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Research Article

Structural, morphological and magnetic properties of fe₃o₄ nanoparticles by co-precipitation method

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Abstract

In recent years nanotechnology much significant potential in different areas of social interest. In this present thesis work Synthesis Fe_3O_4nanoparticles with various ratio of Ammonia solution by Co-Precipitation method and synthesized Fe_3O_4 nanoparticles analyzed by XRD, SEM, FTIR, and VSM for its Structural, Morphology and Magnetic properties. It has been found that the variations in ammonia solution have significant effect on the size and magnetic properties of Fe_3O_4nanoparticles. The prepared Fe_3O_4nanoparticles show applications.

Keywords: *: Fe_3O_4 nanoparticles, XRD, SEM, FTIR, VSM.*

Introduction

The arising fields of Nano-science and Nano-engineering are prompting to unprecedented understanding and control over the basic building blocks of all physical matter. It encompasses areas of research as diverse as engineering, physics, chemistry, material science, and molecular biology (Pooja Moteriya *et al*, 2020).

The research in this area has been set off by the recent availability of revolutionary instruments and approaches that allow the investigation of material properties, with resolution close to an atomic level (Ichinose *et al.*, 1992).The Nano science and Nanotechnology have introduced new trends that involve the ability to synthesize, characterize and manipulate artificial structures, whose features are controlled at the Nano level. It encompasses applications in various sectors such as Agriculture, Food and Biomedicine. Due to their small size they have a high surface-to-volume ratio that increases the surface energy leading to distinctively different chemical, electronic, optical, magnetic, and mechanical properties (Hemlata, Meena *et al.*, 2020: Boccaccini *et al* 2010 :.Shenashen et al .,2014 : Y.F.Goh et al.,2014 : Ciraldo *et al.*, 2018).For example, nanoparticle based semiconductors sensors exhibit higher sensitivity towards air pollutants for lower detection thresholds, at lower operating temperatures (Shen, *et al.*, 1994).

Nanoparticles often exhibit novel properties which are different from the materials (Akshay Dhayagude *et al.*, 2019). Many of these properties show strong dependence on size and surface preparation. The properties of nanocrystalline materials are frequently better than those of regular polycrystalline coarse grained materials. The development of a morphologically controllable synthesis of these semiconductor nanomaterials by a simple and economical method is an important issue (Jin *et al.*, 2001). Nanomaterials offer some unique features including large surface-to-volume ratio, fast charge transport to surface, and controllable morphology, ease for large area processing, and potential for inexpensive fabrication on flexible substrates (Moreno *et al.*, 2002).Within the broad family of functional materials, metal oxides play a very important role in many technological areas and medicinal purposes. Additionally, metal oxides having multivalent oxidation states which have attracted much attention among specialists because they often exhibit superior catalytic reaction performance (Barrodo *et al.*, 2002: Santhoshkumar *et al.*, 2017: Gunalan *et al.*, 2012).Metal oxides play a significant role in many fields of technology including catalysis, sensing, energy storage and conversion, and electro ceramics.

Recently, Nano-size iron oxide particles are widely used in different technological and industrial processes like recording materials; paint formulations, catalytic reactions, oxidizer in termite composition, as electrodes in non-aqueous and alkaline batteries diagnostic imaging, drug delivery, as cathodes in brine electrolysis, for damping in inertial motors, heat-transfer fluids, sorbents and gas sensors materials. In addition, it has been attracted much attention in biomedical applications because of their biocompatibility and low toxicity in the human body. Generally, nano-sized materials exhibit novel physical and chemical properties and consequently, synthesis of nanostructure Fe_3O_4 particles was intentionally studied.

Magnetite is a mineral, one of the three common naturally occurring iron oxides (chemical formula Fe_3O_4) and a member of the spinel group. Magnetite is the most magnetic of all the naturally occurring minerals on Earth (Harrison, R. J et al., 2002). Small grains of magnetite occur in almost all igneous and metamorphic rocks. Magnetite is black or brownish-black with a metallic luster, has a Mohshardness of 5–6 and a black streak. The chemical IUPAC name is iron (II, III) oxide and the common chemical name is ferrous-ferric oxide.

Various methods have been developed to produce ferrous ferric oxide (Fe_3O_4) nanoparticles can be synthesized through mechanical millings, decomposition of organic iron precursor, precipitation, sol–gel, combustion, solvothermal, hydrothermal, thermal decomposition etc. Among the various methods reported for the synthesis of Fe_3O_4 NPs, co precipitation method are commonly employed due to large scale production and relatively improved magnetic properties respectively (Jeong *et al.*, 2007). Chemical methods are promising, in terms of cost reduction and the ability to produce large amounts of small band gap material, which shows interesting size quantization effects (below the Bohr radius, i.e., 30 Å), minimum instrumentation compared to many physical methods (Prakash chand *et al.*, 2015). In recent years most of the metal oxide nanomaterials can be produced by soft chemical methods, such as co-precipitation, sol-gel and hydrothermal synthesis (Hair *et al.*, 1975).

The main aim of the present work is to synthesize magnetite nanoparticles by chemical co -precipitation method. Furthermore, the characterization of such synthesized nanoparticles was investigated by X-ray diffraction analysis, Scanning electron microscopy, Fourier transform infrared spectroscopy and Vibrating sample magnetometer.

Finally, to study the super paramagnetic nature of the synthesized Fe_3O_4 nanoparticles and predict their -medical applications.

Experimental Section

Materials used

(i) Ferric chloride ($FeCl_3$)

Molecular Formula : $FeCl_3.6H_2O$

Molar Mass : 162.2 g/mol (anhydrus)

Appearance : Green-black by reflected light

Density : 2.898 g/cm^3

Melting point : 306 ˚C

Boiling point : 315 ˚C

Solubility : Soluble in water

(ii) Ammonium Hyroxide (NH_4OH)

Molecular Formula : NH_4OH

Molar Mass : 35.04 g/mol

Appearance : Colorless liquid

Density : 0.91 g/cm^3 (25 %)

Melting point : −57.5 °C (25%)

Boiling point : 37.7 °C

Solubility : Miscible

(iii) Ferrous chloride ($FeCl_2$)

Molecular Formula:$FeCl_2$

Molar Mass : 198.81 g/mol (tetrahydrate)

Appearance : Pale green solid

Density : 1.39 g/cm^3(tetrahydrate)

Melting point : 105 ˚C (tetrahydrate)

Boiling point : 1023 ˚C(tetrahydrate)

Solubility : soluble in THF

Co-precipitation method

Precipitation is the formation of a solid in a solution during a chemical reaction occurs.

The solid formed is called the precipitate, and the liquid remaining above the solid is called the supernate. Precipitation reaction can be used for making pigments, removing salts from water in water treatment, and in classical qualitative inorganic analysis.

There are three main mechanisms of co precipitation; inclusion, occlusion, and adsorption. An inclusion occurs when the impurity occupies a lattice sites in the crystal structure of the carrier, resulting in a crystallographic defect; this can happen when the ionic radius and charge of the impurity are similar to those of the carrier. Besides its application in chemical analysis and in radiochemistry, co precipitation is also “ potentially important to many environmental issues closely related to water resources, including acid mine drainage, radionuclide migration in fouled waste repositories, metal contaminant transport at industrial and defines sites, metal concentrations in aquatic systems, and wastewater treatment technology (Martin de Vidales *et al.,* 1999).

Among the various methods reported for the synthesis of magnetite NP’s, co precipitation and decomposition of salt in high boiling organic solvent are more commonly employed due to large scale production and relatively improved magnetic properties. All the commercially based Fe_3O_4 NP’s based contrast agents have been synthesized only by co precipitation method. In chemistry, co precipitation (CPT) or co-precipitation is the carrying down by a precipitate of substances normally soluble under the conditions employed. Co precipitation is an important issue in chemical analysis, where it is often undesirable, but in some cases it can be exploited. In gravimetric analysis, which consists on precipitating the analytic and measuring its mass to determine its concentration or purity, co precipitation is a problem because undesired impurities often co precipitate with the analyze, resulting in excess mass. This problem can often be mitigated by “digestion” (waiting for the precipitate to equilibrate and form larger, purer particles) or by red solving the sample and precipitating it again (Simon *et al.,* 2006 & Jung *et al.,* 1995)

Preparation ofFe$_3$O$_4$ nanoparticles

Magnetites were prepared in laboratory by co precipitation method using following reagents. $FeCl_3.6H_2O$, NH_4OH (25%) and $FeCl_2.4H_2O$, were used with deionized water as solvent. All the chemical reagents were analytical grade, obtained from Merck (India) and used without further purification.

The Fe_3O_4nanopartices were prepared based on co-precipitation of Fe^{3+} and Fe^{2+} under the aqueous ammonia as precipitating agent. Briefly(0.2M) of $FeCl_24H_2O$ and (0.4M) of $FeCl_26H_2O$ were dissolved in 100 ml distilled water, the solution was heated to 80°C under various stirring at 750 rpm, 12ml of ammonium hydroxide (NH_4OH) is dropped slowly into the solution. The resulting suspension was vigorously stirred for another 1 hr the color of solution changed to black precipitates solution changes indicates Fe_3o_4 NP$_{S.}$ The black magnetic precipitates obtained were washed several times with distilled water and ethanol. Finally Fe_3O_4NPs were collected and dried for 6 hr at 70° C in Hot Air Oven.

Characterization

The prepared samples were characterized by adopting various physics chemical methods namely X-ray diffraction (XRD), Fourier transform infrared (FTIR), scanning electron microscopy (SEM) and vibrating sample magnetometer (VSM). The prepared Fe_3O_4 samples were characterized using the powder X-ray diffractometer, XPERT PRO with Cukα X-ray radiation (λ=0.15496 nm). The FTIR spectrum of the as-prepared sample was recorded, with a ‘SHIMADZHU’- FTIR Spectrometer using the KB r-pellet technique at a resolution of 4 cm^{-1} over the range 4000–400 cm^{-1}. The surface morphology of the prepared samples has been carried out using the **FEI Quanta FEG 200 Scanning Electron Microscope**. The magnetic measurements of the prepared samples were taken by a vibrating sample magnetometer model EG & G PARC VSM 155 at room temperature.

Results and Discussions

X-ray Diffraction (XRD) and Structural confirmation of Fe_3O_4.

X-ray diffraction (XRD) is a rapid analytical technique primarily used for the phase identification of a crystalline material, and can provide information on unit cell dimensions (Radhika Parvataneni et al., 2018). The structure identification is made from the X-ray diffraction pattern analysis, comparing it with the internationally recognized database containing the reference pattern (Joint Committee on Powder Diffraction Standards (JCPDS)). Powder X-ray diffraction is usually used to determine the crystal structure, grain size, phase and purity of the sample.

The simplest and most widely used method for estimating the crystallite size is from the Full Width at Half Maximum (FWHM in radian) of a diffraction peak by Debye-Scherrer's formula; $D = k\lambda / \beta\cos\theta$ (Giriraj Tailor et al., 2020)

where,

D = crystallite size,

λ = wavelength of the X-rays,

β = FWHM (in radians),

θ = angle of diffraction.

The size obtained from Scherrer's formula yields the apparent or average particle size for a material.

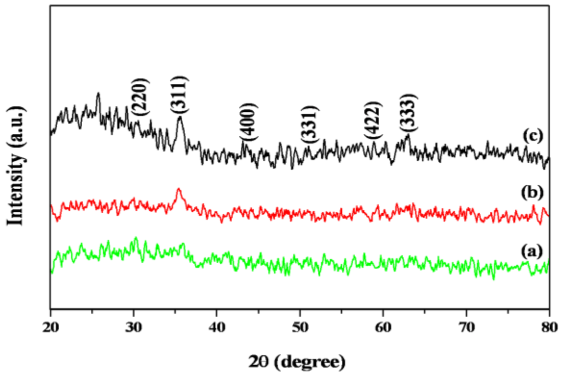


Fig. 1 XRD patterns of Fe_3O_4 nanoparticles prepared with (a) 12, (b) 15 and (c) 25 ml of ammonia solution.

Figure 1(a-c) shows the XRD patterns of Fe_3O_4 samples prepared with different ml of ammonia solution (12, 15 and 25 ml). All the diffraction peaks were readily indexed to a pure cubic phase of Fe_3O_4. The diffraction patterns are well matched with the literature (Safari *et al.*, 2014). Moreover, no other characteristic peaks due to the impurities, such as metallic Fe and other iron oxides were observed, which suggests that the precursors have been thoroughly oxidized to pure Fe_3O_4 nanoparticles. It is known that line broadening of diffraction peaks is influenced by the crystallite size and the internal strains. Fig.5.1 (a) shows a slight broadening of the peaks compared to that of the sample prepared with 15 and 25ml of ammonia (Fig.5.1(b-c)), which clearly reveals that the increased grain growth of the sample during the higher quantity of ammonia solution. Using Scherrer's formula, the average crystallite sizes of the samples are calculated to be 18, 20 and 25 nm for 12, 15 and 25 ml of ammonia solution used for preparation of Fe_3O_4 nanoparticles, respectively.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is one of the most widely used techniques used in characterization of nanomaterials and nanostructures. It provides the image of the morphology and microstructures of the bulk and nanostructured materials and devices (Allafchian *et al.*, 2016). The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography. It has many advantages such as, large depth of field and higher resolution, which allows more of a sample to be in focus at one time and so closely can be magnified at much higher levels.

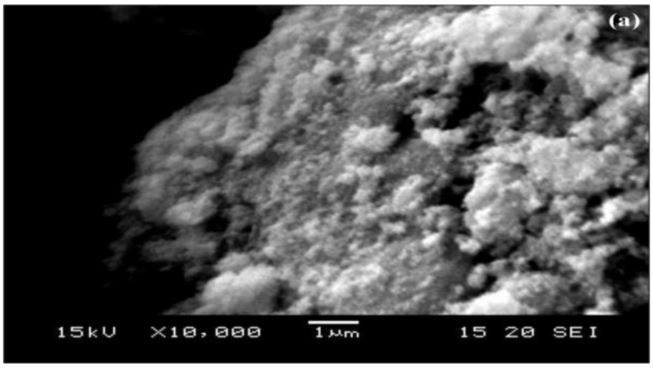


Fig.2 (a) SEM images of Fe_3O_4 nanoparticles prepared with (a) 12of ammonia solution.

The morphologies and microstructures of the as-prepared products were illustrated by SEM observations. Fig.2 (a-c) shows the detailed morphology of the hematite, from which dispersed, weak and highly agglomerated Fe_3O_4 nanoparticles were clearly observed for the prepared samples by using 12, 15 and 25 ml of ammonia solution, respectively.

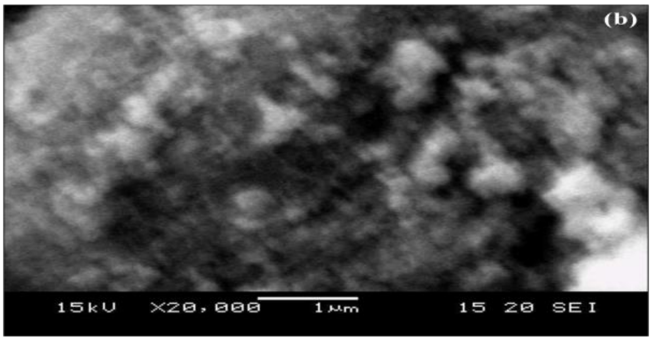


Fig.2(b) SEM images of Fe_3O_4 nanoparticles preparedwith (b 15 of ammonia solution.

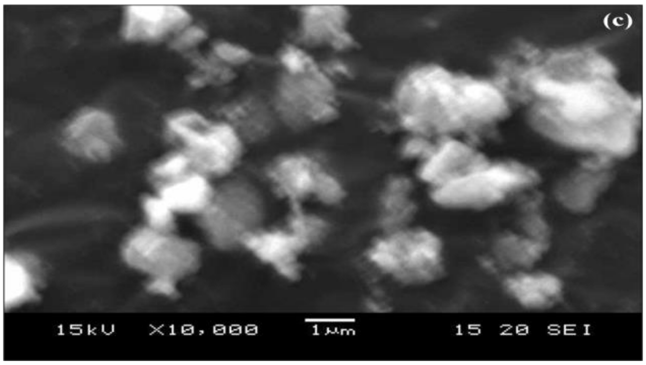


Fig.2(c) SEM images of Fe_3O_4 nanoparticles prepared with (c) 25 ml of ammonia solution.

As can be seen in the SEM images, spherical-like nanoparticles were observed with ~18, 20 and 25 nm in diameter. Moreover, the agglomeration effect was increasing with increasing ammonia solution quantity. The agglomeration of nanocrystals is usually explained as a common way to minimize their surface free energy; however, some reports explained that the agglomeration is assigned to the presence of organic radicals that act as binders (Dhananjaya *et al.*, 2011).

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared (FTIR) spectroscopy is a powerful tool for identifying the types of chemical bonds (functional groups) in a molecule by producing an infrared absorption spectrum that is like a molecular "fingerprint" (Parvathiraja *et al.*, 2020). The wavelength of the light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum. In general, the infrared radiation interacts with the chemical bonds to cause stretches, bends and various other atomic vibrations. For a vibration to give rise to the absorption of infrared radiation, it must cause a change in the dipole moment of the molecule.

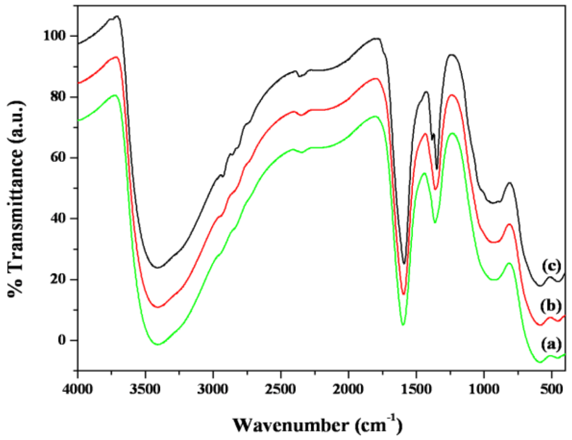


Fig. 3 FTIR spectra of Fe_3O_4 nanoparticles prepared with (a) 12, b) 15 and (c) 25 ml of ammonia solution

Fig.3 (a-c) shows the FTIR spectra of as-prepared Fe_3O_4 sample prepared with different ml of ammonia solutions (12, 15 and 25 ml). The broad absorption band observed in the spectra at 3413 and 1605 cm^{-1} are related to the O–H stretching and H–O–H bending vibration of the adsorbed water on the surface of the sample, respectively (B.D. Terris et al., 2005).

Vibrating Sample Magnetometer (VSM)

Vibrating sample magnetometer (VSM) is employed to determine the magnetization of the samples synthesized. Fig.4(a-c) shows the magnetic hysteresis loops of the Fe_3O_4 nanoparticles prepared with different ml of ammonia solution (12, 15 and 25 ml). It can be seen that the all the samples exhibits super paramagnetic behavior; however, the saturation magnetization (M_s) were differ with samples prepared in different ml ammonia solution.

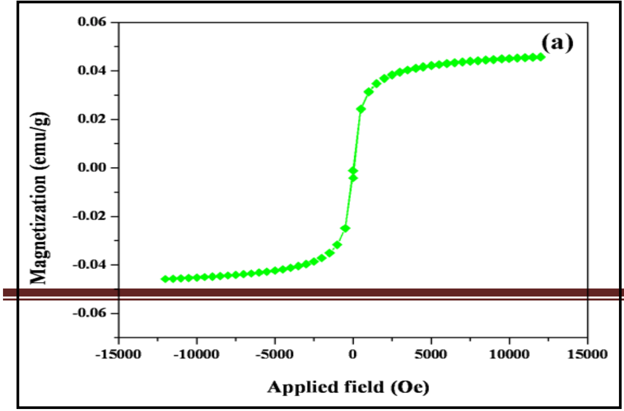
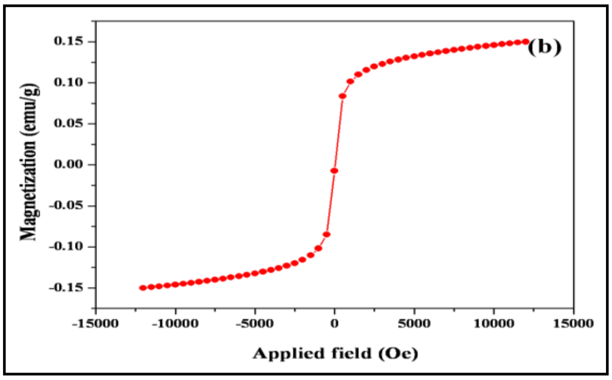
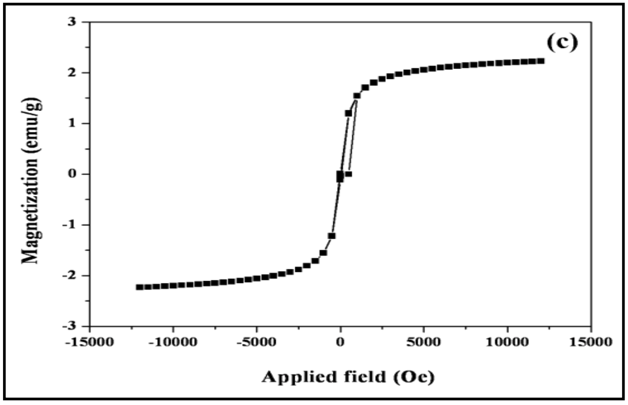


Fig.4 (a) Room temperature magnetic studies of Fe_3O_4 nanoparticles prepared with (a) 12,of ammonia solution.

Fig.4(b) Room temperature magnetic studies of Fe_3O_4 nanoparticles prepared with (b) 15of ammonia solution.

Fig.4 Room temperature magnetic studies of Fe_3O_4 nanoparticles prepared with (c) 25of ammonia solution





The saturation magnetization (M_s) of the Fe_3O_4 nanoparticles were measured to be 0.045874, 0.15010 and 2.2323 emu for the samples prepared with 12, 15 and 25 ml of ammonia solution, respectively, the different magnetization values of the samples may due to their different crystallite size. Therefore, the magnetization has a size-depended behavior for the Fe_3O_4 nanoparticles (Saha *et al.*, 2013). As the particle size decreases, transition takes place from multi-domain to a single domain system. The saturation magnetization decreases with decreasing particle size. On the other hand, coercivity increases because it reaches a maximum value at the critical size for single domain, the prepared Fe_3O_4 should be suitable for spintronic devices (Ramling *et al.*, 2002).These magnetic nanoparticles have a stronger magnetism and a higher relaxation rate, which contribute to their application form MRI (Ting Guo *et al.*, 2018)

Conclusions

In the present work deals with the synthesis, structural, size, morphology and magnetic properties of Fe_3O_4 nanoparticles by using co-precipitation method.The cubic structure of the prepared Fe_3O_4nanoparticles was confirmed by the powder XRD patterns. The particle sizes of the Fe_3O_4nanocrystallites prepared with different ml of ammonia solution (12, 15 and 25 ml) were 18, 20 and 25 nm, respectively. It was found that the ammonia solution quantity played important roles in the particle size effect of the nanocrystalline Fe_3O_4.The presence of functional groups of synthesized Fe_3O_4 samples were confirmed by the FTIR spectra.The spherical-like morphologies were observed with ~18, 20 and 25 nm in diameter for the Fe_3O_4nanocrystallites prepared with different ml of ammonia solution (12, 15 and 25 ml). Moreover, the agglomeration effect was increasing with increasing ammonia solution quantity.The magnetic properties of the samples were confirmed by VSM and the saturation magnetization (M_s) of the Fe_3O_4 samples were measured to be 0.045874, 0.15010 and 2.2323emu for the samples prepared with 12, 15 and 25 ml of ammonia solution, respectively. The different magnetization values of the samples may due to obtained different crystallite size of the samples. It has been found that the variations in ammonia solution have significant effect on the size and magnetic properties of Fe_3O_4nanoparticles.The prepared Fe_3O_4 nanoparticles show applications in the areas of nanoelectronics, sensors, batteries and photo catalysis.

References

Moteriya, Pooja, and Sumitra ChandaJ.Inor Organomet. Polymater: 30, 10(2020) 392 -3932.

Ichinose. N, Ozaki.Y, Kashu. S, Super PartTechonSpringer_Verlag, London, 1992.

Hemlata, Prem Raj Meena, Arvind Pratap Singh and Kiran Kumar Tejavath. ACS omega 5, no. 10 (2020): 5520.

Boccaccini. A.R, Erol. E, Stark W.J, Mohn. D, Hong. Z, Mano. J.F, Compos. Sci. Technol. 70 (2010)1764–1776.

Shenashen. M.A, El-Safty. S.A, Elshehy E.A, Part.Syst. Charact. 31 (2014) 293–316.

Goh. Y.F, Alshemary. A.Z, Akram. M, M. Abdul Kadir M.R, Hussain. R, Int. Appl. J. Glas, Sci. 5 (2014) 255–266.

Ciraldo. F.D, Liverani. L, Gritsch. L, Goldmann. W.H, Boccaccini. A. R, Dent. Mater. 11(2018) 692.

Shen. P.K, Tseung. A.C.C, Electrochem. J. Soc. 141 (1994) 3082.

Dhayagude, Akshay C., Sandeep. K, Newase,Satyawati. S, Joshi, Balasaheb. P, Kapadnis, andSudhir Kapoor. Mater. Sci .Eng : C 94 (2019): 437-444.

Jin.R, G. T. W, Mirkinm. C. A, Kelly. K. L, Schatz. G. C, Zheng. J. G, Science 194 (2001) 1901.

Moreno. E. M, Zayat. M, Morales. M. P, Serna. C. J, Roig. A, Levy. D, Langmuir 18, (2002) 4972.

Barrodo.E, Prieto.F, Medina. J, Lopez.A, Alloys. J.Compd.335,(2002)203.

Santhosh kumar. J, Venkat Kumar. S,and Rajesh kumar. S, Resour-Eff Technol3,no.4(2017):
459- 465.

Gunalan. S, Sivaraj. R, Rajendran. V, Prog. Nat. Sci. 22 (2012) 693–700 .

Harrison.R .J Dunin Borkowski. RE; Putnis, A (2002) ."Direct imaging of nanoscale magnetic interactions in minerals" (free-download pdf). Proceedings of the National Academy of Sciences 99 (26): 16556-16561. Bibcode: 2002PNAS…9916556H. doi:10.1073/pnas. 262514499.PMID 12482930.

Jeong. U, Teng. X, Wang. Y, Yang. H, Xia. Y, Adv. Mater. 19 (2007)33.

Prakash Chand , Anurag Gaur, Ashavani Kumar,
Umesh kumar Gaul,Appl Surf Sci ,356(2015) 438-446.

Hair. M.L, Non-Cryst. J. Solids 19, (1975) 299.

Martin de Vidales. J. L, Lopez-Delgado. A, Vila. E,Lopez. F.A, Alloys. J. Compd.287,(199)276.

Parvataneni, Radhika ,Drug. chem. toxicol 43, no.3 (2020): 307-321.

Tailor, Giriraj, B. L. Yadav, Jyoti Chaudhary,

Manoj Joshi, and Chetana Suvalka.Biochem, Biophy. Report 24 (2020): 100848.

Safari. J, Zrnegar. Z, Mol. J. Struct.1072 (2014)

53-60.

Allafchain, A.R., Mirahmadi-Zara. S. Z, Jalali.S A.H, Hashemi. S. S, and Vahabi. M. R. J. Nanostructure. Chem 6, no. 2 (2016): 129-135.

Dhananjaya. N, Naabhushana. H, Nagabhushana B.M, Rudraswamy. B, Shiakumara. C, Chakradhar. R.P.S, Alloys. J.Compds509 (2011)2368- 2374.

Parvathiraja.C, Shailajha. S, Shanavas. S, and Gurung. J. Appl. Nanosci, 11, no. 2 (2021): 477- 491.

Terris. B. D, Thomson. T, Phys. J, D: Appl. Phys.

38(2005)199.

Reiss. G, Hütten. A, Nature Mater. 4 (2005) 725.

Saha. S, Bhunia. A. K., Physi. J. Sci, 17, 2013, 191– 195.

Ramling. T. P, Winnubst. A. J. A, Van Kats. C. M, Philipse. A. P, J. Colloid Interface Sci. 249 (2002) 346 – 350.

Ting Guo, Mei Lin, Junxing Huang, Chenglin Zhou, WeizhongTian, XuefengBian and XiaoqianFeng., Hindawi–Journal of Nano materials Volume 2018. Article ID 7805147.