Synthesis and Characterization of Transition Metals Doped Zinc Oxides Nanocrystalline Materials by Solution Based Precipitation Technique.

S.T.SHINDE[1], K. G. KANADE*[2], B.K.KARALE[1],
S. S. ARBUJ[4], A.A.KALE[3], D.B.BANKAR[3], S.P.KUNDE[1]

[1]*Post Graduate Department of Chemistry, Radhabai Kale Mahila Mahavidyalaya, Ahmednagar, India*
[2]*Post graduate Department of Chemistry, Yashvantrao Chavan Institute of Science, Satara, India*
[3]*Post Graduate Department of Chemistry, Annasaheb Awate College, Manchar, Ambegaon, India*
[4]*Centre for Materials for Electronic Technology (C-MET), Off Pashan Road, Panchwati, Pune, India.*
*****Corresponding Author email: kgkanade@yahoo.co.in

Abstract

A green synthesis of pure zinc oxide and transition metal doped zinc oxides such as Mn-ZnO, Fe-ZnO, Co-ZnO, Ni-ZnO and Cu-ZnO has been carried out by solution based precipitation technique. The pure ZnO and transition metal doped ZnO were characterized by FTIR, XRD, FE-SEM and EDS analysis. The FTIR analysis shows the formation of Metal oxide peaks of ZnO and the redshift value of FTIR shows transition metal doped on zinc oxide. The XRD analysis shows formation of highly crystalline hexagonal phase wurtzite structure of ZnO. The XRD of Mn doped ZnO shows presence of pure spinel phases of Mn along with hexagonal ZnO. The XRD of Fe-ZnO/Co-ZnO/Ni-ZnO shows cubic phase of Fe/Co/Ni along with hexagonal ZnO and Cu-ZnO shows monoclinic phase of Cu along with hexagonal ZnO. The FE-SEM images of ZnO shows the agglomerated clumpy particles with size 150-200nm, and the FE-SEM of doped image of Mn-ZnO, Fe-ZnO, Co-ZnO, Ni-ZnO, and Cu-ZnO was found spherical, rectangular and spongy morphology with the particle size 30-40, 35-45, 25-35, 15-25 and 20-30 nm respectively. The EDS analysis is well concurrence with the elemental analysis of transition metal doped ZnO. Overall our methodology for the preparation of nanocrystalline ZnO and transition metal doped nanocrystalline ZnO is easy and environmentally friendly.

Keywords: Solution based technique, ZnO NPs, Mn/Fe/Cu/Ni/Cu doped ZnO, and Characterization of NPs.

Introduction

Nowadays, the synthesis of nano material's and its use as environmentally friendly catalyst for organic transformation [1-2] as well as degradation of organic waste is an important area of research [3-4] in chemistry. Numbers of physicals and chemicals methods are routinely used for the synthesis of nonomaterial such as solution based precipitation technique [5-6], molten salt synthesis technique [7-8], sol-gel method [9-10] and hydrothermal method [11-12] for the find out unique morphology and uniform particle size. It has observed that nanosized materials exhibit altogether superior physical and chemical properties such as magnetic [13], electrical [14], catalytic [15], optical [16] and mechanical properties[17] than large particle sized materials due to their smaller size they have high surface-to-volume ratio that increases the surface leading energy.

Therefore we have used economically cheap and easily available transition metals such as Mn, Fe, Co, Ni and Cu for the doping with ZnO nanomaterials by solution based precipitation technique.

Those materials further can be used as heterogeneous recyclable catalyst in number of organic transformation and dye degradation.

Experimental Work

a) Synthesis of ZnO and transition metal doped ZnO.

For the synthesis of ZnO and transition metal doped ZnO, oxalic acid (99.9 %, SD-fine chemicals), zinc sulphate, manganese sulphate, ferrous sulphate, cobalt sulphate, nickel sulphate and copper sulphate (99.9%, SD-fine chemicals) has been used as precursors materials. The oxalic acid (0.1N) solution was added drop wise into different solution of zinc sulphate (0.1N) solution, as well as mixture of zinc sulphate (0.1N) and manganese sulphate (0.1N), zinc sulphate (0.1N) and ferrous sulphate (0.1N), zinc sulphate (0.1N) and cobalt sulphate (0.1N), zinc sulphate (0.1N) and nickel sulphate (0.1N), zinc sulphate (0.1N) and copper sulphate (0.1N) with constant stirring till the formation of zinc oxalate, Mn-Zn oxalate, Fe-Zn oxalate, Co-Zn oxalate, Ni-Zn oxalate and Cu-Zn oxalate complex. The formed precipitate of zinc oxalate and Mn/Fe/Co/Ni/Cu-zinc oxalate was washed by distilled water (~1lit) with multiple times and dried at 120ºC in the oven. Further, this intermediate complex was decomposed at 520ºC for 6 hr in order to achieve nanocrystalline ZnO, Mn-ZnO, Fe-ZnO, Co-ZnO, Ni-ZnO and Cu-ZnO.

b) Characterization of powdered ZnO and transition metal doped ZnO.

Fourier Transform Infra-Red spectroscopy (FTIR) (IR Affinity-1S) in the wavelength range of 400 - 4000 cm^{-1} was used to study the formation of nanocrystalline ZnO and Mn-ZnO, Fe-ZnO, Co-ZnO, Ni-ZnO and Cu-ZnO. The Powder X-ray Diffractograms (XRD) was recorded on X-ray diffractometer (Rigaku-D8/MaX-2200V) using CuK α-radiation with Ni filter. The field emission scanning electron microscope (FESEM HITACHI S-4800 and Nova Nano SEM 303) was used to determine surface morphology and particle size. Percent doping was showed by Energy-dispersive X-ray spectroscopy (EDS) study.

Results and Discussion

Structural study by FT-IR:

From the studies, the stretching mode of undoped ZnO is at 510.34 cm^{-1}. In this work, for (Mn-ZnO, Fe-ZnO, Co-ZnO, Ni-ZnO and Cu-ZnO), the values of absorption were found to be redshifted at 515.73, 532.37, 565.54, 551.50, and 516.18 cm^{-1} (Figure 1a-1f) respectively. Definitely, this can prove that the Zn–O–Zn network was perturbed by the occurrence of Mn, Fe, Co, Ni and Cu in its environment with the change in the peak position of the ZnO absorption bands. The overall FTIR analysis data is well matched with the reported frequencies of all doped nanomaterials.

Structural study by XRD:

Figure 2 showed typical X-ray diffraction pattern of as-synthesized nanocrystalline ZnO and Mn-ZnO, Fe-ZnO, Co-ZnO, Ni-ZnO and Cu-ZnO. The strong and intense XRD peaks (Fig. 2a) indicate the formation of highly crystalline hexagonal phase of ZnO with wurtzite structure. The lattice constant values acquired from the XRD patterns of ZnO [18] and Mn/Fe/Co/Ni/Cu-ZnO were in good agreement with the reported JCPDS values (100), (002), (101), (102), (110), (103) and (201). The XRD patterns of as synthesized materials such as of Mn doped ZnO [19] (Fig. 2b) depicts the presence of wurtzite ZnO along with pure spinel phases of Mn. The Fe/Co/Ni doped ZnO (Fig. 2c, 2d and 2e) depicts the presence of wurtzite ZnO along with cubic phases of Fe/Co/Ni [20-22], and Cu doped ZnO (Fig. 2f) depicts the presence of wurtzite ZnO along with pure monoclinic phases of Cu [23].

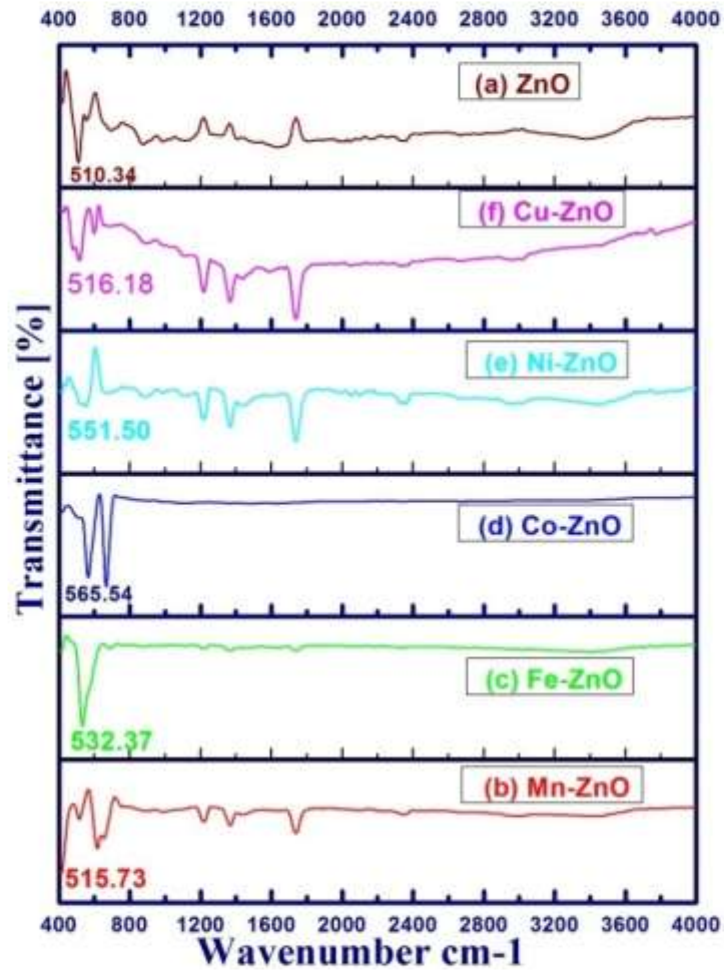

Figure 1: FT-IR pattern of as synthesized (a) ZnO, (b) Mn-ZnO, (c) Fe-ZnO, (d) Co-ZnO, (e) Ni-ZnO and (f) Cu-ZnO

The crystallite size of nanocrystalline materials are calculated using Scherrer's equation,

$$D_p = \frac{0.94\lambda}{\beta_{1/2}\cos\theta}$$

The average particle size was found to be in the range 40-50 nm for pure ZnO. As well as the particle size of Mn-ZnO, Fe-ZnO, Co-ZnO, Ni-ZnO, and Cu-ZnO was found in the range 30-40, 35-45, 25-35, 15-25 and 20-30 nm respectively.

FE-SEM study:

The FE-SEM images of ZnO nanomaterials depict the formation of agglomerated nanosheet like structures with particle size 120-180 nm (Fig. 3a, 3b). In case of Mn-ZnO, the formation flower shape morphology (Figure 3c and 3d) with particle size 20-40nm. The Fe-ZnO shows the rectangular shape at lower resolution (Fig. 3e) and at higher resolution shows spherical morphology with size 40-60 nm (Fig. 3f). The Co-ZnO depicts the formation irregular shape morphology with particle size 100-150 nm (Fig. 3g and 3h). Ni-ZnO shows the round shape nano particle with size 50-80nm (Fig. 3i and 3j). The figure 3k and 3l shows the agglomerated clumpy morphology of Cu doped ZnO materials with particle size 30-50nm.

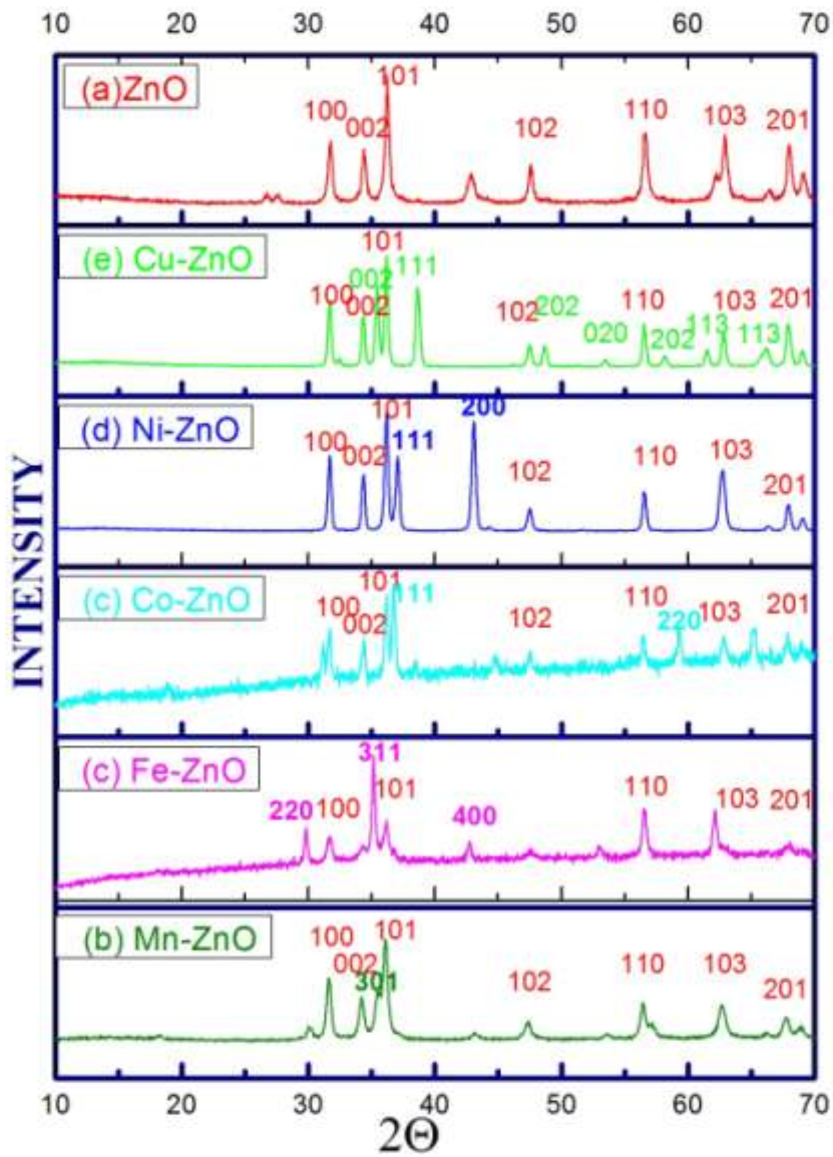

Figure 2: X-ray diffraction pattern of (a) ZnO, (b) Mn-ZnO, (c) Fe-ZnO, (d) Co-ZnO, (e) Ni-ZnO, and (f) Cu-ZnO

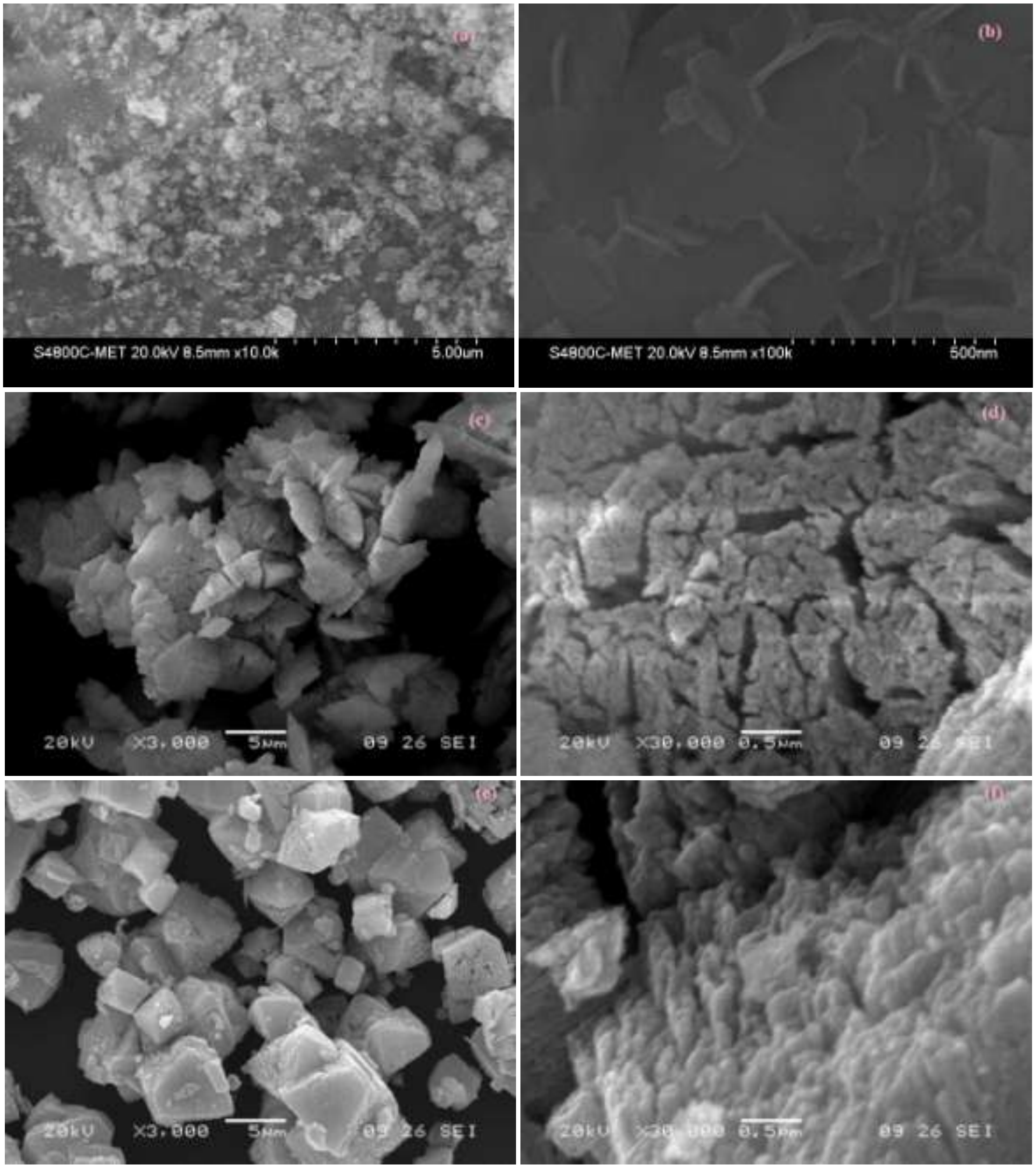

Figure 3: Morphology by FE-SEM of ZnO (a and b), Mn-ZnO (c and d), Fe-ZnO (e and f)

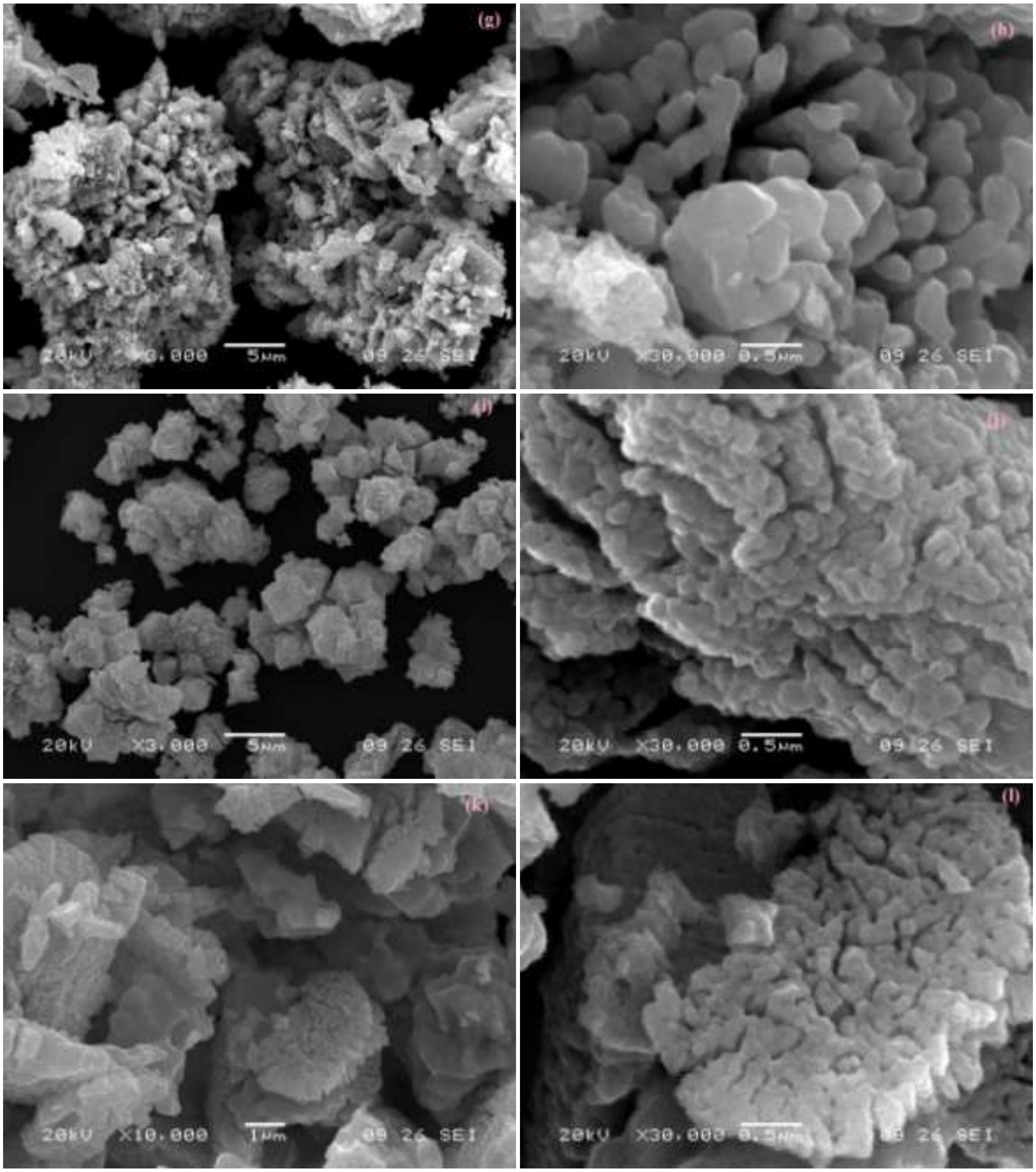

Figure 3: Morphology by Co-ZnO (g and h), Ni-ZnO (i and j), Cu-ZnO (k and l).

EDS analysis:

Figure 4, shows the Energy-dispersive X-ray spectroscopy (EDS) analysis of as synthesized Mn-ZnO, Fe-ZnO, Co-ZnO, and Ni-ZnO. The EDS analysis of figure 4a showed presence of Zn, O and Mn elements in the material. The EDS analysis illustrates nearby 41.52 wt. % Oxygen, 9.01 wt. % Mn and 49.47 wt. % Zn elements present in the material. The EDS analysis of figure 4b showed presence of Zn, O and Fe elements in the material. The EDS analysis illustrates nearby 45.38 wt. % Oxygen, 21.73 wt. % Fe and 32.89 wt. % Zn elements present in the material. The EDS analysis of figure 4c showed presence of

Zn, O and Co elements in the material. The EDS analysis illustrates nearby 42.21 wt. % Oxygen, 32.47 wt. % Co and 25.32 wt. % Zn elements present in the material. The EDS analysis of figure 4d showed presence of Zn, O and Ni elements in the material. The EDS analysis illustrates nearby 39.93 wt. % Oxygen, 25.98 wt. % Ni and 34.09 wt. % Zn elements present in the material. The percent loading by wet impregnation method is well concurrences with EDS report.

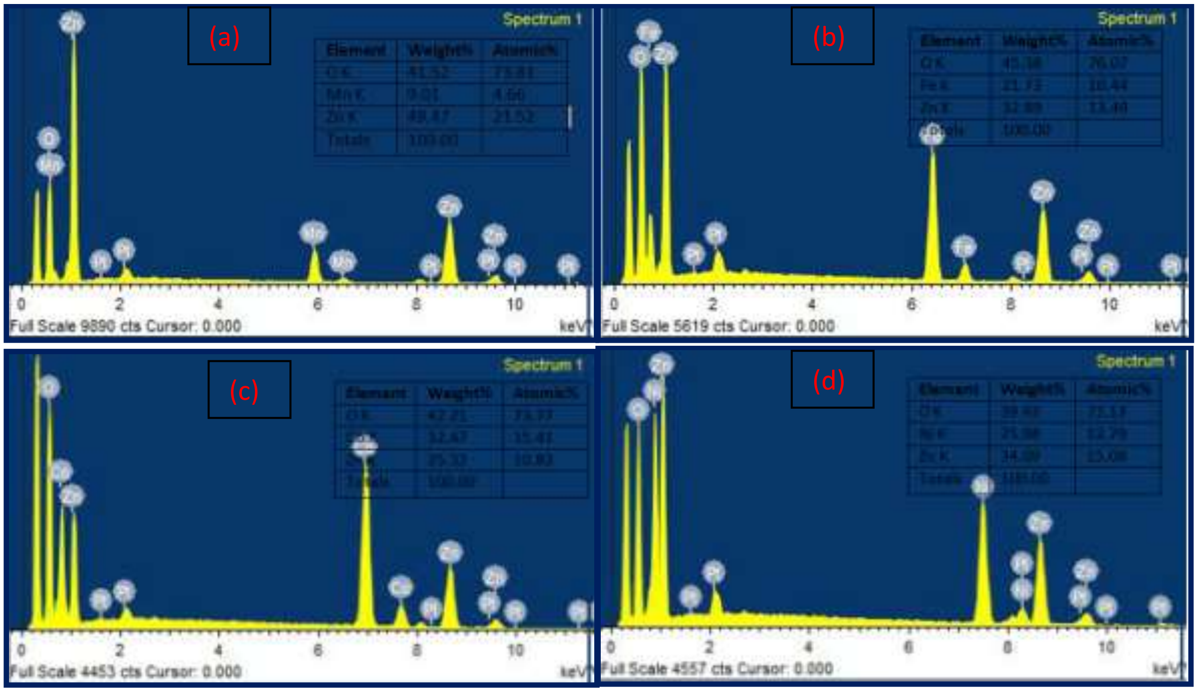

Figure 4: EDS image of as synthesized a) Mn-ZnO, b) Fe-ZnO, c) Co-ZnO, d) Ni-ZnO

Conclusion

We have successfully accomplished synthesis of nanocrystalline ZnO and Mn/Fe/Co/Ni/Cu-ZnO by solution based precipitation technique. The morphology and particle size of as synthesized materials is found to be more uniform and at nanoscale. The as synthesized materials can be act as a heterogeneous recyclable catalyst for different organic transformation. Overall we have used as an environmentally friendly route for the synthesis of nanomaterials and its catalytic application.

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