

The effect of PVP on morphology, optical properties and electron paramagnetic resonance of $\text{Zn}_{0.5}\text{Co}_{0.5}\text{Fe}_{2-x}\text{Pr}_x\text{O}_4$ nanoparticles

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Abstract. Zinc Cobalt nano ferrite doped with Praseodymium, $\text{Zn}_{0.5}\text{Co}_{0.5}\text{Fe}_{2-x}\text{Pr}_x\text{O}_4$ ($0 \leq x \leq 0.2$), were prepared by co-precipitation method from an aqueous solution containing metal chlorides and two concentrations of poly(vinylpyrrolidone) (PVP) 0 and 30g/L as capping agent. The samples were characterized using X-ray powder diffraction (XRD), Transmission Electron Microscope (TEM), UV-visible optical spectroscopy, Fourier transform infrared (FTIR) and Electron Paramagnetic Resonance (EPR). XRD results display the formation of cubic spinel structure with space group $\text{Fd}\bar{3}\text{m}$ and the lattice parameter (a) is slightly decreased for PVP capping samples. The particle size that determined by TEM, decreases for PVP capping samples. The optical band energy E_g increases for PVP capping samples, confirming the variation of energy gap with the particle size. The FTIR results indicate that the metal oxide bands were shifted for the PVP capping samples. EPR data shows that the PVP addition increases the magnetic resonance field and hence decreases the g-factor.

1. Introduction

The interest in research of metal spinel ferrite nanoparticle, with the formula MFe_2O_4 , $\text{M} = \text{metal(s)}$, has increased significantly in the last 10 years due to their potential applications in spintronics, biomedical and magnetic refrigeration [1-4]. MFe_2O_4 can be described as a cubic, closely packed arrangement of oxygen atoms, and M^{2+} and Fe^{2+} ions can occupy either tetrahedral (A) or octahedral (B) sites. Among all methods, chemical co-precipitation is most suitable because of its simplicity, better control on particle size and other properties of materials. To control the growth of the spinel ferrite nanoparticles, poly(vinyl pyrrolidone) (PVP) is added during the synthesis for capping the surface of the particles [5-6]. The results indicate a decrease in the particle size for PVP capping samples.

The aim of the work is to study the effect of PVP on zinc cobalt nano ferrite doped with a rare earth element through structural, optical and magnetic measurements.

2. Experimental

Metal chlorides reagents, poly (vinyl pyrrolidone) (PVP), and deionized water were used as precursors. A separate solution of PVP was prepared by dissolving 3g of PVP in 100 ml before mixing the suitable stoichiometric amounts of metal chloride reagents. For co-precipitation of such prepared solution, solution of NaOH (4M) was added in drop wise with constant stirring produced by a magnetic stirrer. The pH of the solution was maintained at 12.5-13, in order to transform the hydroxides of metals into nanoparticles. The solution was maintained at 333K with constant stirring for 2 hours. This duration was sufficient for the transformation of hydroxides into spinel ferrite. The precipitated particles were then washed several times with distilled water to remove the impurities. The precipitated particles were then dried in an oven at 373K for 24 hours. The resulting solid was grounded into powder and calcined at temperature 823K for 6 hours. The nanosized ($\text{Zn}_{0.5}\text{Co}_{0.5}\text{Fe}_{2-x}\text{Pr}_x\text{O}_4$) were characterized by XRD using Bruker D8 advance powder diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) in the range $10^\circ \leq 2\theta \leq 80^\circ$. The surface morphology was examined using Jeol transmission electron microscope JEM-



100CX, operated at 80 kV. The FTIR analysis was carried by FTIR 8400S Shimadzu in the range 350-700 cm^{-1} . UV-visible absorbance spectrum of sample has been taken in the wavelength range from 200 nm to 600 nm by using Jasco-V-670 - UV-Vis spectrometer. EPR spectrum of samples was recorded on X- band EPR Spectrometer Model: ER0485 Make: Bruker, for determining g-value and resonance magnetic field.

3. Results and discussion

The XRD results of the $(\text{Zn}_{0.5}\text{Co}_{0.5}\text{Fe}_{2-x}\text{Pr}_x\text{O}_4)$ nanoparticles with $x=0.04$ and 0.08 , free and PVP capping are shown in Figure 1. The XRD results confirm the presence of nanoferrite with a face-centered cubic structure [7]. The XRD patterns also show that the peaks become broader for PVP capping samples and their intensity decrease contributing to the decrease in the crystallite size.

Table1. Various parameters of Zn-Co nano ferrite measured by XRD and TEM with and without PVP capping.

	Free from PVP				Capped with PVP			
	$x=0$	$x=0.04$	$x=0.08$	$x=0.2$	$x=0$	$x=0.04$	$x=0.08$	$x=0.2$
Crystallite size XRD(nm)	28.3	19.4	18.7	14.7	13.3	12.24	8.51	14.63
Particle size TEM(nm)	24.69	17.24	15.9	12.06	13.08	10.34	7.58	7.04
Lattice parameter a ($\text{\AA}$)	8.4404	8.4349	8.4291	8.4057	8.3948	8.4020	8.4022	8.4092
v_1 (cm^{-1})	570.74	576.74	586.38	632.67	577.02	591.341	583.141	571.458
v_2 (cm^{-1})	434	449.43	430.14	441.71	403.957	419.444	397.853	433.333
Band gap energy (eV)	3.05	3.06	3.07	3.10	3.064	3.075	3.081	3.085
Hr (G)	2171	2500	2518	2826	2399	2663	2678	3116
g-factor	3.041	2.641	2.622	2.337	2.752	2.479	2.465	2.119

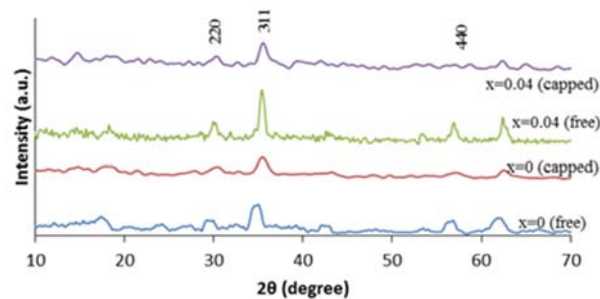


Figure 1. XRD patterns of $\text{Zn}_{0.5}\text{Co}_{0.5}\text{Fe}_{2-x}\text{Pr}_x\text{O}_4$ nanoparticles with $x=0$ and 0.04 for free and PVP capping samples.

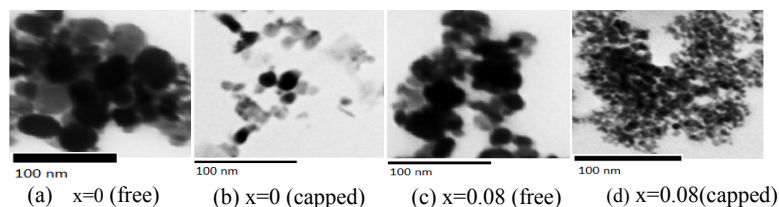


Figure 2. TEM images of $\text{Zn}_{0.5}\text{Co}_{0.5}\text{Fe}_{2-x}\text{Pr}_x\text{O}_4$ nanoparticles.

The average crystallite size (D) was calculated from the full width at the half maximum (FWHM) of the XRD patterns and the lattice parameter, by using Debye-Scherrer formula and Bragg's equation respectively [8].

Table 1 shows that both the lattice parameter and the average crystallite size decrease for PVP capping samples. This means that PVP reduces the agglomeration of the nanoparticles [9]. Figure 2 (a, b, c and d)) shows the TEM images for free and PVP capping samples of $\text{Zn}_{0.5}\text{Co}_{0.5}\text{Fe}_{2-x}\text{Pr}_x\text{O}_4$ nanoparticles with $x=0$ and 0.08. It is clear that the presence of PVP significantly affects the crystallite size, distributions and dispersion of the resulting nanoparticles. Uniform nanoparticles with narrow size distribution and sphere shapes with weak agglomeration were obtained for PVP capping samples [10]. PVP results in significant size reduction of nanoparticles. The crystallite size obtained from TEM, is quiet similar to that obtained from XRD with approximate deviation from 2 to 15% as listed in the table 1.

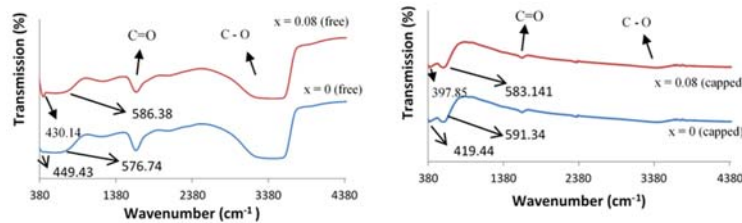


Figure 3. FTIR spectra of $\text{Zn}_{0.5}\text{Co}_{0.5}\text{Fe}_{2-x}\text{Pr}_x\text{O}_4$ with $x=0$ and 0.08 for free and PVP capping

Figure 3 shows the FTIR spectra for $\text{Zn}_{0.5}\text{Co}_{0.5}\text{Fe}_{2-x}\text{Pr}_x\text{O}_4$ with $x=0$ and 0.08. The FTIR spectra indicate the two principle absorption bands in the range $350\text{--}700\text{ cm}^{-1}$, which correspond to intrinsic stretching vibrations of the metal at the octahedral site, $\text{M}_{\text{oct}}\leftrightarrow\text{O}$ (observed from $\nu_2=382$ to 456 cm^{-1}) and at the octahedral site, $\text{M}_{\text{tet}}\leftrightarrow\text{O}$ (observed from $\nu_1=570$ to 633 cm^{-1}). For PVP capping samples, a shift in these two vibration bands is observed, as listed in table 1. For PVP capping samples, the broad band between 3000 and 3600 cm^{-1} related to stretching hydroxyl (O-H) group is replaced by sharper peak [11]; Also a shift in the peaks between 1620 and 1650 cm^{-1} towards lower wave number region is observed which indicates that C=O bond is getting weakened, and there exists an interaction between metal ions and PVP through oxygen of C=O group of the polymer [12].

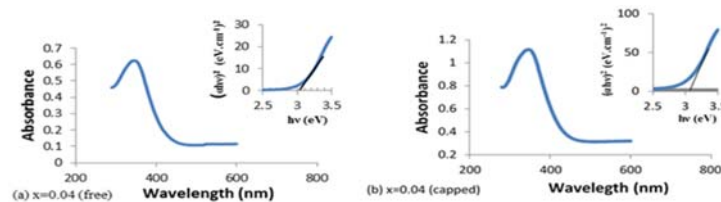


Figure 4. Plot of Absorbance as a function of wavelength $\text{Zn}_{0.5}\text{Co}_{0.5}\text{Fe}_{2-x}\text{Pr}_x\text{O}_4$ with $x=0.04$ for (a) free and (b) PVP capping samples; The inset figures are for Tauc plot.

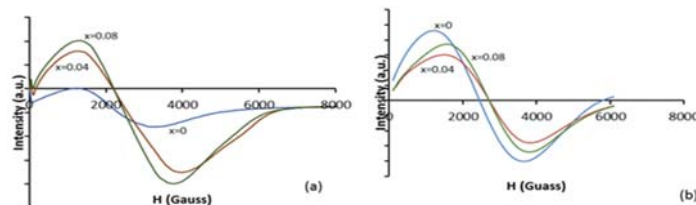


Figure 5. EPR spectra for $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_{2-x}\text{Pr}_x\text{O}_4$: (a) without (b) with PVP capping

Table 1 shows the values of bandgap energy of free and PVP capping samples. The energy bandgap E_g was obtained from the Tauc plot, using the intercept of the linear portion of the curve $(\alpha h\nu)^2$ versus $h\nu$ to $y=0$ as shown in figure 4. For the obtained energy gap of PVP-capped nanoparticles was found to increase which confirms the decrease of particle size when PVP was added. Such increase in the band gap may be attributed to the quantum confinement effect created by PVP surfactant [13].

X-band EPR spectra (9.24 GHz) recorded at room temperature for free and PVP capping $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_{2-x}\text{Pr}_x\text{O}_4$ are shown in figure 5. A single and strong symmetric EPR signal was observed for all samples with the resonance magnetic field H_r . For PVP capping samples, the value of H_r was increased as listed in table 1.

The spectroscopic Landé factor (g-value) was determined from the magnetic resonance field H_r by:

$$g = hv(\beta H_r)^{-1}, \quad (1)$$

where h is Planck's constant, v is the microwave frequency (9.24×10^9 Hz), β is the Bohr magneton. All the spectra were analysed and fitted to single EPR absorption line to obtain the values of magnetic resonance fields H_r and g-values as listed in table 1.

The increase of resonance field, as shown in figure 5, could be contributed to the decrease in super exchange interactions for the PVP capping samples. The g-values decreased for PVP capping samples, as listed in table 1; this is probably due to the enhanced exchange interaction between ferromagnetic core and antiferromagnetic surface layer [14].

4. Conclusion

The nanoparticles of $\text{Zn}_{0.5}\text{Co}_{0.5}\text{Fe}_{2-x}\text{Pr}_x\text{O}_4$ were successfully fabricated by the co-precipitation method with PVP as a capping agent with concentrations 0g/L and 30g/L. This work focused on the effect of PVP on Zn-Co nano ferrite doped with rare earth element. The average particle size was determined by TEM is in agreement with that calculated from XRD. For PVP capping samples, the particle size and the band gap energy was decreased. The FTIR confirmed the presence of metal oxide bands where their corresponding wavenumbers were shifted when PVP was added. The EPR spectra show that the resonance magnetic field was increased and the g-factor was decreased for the PVP capping samples. The effect of PVP in reducing the size and improving the EPR spectra of nanoparticles can have benefit in biomedical applications such as Magnetic Resonance Imaging MRI. Furthermore, this work can be extended by adding different concentrations of PVP, in order to find the optimum quantity.

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