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Structural and Optical Properties of Ni-substituted Barium Titanate/ Polyaniline as a Nanocomposites for Optical Sensing

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Abstract

Ni^{2+} substituted $BaTiO_3$ tetragonal perovskite ceramic with composition formula $Ba_{1-x}NixTiO_3$ was synthesized via sol-gel method route, the synthesized ceramics was ground, pre-calcinated at 800°C and calcinated at 950°C to get nano-sized particle. Polyaniline (PANI) was synthesized via oxidative polymerization of aniline monomer using ammonium persulphate. Barium nickel titanate and polyaniline composite were made by mixing the duo in 1:1 ratio after which they were ground thoroughly to make the homogeneous mixture for analyses. The composites were characterized using X-ray diffraction (XRD), Fourier transforms infrared (FTIR), UV-vis spectroscopy, field emission scanning electron microscopy (FE-SEM) characterization techniques. The band gaps are 2.63, 2.49 and 2.02 for $BaTiO_3$/polyaniline, $Ba_{0.9}Ni_{0.1}TiO_3$/polyaniline, and $Ba_{0.8}Ni_{0.2}TiO_3$/polyaniline respectively. The band gap values are much lower than that of normal barium titanate (3.2eV) as observed from the literature and this is due to the presence of polyaniline which is conducting material minimizing the Fermi level between valance and conductive band. The nanocomposites may useful as optical sensor.

Keywords: Polyaniline, barium titanate, band gap, optical sensing

1. INTRODUCTION

Semiconducting properties of ferroelectric materials have attracted much of scientist's attention due to its application to various electronic devices such as memory cell capacitors, high-density random access memories (ferroelectric RAMs), and dynamic RAMs. As it is known that perovskite ABO_3-type $BaTiO_3$ (BTO) has been an excellent ferroelectric crystal with the band gap about 3.8 eV and the ferroelectric–paraelectric transition temperature above 400 K. And it is extensively used as dielectric in multilayer ceramic capacitor (MLCC) because of its high permittivity and low loss. Their applications does not stop there, $BaTiO_3$ can be used in devices like sensor, transducer, microwave filter, infrared detector, heater and dynamic random access memory.[2] In recent years, fruitful researches are being conducted on the doped barium titanate materials to examine the impact incorporation of impurities on ferroelectricity, dielectric constant, capacitance, optical properties and phase transition nature of $BaTiO_3$ ceramics.[3] A considerable number of works focused on how to modify those properties, this can be achieved introducing the impurities by doping with some

transition or rare earth metals or composites with some conductive polymers such as polyaniline.

Polyaniline (PANI) is homopolymer having benzenoid, quinonoid or both molecular formulas that exist in different proportions. Polyaniline has been known as conducting polymer since 1862 discovered by D.H.Letheby[4,5,6]. It drew greater attention of scientists, this is due to its' high electrical conductivity, optical properties. Polyaniline can be easily synthesized in two ways chemically or eletrochemically from acidic aqueous solutions. The chemical method has a large significance because it is very reasonable method for the mass production of PANI. The most simple and commonest preparation method is oxidative polymerization of aniline, ammonium peroxodisulfate serve as an oxidant in the process. Composites of polyaniline with metals, metalloids and non-metals were studied and got considerable progress. Composite of polyaniline with inorganic materials like $BaTiO_3$, and other inorganic salts were investigated for optical properties.

2. EXPERIMENTAL DETAILS

Sample code	Sample composition
BTP1	$BaTiO_3$/polyaniline
BTP2	$Ba_{0.9}Ni_{0.1}TiO_3$/polyaniline
BTP3	$Ba_{0.8}Ni_{0.2}TiO_3$/polyaniline

$Ba_{1-x}Ni_xTiO_3$ (x=0.0, 0.1, 0.2) powder of pure and doped $BaTiO_3$ ware synthesized by sol–gel method. This chemical route has the advantage that it is relatively simple, easy, stoichiometric composition control and low cost. Weighted amounts of the appropriate proportions of high purity barium nitrate, nickel nitrate, titanium dioxide and citric acid precursors, were dissolved in 100ml of distilled water contained in 500ml beaker. The solution was heated on magnetic stirrer at 100°C stirred by magnetic bit until the solution turned into gel and finally into ceramic. The ceramic was ground, pre-calcined at 800 ^{0}C and calcined at 950 ^{0}C in muffle furnace to obtain- nickel doped barium titananate. Polyaniline synthesis was done via oxidative polymerization method. In this process, about 23.30gram of aniline monomer was being poured stepwisely into 91.20 ml of HCl acid at 0 ^{0}C in chilled ice bath followed by addition of 40.50gram Ammonium persulphate solution which was initially dissolved in distilled water. The polymer confirmed to be formed as the solution turned into dark green precipitate. The solution was continuously stirred for 60mins; after that distilled water was poured rinse it. The solution was filtered and washed with both distilled water followed by methanol until the clear filtrate was obtained. The polyaniline polymer obtained was dried in an oven at 60°C for 48 hours.

3. RESULT

3.1 XRD analysis

Fig. 1 shows the XRD spectra pattern of Ni doped $BaTiO_3$/PANI nanocomposite. According the JCPDS card no (050625), single phase $BaTiO_3$ with presence of traces of barium carbonate as secondary phase formed during the synthesis was observed at undoped (0.0) and first doping (0.1) peaks at 950°C.Crystal peaks appeared in all patterns but increases as the Ni contents increases. Shoulder at the peak with hkl (002)

45.5-45°C appeared at the first doping which indicates changing from cubic to tetragonal phase. Splitting of this peak, (002) and (200) indicated clearly the presence of tetragonal phase of $BaTiO_3$ in these powders. As the concentration of Ni in $BaTiO_3$ increases, the (002) intensity at 45°C is increasing. The analyses showed that $Ba_{1-x}Ni_XTiO_3$ Ceramics are tetragonal symmetry in the space group P4mm.In the same fig small broad peak at 2θ = 25° show the presence of PANI and also show some degree of crystallinity in undoped and first doping of nickel in barium titanate.

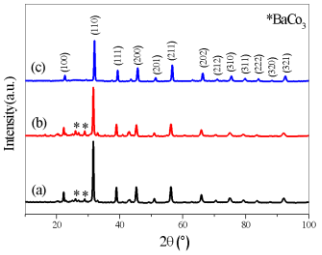

Fig. 1. XRD spectra for barium titanate/polyaniline composites.
(a) $BaTiO_3$/polyaniline, (b) $Ba_{0.9}Ni_{0.1}TiO_3$/polyaniline, and (c) $Ba_{0.8}Ni_{0.2}TiO_3$/polyaniline

3.2 FTIR analysis

Fig. 2 shows the FTIR pattern for synthesized $Ba_xNi_{1-x}TiO_3$ which pre-calcinated at 800 °C and calcinated at 950°C for 6 hours and the spectra showed the peak around 300-500 cm^{-1} which is due to **Ti-O** vibration and carbonate peaks (**CO_3^{-2}**) at 851.71, 1051.15, 1425.45, 164766 and 2337.07 cm^{-1}. The carbonates peaks realized are due to the presence of $BaCO_3$ secondary phase. The **Ti-O** absorption peak got narrower and sharper which shows the crystallinity of the material as the number of vibrational molecules decreases and amorphous TiO_2 transform into octahedrally TiO_6 as confirmed by XRD in fig 5.[12] The intensity of carbonate peaks diminish as the nickel doping increases, which shows the decreasing of impurities. The bands present in the TiO_6 octahedral are O-Ti-O bending (390 cm^{-1}) and Ti-O stretching (538 and 630cm^{-1}).[13] In addition to the peaks of **T-O, CO_3^{-2}** , various peaks are observed which indicates the presence of polyaniline in the composite. The peaks include C-C, C=C, C-N, C-H, N-H and 1-4 disubstituted aromatic ring (benzenoid) at 1141, 1588, 1330.75, 2948.23, 3464 and 814.45 cm^{-1} respectively. The carbonate peaks around 2380 cm^{-1} increased at the first nickel doping (0.1) and then dramatically decreased at the second doping of nickel (0.2) to show the a little or absence of carbonates impurity from barium carbonate ($BaCO_3$).The spectra also show the peak at 1500 cm^{-1} and 1550 cm^{-1} may be due to presence of quinanoid and benzenoid rings respectively.

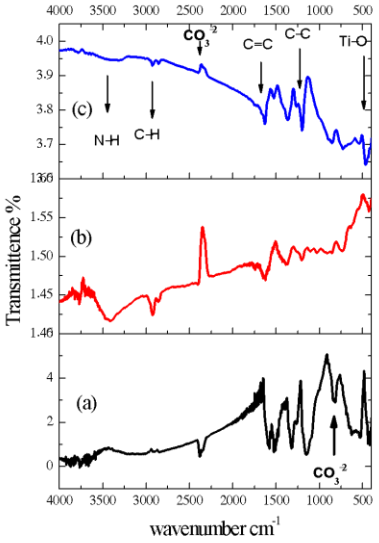

Fig.2 FTIR spectra of barium titanate/polyaniline nanocomposites (a) $BaTiO_3$/polyaniline, (b) $Ba_{0.9}Ni_{0.1}TiO_3$/polyaniline, and (c) $Ba_{0.8}Ni_{0.2}TiO_3$/polyaniline

3.3FESEM/EDX/mapping analysis

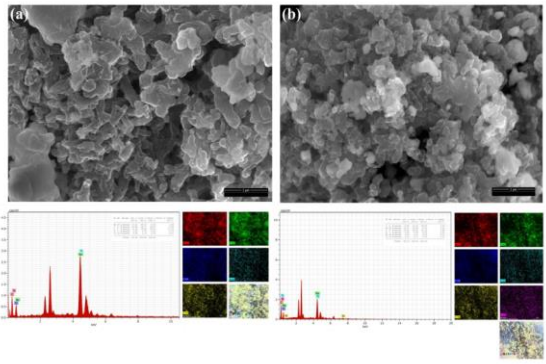

Fig. 3 FESEM, EDX spectra and elemental mapping of barium titanate/PANI nanocomposites (a) $BaTiO_3$/polyaniline and (b) $Ba_{0.9}Ni_{0.1}TiO_3$/polyaniline

Fig. 3 (a) and (b) presents the FESEM, EDX spectra and elemental mapping of barium titanate/PANI for nanocomposites $BaTiO_3$/polyaniline and $Ba_{0.9}Ni_{0.1}TiO_3$/polyaniline respectively. Both nanocomposites show different morphologies with agglomeration of the nanoparticles of barium titanate and polyaniline. The barium titanate nanoparticles are well embedded in the polyaniline. Two possible scenario results in the current morphology, the first being the surface amorphous structures of the polyaniline crystallized in situ and the small nanoparticles of barium titanate merged into larger ones. The second is that the surface amorphous structure of polyaniline nanoparticles

diffused quickly to the surface of the barium titanate particles and then crystallized. The EDX spectra and elemental mapping shows all the substituted elements for polyaniline and barium titanate. Hence, the stoichiometry of the prepared nanocomposites is maintained.

3.4. Optical properties

The optical band gap energy (E_{gap}) was determined using Wood -Tauc formula. Thus the value of band gap (E_{gap}) of barium nickel titanate/polyaniline composite was obtained by extrapolating (tangent) the linear portion of the curve or tail (y=0) in the UV-Vis Absorbance spectrum. The Wood and Tauc formula is given as

$$\alpha h\upsilon = A(hv - Eg)$$

Where Eg is band gap energy, A is constant, h is plank's constant, υ is frequency and α is absorption.

From the **Fig. 4** the band gap spectra values are much lower than that of normal barium titanate (3.2eV) as observed from the literature and this is due to the presence of polyaniline which is conducting material minimizing the Fermi level between valance and conductive band. The band gap for $BaTiO_3$/polyaniline, $Ba_{0.9}Ni_{0.1}TiO_3$/polyaniline, and $Ba_{0.8}Ni_{0.2}TiO_3$/polyaniline are 2.63, 2.49 and 2.02 respectively.

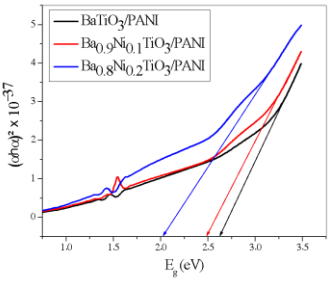

Fig. 4 Band gap of barium titanate/PANI nanocomposites

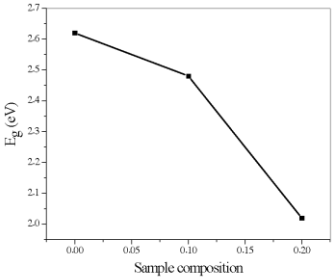

Fig.5. Variation of band gap with composition of barium titanate/PANI nanocomposites

5. CONCLUSION

BNT/PANI composites were successfully synthesized by thorough mixing of barium nickel titanate and polyaniline in 1:1 ratio. Nanoparticles formations in the composites were confirmed by XRD, FTIR, FE-SEM and ultraviolet (UV) visible spectroscopy. The

XRD spectra pattern shows the intensity of the peak transforming from cubic to tetragonal as the nickel concentration increases. FTIR pattern shows the formation of Ti-O stretching, C=C, N-H, disubstituted benzenoid fuctional groups confirming the formation of polyaniline and traces of carbonates impurities which disappear as nickel concentration increases. FE-SEM.UV analyses gives the ban gap which is decreases drastically as compare with BNT as the nickel concentration increases, the drastic falling of band gap may be due conducting property of polyaniline. Polyaniline is good for reducing the Fermi level which also decreases the energy gap from valence bond and conducting band.

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