Comparative Study between Co-Precipitation and Sol Gel Method for the Preparation of Ferrites

Digmbar D. Kulkarni[1], Vishwesh R. Joshi[2], Sneha N. Shetty[3], Safa B. Patel[4], Misbah S. Khalfe[5]

Department of Physics[1,2,3,4,5]

Dapoli Urban Bank Senior Science College, Dapoli, Ratnagiri, Maharashtra, India

ddkulkarni50@gmail.com, joshiv97@gmail.com, snehashetty499@gmail.com, safapatel85@gmail.com, misbahkhalfe@gmail.com

Abstract: *The preparation of cobalt zinc ferrite that is crystallite magnetic material has been prepared by the famous methods co-precipitation and sol gel. The sol gel auto-combustion method requires low temperature and less time, produces homogeneous particles of uniform size. Whereas the co-precipitation method has possibility of producing pure and homogenous material. Though sol gel method produces high quality materials, co-precipitation has been effective and proved technology. Co1-xZnxFe2O4 can be prepared by the co-precipitation and sol gel auto combustion method for the full range of compositions with x varying from x=0.1-0.9. To study the structural properties of spinel structure ferrites XRD characterisation has been done. FTIR characterisation used to understand the metal ion bond formation. The formation of Co1-xZnxFe2O4 using both the methods was confirmed by the XRD. The transmission wave bond for specific range for both the methods, which corresponds to formation of oxygen bond and it confirms the formation of cobalt zinc ferrite. Spinel structure of ferrite represents the class of magnetic material. Sol gel and coprecipitation are widely used methods. The size and the properties of spinel ferrite nanoparticles can be greatly depends upon on pH, fuel, stirring time and speed, compound, etc. Ferrites are ferromagnetic oxides consisting of ferric oxide and metal oxides. The spinel ferrites are widely studied because of their numerous applications in several fields. Among the different spinel ferrites cobalt ferrite (CoFe2O4) with inverse spinel structure are promising magnetization, High electrical properties, good mechanical properties and chemical stability.*

Keywords: Cobalt Zinc Ferrite, Sol Gel, Co-Precipitation, XRD, FTIR.

I. Introduction

Ferrites are mixed oxide magnetic materials in which the iron oxide is main component. Ferrites have opened a new era in the physics of magnetic materials. Many researchers have made efforts to synthesis the ferrite materials for various applications.

The loadstone Fe_3O_4 was the first magnetic material known to man. It is also called as ***magnetite or Ferrous Ferrite***[10] . The magnetization phenomenon occurring in the ferrite material was studied by Du Boise et.al [1] to give quantitative idea about saturation magnetization in 1890. Pierre Weiss [2] has studied the magnetic properties of Fe_2O4 and found its saturation magnetization and Curie temperature. Hilpert et al [3] was first laid down the foundation stone for ceramic magnetic and suggested the formula AFe_2O_4 where A is divalent metal ion and also prepared the ferrites in laboratory.

Hedvall et al [4], Tammann et al [5] and Jander et.al [6] have explained the preparation of ferrites by solid state reaction. Kato and Takel [7] developed and realized that this magnetic oxide is the best material to use as a core for inductor.

The first application of magnetite was as ‘Lodestones’ used by early navigators to locate magnetic North. Naturally occurring magnetite is a ‘hard’ ferrite. ‘Hard’ ferrites have permanent magnetization. In time, man-made ‘hard’ ferrites with superior properties were developed but producing corresponding ‘soft’ magnetic material in the laboratory was a task.

Ferrites are used predominately in three areas of electronics: low level applications, power applications, and Electro-Magnetic Interference (EMI) suppression. Ferrite are found in the city Magnesia that’s why named Magnetite. Ferrites are mixed metallic oxides of high resistivity and are members of semiconductor family. They are ceramic ferromagnetic material with a general composition MFe_2O_4, where M is divalent metal. Fe, Mn, Mg, Ni, Zn, Cd, Cu, Co.**[8].**

II. Structure Of Ferrites:

1. Spinel Structure
2. Garnet Structure
3. Hexagonal Structure

Here in this article we are going to study spinel type Ferrite nano materials.

2.1 Spinel Structure

The spinel ferrite structure can be described as cubic close packed arrangements of oxygen atoms in which 32 oxygen ions forms a unit cell. Layers of oxygen ions contain 64 tetrahedral (A) sites and octahedral (B) sites.

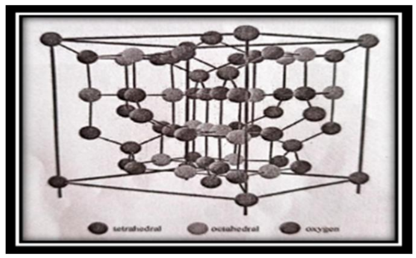

Figure 1: Schematic representation of crystal structure of Spinel Ferrite

Why choose Sol Gel Method and Co-precipitation Method?

Studies of spinel structure ferrite synthesis methods have caused to the development of different chemical synthesis techniques, which have a common features that all reagents are mixed in atomic and molecular level. Most popular methods used for the synthesis are ***Co-precipitation, Sol Gel Method.***

Sol Gel Auto-combustion synthesis method (also called low temperature, self combustion, auto ignition or self propagation) where the chemical sol gel and combustion process is combined has shown great potential in the preparation of spinel type ferrites nanomaterial. Generally this method can be considered as solution combustion techniques. During the last decade, the application of the Sol Gel combustion method for the synthesis of spinel ferrite power has been used in an increasing intensity.

Co-precipitation method is one of the convenient way to synthesis of iron oxide particles (Fe_3O_4) from aqueous salt solution by the addition of base (NaOH) at room temperature. The advantages of Co-precipitation method are high yield, high purity product, easily reproducible, etc.

III. Applications Of Ferrites

Now a day the magnetic materials are found in numerous products such as home appliances, electronic products, automobiles, communication equipment and data processing devices etc. These materials have now become a vital part of everyday life in modern times. It has wide applications in motors, generators, loudspeakers and telephones. Soft ferrites, used for low and high frequency applications. The low frequency applications of soft ferrites include magnetic recording heads, inductor and transformer and filter cores. The high frequency applications of soft ferrites include a large number of microwave components such as circulators, isolators. Now a days ferrites are used in radio, television, microwave and satellite communication, bubble devices, audio, video, digital recording.

3.1 Comparative Study

Co-precipitation Method	Sol Gel Method
1. Depends on parameters such as reaction temperature, pH, initial molar concentration.	1. Low temperature, less time, pH, ratio of citric acid to the metal nitrate.
2. Samples produced by Co-precipitation method showed super paramagnetic behaviour.	2. Produces homogeneous particles of uniform size.
3. High resistivity.	3. High resistivity.
4. Soft magnetic material.	4. Soft magnetic material

5. FTIR used to confirm the formation of Fe-O bond.	5. FTIR shows oxygen bonds at range of 500-600 cm^{-1} confirming formation of Co^{2+}.
6. The average Crystallite size of the particles were determined from XRD.	6. The average Crystallite size of the particles were determined from XRD

Table 1: Comparative study of Sol Gel and co-precipitation method

3.2 Preparation of Ferrites

A. Preparation of Ferrites by SOL-GEL Auto combustion Method

In present work, all the samples were prepared by using Sol-gel auto combustion technique. In sol-gel auto combustion technique, oxidizing metal salts and combustion agent (fuel) are essential for the combustion process. Metal nitrates and citric acid were used as oxidizing salts and combustion fuel for all the sample preparations. The Sol-gel auto combustion technique has been proved to be extremely facile, time-saving and energy-efficient route for the synthesis of ultra-fine hexaferrite powders.

B. Sol Gel Process

1. The starting materials used in the preparation of high purity metal nitrates i.e. ferric nitrate, cobalt nitrate and zinc nitrate and citric acid (as fuel) with high purity (for the formation of high quality nanoparticles).
2. Moreover, using distilled water for preparation of the solution is important to reduce the chances of the presence of impurities in the final product.
3. The solution was prepared with the molar ratio of citric acid to the total moles of chloride at 1:1 , where the stoichiometric amount of ferric nitrate, zinc nitrate and cobalt nitrate and citric acid were used.
4. The pH of the prepared solution was adjusted to 7 with the drop wise addition of ammonia and stirring.
5. The neutral solution of stoichiometric amounts of starting material and citric acid place it on hot plate with stirring.
6. First any water present was evaporated, and then as a result of continuous heating the gel was formed at approximately 90°C.
7. With continuous heating it began to dry until it became viscous gel.
8. Then self-ignition reaction took place at approximately 120-200°C. Without further heating the product formed is a "porous product".
9. The dried gel burnt completely in a self-propagating combustion manner to form Loose powder.
10. Finally the burnt powder was annealed at temperature 550°C for 4hrs with a heating rate of 50°C per minute to obtain the spinel phase.
11. Structural characterization was carried out by the x-ray diffraction.

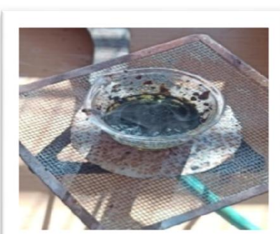

Fig 2. Viscous Gel formed at 100-120°C

Fig 3. Formed Ferrite crushed in mortar and pestle to form fine ferrite powder

B. Formation of Spinel Ferrites by Co-precipitation Method

For the synthesis of ferrite nano-particles the co-precipitation Technique is probably the uncomplicated and most productive chemical Route. This method also provides favourable production of nanoparticles. By Maintaining pH, temperature, ionic strength, nature of the salts, or the Fe(II)/Fe(III) concentration ratio the shape and size of the nanoparticles Can be customized.

IJARSCT

ISSN (Online) 2581-9429

International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)

Impact Factor: 6.252

Volume 2, Issue 4, April 2022

Co-Precipitation Process

1. Ultra-fine particles of with x varying from 0 to 1.0, were prepared by Co-precipitating aqueous solutions of $CoCl_2$, $ZnCl_2$ and $FeCl_3$ mixtures respectively in alkaline medium.
2. The mixed solution of $CoCl_2$, $ZnCl_2$ and $FeCl_3$ in their respective stoichiometry was prepared and kept at 60°C.
3. (100 ml of 0.5 M $CoCl_2$, 100ml of 0.5M $ZnCl_2$ and 100ml of 2M $FeCl_3$ in the case of $Co0.5Zn0.5Fe_2O_4$ and similarly for the other values x)
4. The mixtures of salts were stirred on magnetic stirrer for 30 minutes in order to have homogeneous solution.
5. This mixture was added to the boiling solution of NaOH (0.63M dissolved in 1200ml of distilled water) within 10 second under constant stirring.
6. The solid solution of metal hydroxide was transformed to complex zinc substituted ferrites when subject to heating in the alkaline medium.
7. The solution was maintained at 85°C for 1 hr.

Precipitated solution was filtered. This residue may contain salt in large amount which is removed by washing under ultra pure distilled water. The setup is shown as below-

Co-precipitation	Sol Gel
1. Stirring the starting materials i.e. Cobalt chloride, zinc chloride and ferric chloride with distilled water for 20-30 minutes.	1. Stirring the starting materials i.e. Cobalt nitrate, zinc nitrate and ferric nitrate with distilled water for 20-30 minutes.
2. Adding NaOH in boiling solution in 10, second under constant stirring.	2. Solution prepared with molar ratio of citric acid 1:1 with nitrate and stirs the solution for 30 minutes.
3. pH adjusted to 7, for that solution was and wash out by pure distilled water.	3. pH adjusted to 7 with drop wise addition to Ammonia (30%).
4. The residue initially dried at room temperature.	4. Heating at 90°C so that viscous Gel formed.
5. The compound maintain at 85° c until it becomes dry.	5. Self-ignition reaction took place at 120-200°C,and porous product formed.
6. Sintering at 550°C for 4hrs in muffle furnace.	6. Sintering at 550°C for 4hrs in muffle furnace
7. Crushed the formed ferrite in motor and pestle to form fine ferrite powder.	7. Crushed the formed ferrite in motor and pestle to form fine ferrite powder.

Table 2: Comparison between procedures of both the methods.

IV. X-Ray Diffraction

4.1 Introduction

The most widely accepted X-ray diffraction technique is used to characterize the crystallinity of nanoparticles. It gives average diameters of all the nanoparticles. Laue had suggested that the X-rays could undergo diffraction by the crystals, since the crystal planes can acts as the grating for the X-rays.

Analysis of the diffraction pattern confirms the formation of cubic spinel structure for all the samples. The strongest reflection comes from the (311) plane, which denotes the spinel phase. All the compositions had a Spinel structure. The peaks indexed to 220, 311, 400, 422, 511 and 440 planes of a cubic unit cell, corresponding to cubic spinel structure.

IJARSCT
ISSN (Online) 2581-9429
International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)
Impact Factor: 6.252
Volume 2, Issue 4, April 2022

V. Result

5.1 Sol Gel Method:

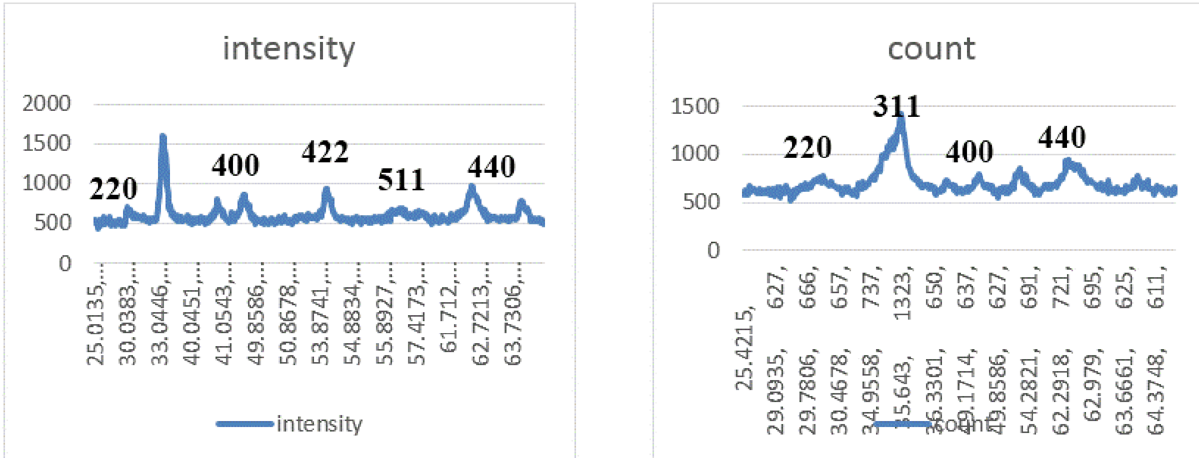

Figure 7: Shows the X-ray diffractogram of Zinc cobalt ferrite with x= 0.1, 0.3

hkl	0.1	0.3
220	25.83724	30.1345
311	33.173	35.554

Table3: XRD characterization of sol gel

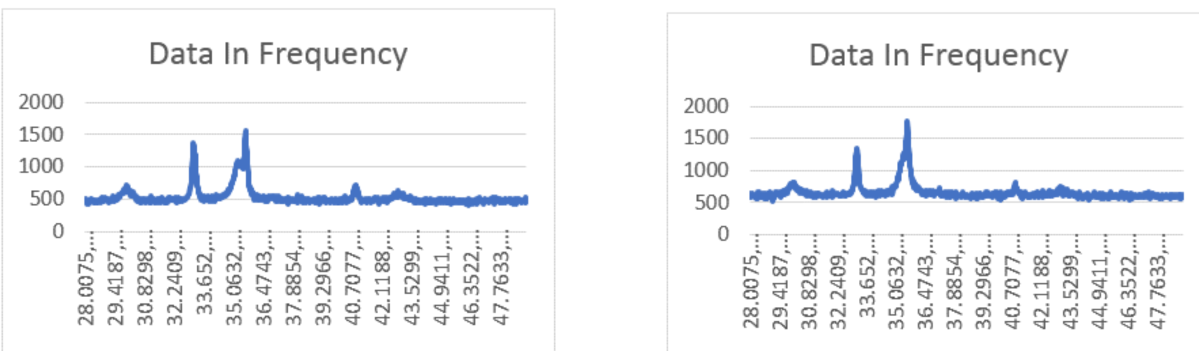

Figure 8: Shows the X-ray diffractogram of Zinc cobalt ferrite with x= 0.2, 0.1

VI. Conclusion

It is concluded that fig-1and2 shows the X-ray diffraction pattern zinc cobalt ferrite nanoparticles. All the peak belongs to cubic spinel structure and the analysis of XRD pattern prove the formation of spinel ferrite structure. XRD peak corresponding to most intense 311 peak of the XRD pattern[11]. Similar results found in Nano particulate crystalline cobalt ferrite for permanent magnet applications journal. [9]

6.1 Far Infrared Absorption Spectroscopy

The FTIR characterization has been done to understand the bond formation and synthesis material is ferrite. It is rapid method of characterization. These methods help us to understand the structure of functional groups and their linkages. The results of IR absorption study help us to understand electrical and magnetic properties of ferrites. In this report, the IR absorption analysis of Zn substituted Co- ferrites have been discussed. The IR spectra of samples in present case were obtained from common facility Centre, Shivaji University Kolhapur Maharashtra.

A. Sol Gel Method:

Zn content in cobalt Ferrite	ν_1	ν_2	ν_3	ν_4
0.4	3495.49	1591.50	1136.51	602.31
0.8	3488.50	1586.95	1041.85	602.28

Table 5: IR characterization of sol-gel

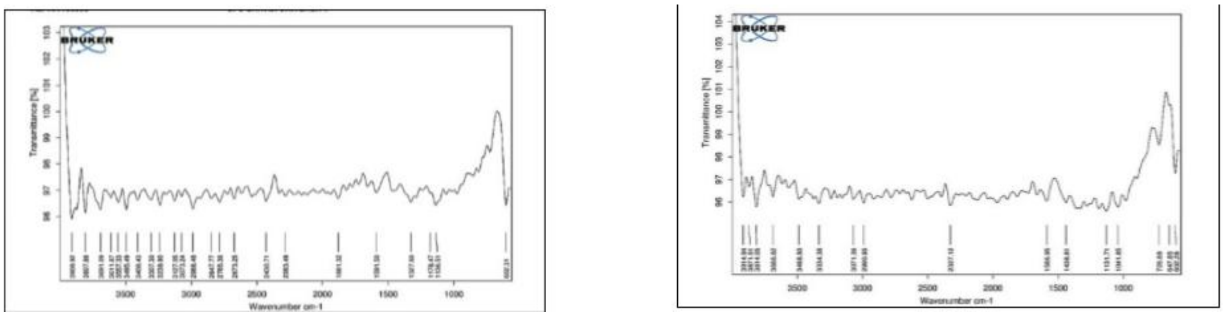

Figure 9: Shows the IR diffractogram of Zinc cobalt ferrite with x= 0.4,0.8

Zn content in cobalt Ferrite	ν_1	ν_2	ν_3	ν_4
0.6	3488.92	1520.13	1139.52	640.89
0.2	3474.71	1518.08	1139.12	723.55

Table 6: FTIR characterization of co-precipitation

Co-precipitation Method

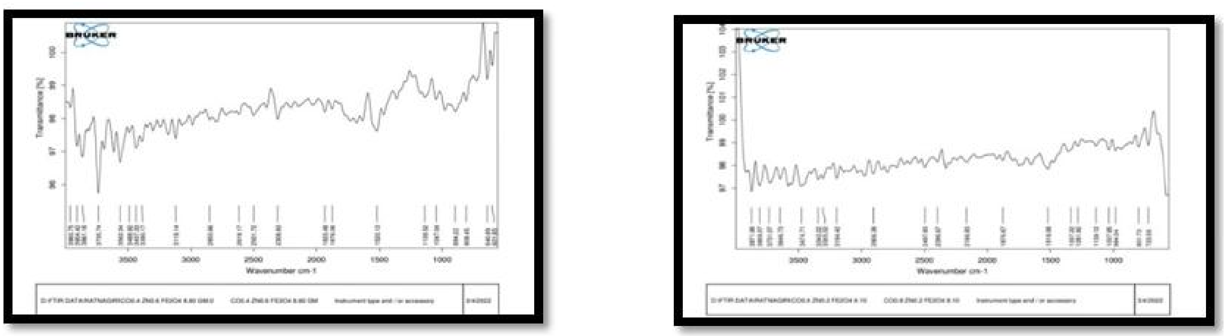

Figure 10: Shows the IR diffractogram of Zinc cobalt ferrite with x= 0.6,0.2

Conclusion

FTIR characterization from fig. shows the formation of metal-oxygen bonds. The transmission wave bond ϑ_1- ϑ_4 (3495.49- 602.31) which corresponds to formation of oxygen bond and it confirms the formation of cobalt zinc ferrite. Bond length increases with increase in zinc concentration[12]. Similar results found in Nano particulate crystalline cobalt ferrite for permanent magnet applications journal. [9].

Comparative study: (Characterization)

XRD of Sol-gel	XRD of Co-precipitation
1. Most intense 311 peak at 33.173 for x=0.1.	1. Most intense 311 peak at 35.6542 for x=0.1.
2. Peaks indexed to 220,311,400,422,511 and 440 corresponding to cubic unit cell.	2. Peaks indexed to 220,311,400,422,511 and 440 corresponding to cubic unit cell.

IR of Sol-gel	IR of Co-precipitation
1. Transmission of wave bond $\nu_1 - \nu_4$ (3495.49-49.602.31).	1. Transmission of wave bond $\nu_1 - \nu_4$ (3488.92-723.55).
2. Formation of metal oxygen bond has been confirmed.	2. Formation of metal oxygen bond has been confirmed.

Table 7: Comparison between results of both the methods

VII. Summary and Conclusion

Preparation techniques suitable for preparation of CoZn substituted ferrite nanoparticle using co-precipitation and Sol Gel are prepared. $Co_{1-x}Zn_xFe_2O_4$ nanoparticles can be prepared by the co-precipitation method for the full range of compositions with x varying from x= 0 to 1. Preparation of COF nanoparticles with the Citric acid Auto-combustion method relatively low temperature without further sintering was successful. The formation of $Co_{1-x}Zn_xFe_2O_4$ using both the methods were confirmed by the XRD.

In present work the samples prepared by Co-precipitation method showed superparamagnetic behaviour. Here the $CoFe_2O_4$ prepared by Co-precipitation method shows that it is not very small and it is known that $ZnFe_2O_4$ is a soft magnetic material. This soft magnetic nano-particles have interesting applications in magnetic costing and in the preparation of ferrofluids.

The Sol Gel Auto-combustion method requires low temperature and less time produces homogeneous particles of uniform size. With their key characteristics, nano dimensional Crystallite magnetic material systems have been recently used in a wide range of fields such as magnetic drug delivery, hyperthermia for cancer treatment, ferrofluids, magnetic storage data and many other applications. It has wide range of applications in biomedical, industry and other.

7.1 Comparative Study

Sol gel method	Co-precipitation method
1. Used citric acid as fuel agent.	1. Used NaOH as fuel agent.
2. Proceed at 120℃-200℃ temperature.	2. Relatively low temperature.
3. It takes less time.	3. Relatively much time for the process.
4. Used on commercial level.	4. Also used on commercial level but at least.
5. Energy saving due to low annealing temperature.	5. High yield, high product purity.
6. Low cost	6. Low cost

Table 8: Comparison between both the methods

Acknowledgement

Our special thanks to D.D.Kulkarni sir (HOD), Aniket Nandiskar sir, our guide Vishwesh R. Joshi sir, for their right directional and valuable guidance. We sincerely thanks our physics department staff for providing us laboratory facilities and instruments which were very essential for our experimental work. We also thankful to chemistry department for providing us glass wears and muffle furnace and thanks to head of chemistry department Sathe Sir for giving permission to use the lab. We thankful to Mr. D. D. Kulkarni sir, whose very important spiritual blessings gives moral support during this work.

List of Figures

1. Fig 1. Schematic representation of crystal structure of Spinel Ferrite
2. Fig 2. Viscous Gel formed at 100-120°C
3. Fig 3. Formed Ferrite crushed in mortar and pestle to form fine
4. Fig 4. Vertical Mechanical Stirrer Set-up
5. Fig 5. Filtration Method Set-up
6. Fig 6. Drying the residue at room temperature
7. Fig 7. Shows the X-ray diffract gram of Zinc cobalt ferrite with x= 0.1, 0.3
8. Fig 8. Shows the X-ray diffract gram of Zinc cobalt ferrite with x= 0.2, 0.1
9. Fig 9. Shows the IR diffract gram of Zinc cobalt ferrite with x= 0.4,0.8
10. Fig 10. Shows the IR diffract gram of Zinc cobalt ferrite with x= 0.6,0.2

IJARSCT

ISSN (Online) 2581-9429

International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)

Impact Factor: 6.252

Volume 2, Issue 4, April 2022

List of Tables:

REFERENCES

[1]. D.U. Bois, Phil. Mag. 29 (1890) 295.

[2]. Pierre Weiss Phys., 6 (1907) 66.

[3]. Hilpert S., Ber. Deut. Chem. 12 (1912) 2248.

[4]. Hedvell J.A Ber. Duet. Chem. 45 (1912) 401.

[5]. Tammann G.Z.Anorg. Allegaem. Chem. (1927) 87.

[6]. Jander W.Z. Anorg Allegaem chem. (1927) 1631.

[7]. Kato and Takei T., Jour. of Institute of Electrical Engineers, Japan

[8]. https://youtu.be/JjcRtQ7druY - video on ferrites

[9]. Nano particulate crystalline cobalt ferrite for permanent magnet applications journal.

[10]. https://youtu.be/JjcRtQ7druY (Ref. video of ferrite).

[11]. Standard values of 'hkl' planes were Ref. from jrnl of magnetism and magnetic materials 313 (2007) 293-299.

[12]. Std. values of IR absorption band ref. from jrnl of magnetism and magnetic materials 313 (2007) 293-299.