\omega) = -\left(\frac{\omega}{\pi}\right) P\int_0^\infty \frac{\ln(R(\omega))}{\omega'^2 - \omega^2} d\omega$$
(۲)

For solid materials, if R(ω) and φ(ω) are known, the refractive index n(ω) and extinction coefficient k(ω) of that material are given by:

$$n(\omega) = \frac{1 - R(\omega)}{1 + R(\omega) - 2\sqrt{R(\omega)}\cos\varphi(\omega)}$$
(۳)

$$k(\omega) = \frac{2\sqrt{R(\omega)}\sin\varphi(\omega)}{1 + R(\omega) - 2\sqrt{R(\omega)}\cos\varphi(\omega)}$$
(٤)

Figure 4 shows typical single resonance spectra of n(ω) and k(ω) for PZT nanotube in IR region. From these figures the transverse optical (TO) and longitudinal optical (LO) phonons mode may also be obtained.

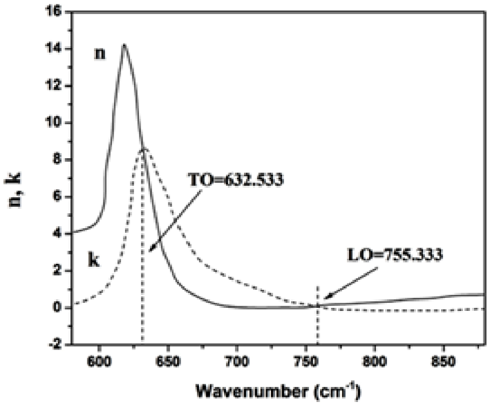

Figure 5: n, k, TO and LO of PZT nanotube

Also, real and imaginary parts are related to n(ω) and k(ω) as:

$$\varepsilon_1(\omega) = n(\omega)^2 - k(\omega)^2 \qquad (۵)$$

$$\varepsilon_2(\omega) = 2n(\omega)k(\omega) \qquad (۶)$$

The real and imaginary parts of the dielectric function of PZT nanotube are shown in Figure 6.

4 Conclusions

The PZT nanotubes were fabricated using the sol-gel alumina-membrane template method and spin-coating technique. The prepared materials were characterized and investigated using FTIR and FE-SEM techniques. Phonon vibration modes of the samples were investigated using K–K relations and FTIR spectra. It was observed that the LO and TO optical phonon modes of PZT nanotubes are632.533 and 755.333 respectively. From FE-SEM images it was revealed that the single crystalline structure with a diameter of about 50 nm and a length of several tens of micrometers. The Kramers–Kronig method was used to evaluate the optical constants (n, k, ε_1 and ε_2) of PZT nanotubes.

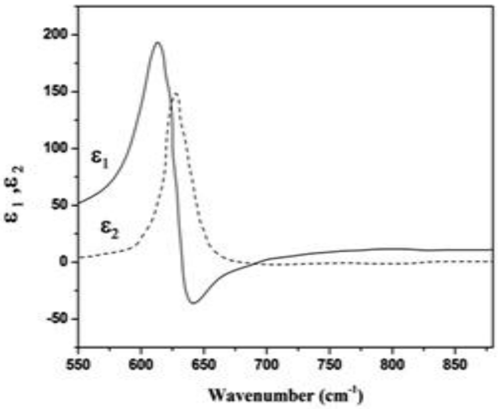

Figure 6: ε_1 and ε_2 of PZT nanotube

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