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Analytical studies of ferrite nanoparticles

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Nanomaterials based on ferrites represent a very attractive area to explore. The results show that the magnetic properties were improved by using dispersed nanoparticles, as ferrites. Nanometer-sized magnetic particles hosted on network material were successfully prepared by a simple chemical process. The aim of this work was to prepare ultra fine cobalt ferrite by a wet chemical method. Ammonium oxalate and a solution of hydrazine hydrate were mixed and stirred under argon atmosphere at 80^{o}C to provide ammonium oxalate hydrazinate. All the produced spherical beads have presented metallic particles ($NiFe_2O_4$, $CuFe_2O_4$, $CoFe_2O_4$, or $MnFe_2O_4$), either as isolated particles or agglomerates, located on their external and internal (within pores). Low temperature synthesis of such materials has been found to yield to ultra fine particles with unique and unusual particle size by means of chemical stoichiometry reaction. The energy dispersive X-ray spectroscopy (XRF) allowed the observation of submicron particles. Also, for characterization, we have used chemical analyses, X-ray diffraction (XRD), UV-Vis absorbance spectroscopy, thermal analyses TG-DTG, Mossbauer spectroscopy and electron microscopy. The analyses show the presence of a homogenous compound with characteristic properties and well crystallized spinel structure, with formula $MeFe_2O_4$ (Me = Co, Mn, Ni).

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1. Introduction

Nanotechnology is a science of the future, which began with John Dalton - the father of modern physics who develop the molecular – atomic structural theory. Nanotechnology developing new materials with dimensions on the nano scale called nano particles and investigate whether we can directly control matter on the atomic scale. This science has applications in a range of fields such as medicine, electronics, energy production and she satisfies growing demands of society [1-3].

Nanophase spinel ferrite particles ($NiFe_2O_4$, $CuFe_2O_4$, $CoFe_2O_4$ or $MnFe_2O_4$) have attracted considerable attention owing to magnetic properties, chemical and thermal stability. The application of $NiFe_2O_4$ nanoparticles are like hyperthermia agent and applied magnetic field product; $CuFe_2O_4$ has practical applications in radioelectronic devices [4], in information storage magnetic fluids ferrofluids and magnetic refrigeration [5]. $CoFe_2O_4$ has some applications in medicine: magnetic resonance imaging (MRI), targeted drug delivery, hyperthermia for cancer treatment and, also the applications in electronic fields are: high density storage devices, magnetic fluids, transformer cores, microwave devices, humidity and gas sensors [6]. $MnFe_2O_4$ has applications in cancer therapy [7]. Other ferrites like (Mn, Ni)-Zn ferrites have high frequency power applications using low-cost raw materials and by inexpensive preparation methodology [8, 9].

Nanosized functional particles present many different anomalous properties. Thus, due to the significant surface-to-volume ratio, anomalous magnetic behaviors, derived from surface spin disorder, have been observed in mechanically activated $NiFe_2O_4$ nanoparticles [10].

Spinel compounds have a general formula $A[B_2]O_4$ where A represent divalent metal ions Fe^{2+}, Mg^{2+}, Ni^{2+} and B represent trivalent metal ions such as: Fe^{3+}, Cr^{3+}, Al^{3+}, Mn^{3+}. These kind of spinel compounds have a cubic close packing of O^{2-}ions structure and two types of sites: Octahedral sites (B-sites) and Tetrahedral sites (A-sites) as you see in Fig. 1 [6].

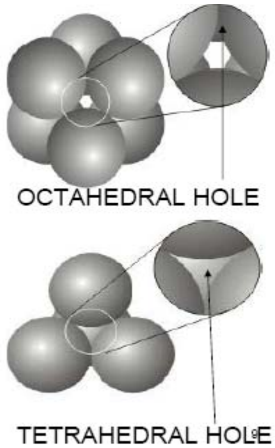

Fig. 1. Structure of Spinel with : a) octahedral hole and b) tetrahedral hole [6].

Physical, chemical and structural properties of oxide powders depend on preparation method and on the applied thermal treatment [11,12]. Therefore, in the last time, considerable efforts have been made to develop a synthesis method for oxide powders from chemical precursors. Such a method seems to be the method of the thermal decomposition of coordination compounds. Compared to the classical methods for synthesis of oxide powders that involve repeated firings of the component oxides, hydroxides or carbonates at high temperatures with frequent grindings and mixings, the precursor method offers some advantages:

- the decomposition of coordination compounds is simultaneous with (or followed immediately by) formation of a mixed oxide;
- the temperature of formation of mixed oxide is much lower than sintering or calcination temperature of some mechanical mixtures of single oxides;
- thanks to the relatively low temperature of formation, the mixed oxides obtained are characterized by fine granulation, high specific surface area and porosity (features that are very important for the catalytic activity of oxides);
- the homogeneity at molecular scale;
- a lower content of impurity.

The coordination compounds used as chemical precursors have to include ligands that generate, by decomposition, volatile products. Carboxylic acids are ligands that correspond to this requirement. It is well known that the time required for thermal decomposition of oxalates can be considerably shortened if the precursors are heated in the presence of a reducing agent, such as hydrazine [13].

The hydrazine can run as unidentate and bidentate ligand due to the variety of ways in which it may be bounded. Thus, there are a very large number of its derivatives. About oxalate hydrazinate complexes the literature is relatively poor [14]. Only oxalate hydrazinate of Fe was studied and published [15]. In this context, chemical analyses and establishes chemical composition of the complex is very important.

The purpose of our study was the incorporation hydrazine together with metallic cations in the structure of some oxalates for yielding coordination compounds, chemical precursors for low temperature synthesis of oxide powders. It was obtained oxalate hydrazinate complex of Fe, Mn, Ni and Co. For these compounds have been established the chemical composition, spectral properties and thermal behavior in order to determine the conditions for ferrite powder synthesis.

2. Experimental work

2.1. Synthesis

Nanometer-sized magnetic particles of $CoFe_2O_4$, Mn-Zn and Ni-Zn ferrite were prepared by oxalate-hydrazinate wet method [16].

Ammonium oxalate and a solution of hydrazine hydrate in a 1:3 molar ratio were mixed and stirred under a nitrogen atmosphere at 80 ^{o}C for one hour to provide ammonium oxalate hydrazinate. A saturated mixture of cobalt or manganese or nickel and ferrous chloride solutions in a 1:2 molar ratio was added slowly to the ammonium oxalate hydrazinate complex in a 1:1 molar ratio to obtain a tawny precipitate of cobalt and ferrous oxalate hydrazinate complex. The precipitate was washed, filtered, and dried at 70 ^{o}C to avoid the thermal decomposition. Heated in air at 260 ^{o}C, the precursor decomposes exothermic producing a fine, crystalline powder of oxide ceramic material. This material was analyzed after a thermal treatment at 500 ^{o}C, in air, for one hour. The product has the chemical formula $MeFe_2O_4$ (Me = Co, Mn, Ni).

All the reactants were purchased from Aldrich and Merck. In all experiments it has been used distilled water.

2.2. Apparatus and analysis methods

For the characterization of polynuclear complexes of oxalate hydrazinate it is necessary a complex analytical system capable to elucidate the mechanism of the reaction, to determine the composition and the properties of the substances.

The Elemental Analysis of samples and spectrum analysis was made with Elva X spectrometer with energy dispersive X-ray spectroscopy (XRF) at “XRF” Laboratory - Multidisciplinary Scientific and Technological Researche Institute, Valahia University, Targoviste. It is a non-destructive modern method for quantitative determination of elemental composition. The method allows applying alternative techniques to the same samples for getting more accurate results. XRF spectrometry is based on measuring energies and intensities of spectral lines of secondary X-ray emission. The spectrometer emits primary X-rays and causes each analyte of a sample to emit secondary X-rays. The energies of the secondary X-rays are peculiar to this analyte only. The intensity of the secondary X-rays depends on concentration of the analyte in the sample X-ray spectra relate to electron transitions in the inner atomic levels and are insensitive to chemical bonds [17].

By chemical analysis we determined the content of Co and Fe in $MeFe_2O_4$ compounds and by X-ray diffraction (XRD) we analysed the presence and size of oxide powders`crystals. The XRD has been recorded on DRON 2 type diffractometer.

The absorption spectroscopy in the UV-visible spectral region help us to perceived colour of $MeFe_2O_4$oxide powders involved. In the region of electromagnetic spectrum, molecules undergo electronic transitions.

Thermogravimetry measurements (TG) were examined by: Mettler 4000 TA, TG 50 analyzer system at a rate of 10°C·min^{-1} in a static air atmosphere; Perkin-Elmer thermo analyzer TG S-2 and DTA 1700 at a rate of 10°C · min^{-1}. Also, a TG (Du PontTGA) thermobalance is connected to a PC running Du Pont data processing software. About 15 mg of gently ground stones are subjected to analysis in a Pt plate in a temperature range 35 - 1000 °C (10°C·min^{-1}).

The Mössbauer spectra of the obtained ferrites were recorded on electromechanical spectrometer, at room temperature, whit ^{57}Ca/Cr source (20mCi activity), and standard α-Fe.

For determine the shape and the particle size of the ferrite was used an electronic microscope TESLA BS 301. The samples were prepared by dried method (dispersion on the support).

3. Results and discussion

The ferrite powder prepared by thermal decomposition of Co-Fe oxalate - hydrazinate at 500^{o}C for 1 hour, was analyzed by chemical methods, XRF, XRD, UV-ViS absorbance spectroscopy, TG-DTG (thermal analysis), Mössbauer spectrometry and electron microscopy.

We chose to study $CoFe_2O_4$ ferrite because it has: perfect chemical stability (metal & alloys unstable under atmospheric conditions); good thermal stability; high electrical resistivity (high frequency devices, memory cores, recording media); high saturation magnetization (high density recording media); low coercivity (for recording and reading of data); super-exchange interaction; super-paramagnetism (Biomedical applications) [6]. MnZn ferrites (MZFs) have become important to industry because of their dielectric and magnetic properties.

In the case of $CoFe_2O_4$, the chemical analyses confirm the molar ratio Co: Fe = 1:2 in ferrite powder. The content of Co is 25.2 % and Fe 47.2 % in the obtained powder, comparable with the content of Co and Fe in $CoFe_2O_4$.

The results of spectrum analysis of $CoFe_2O_4$, MnZn and NiZn ferrites are presented in Figures 2 and 7-10.

Spectrum Analysis using XRF spectrometry of sample $CoFe_2O_4$ are presented in Fig. 2.

Fig. 2. Spectrum Analysis of sample $CoFe_2O_4$

In Fig. 2 we observe that $CoFe_2O_4$ has a unitary composition, without impurities.

The X-ray diffraction shown in Fig. 3, indicated a pure nano cristaline cobalt ferrite, with the grain size in the range 10 - 30 nm.

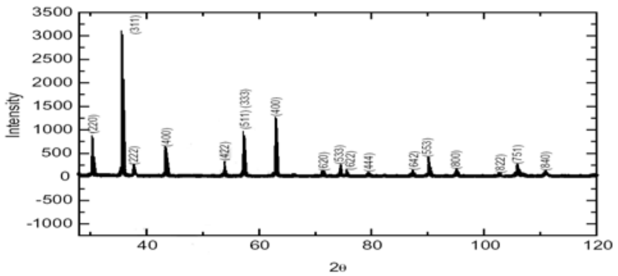

Fig. 3. X-ray diffractogram of the $CoFe_2O_4$ powder.

The UV-Vis spectrum show that the ferrite powder is identified by the charge transfer band at $\gamma_{max} = 28753\ cm^{-1}$.

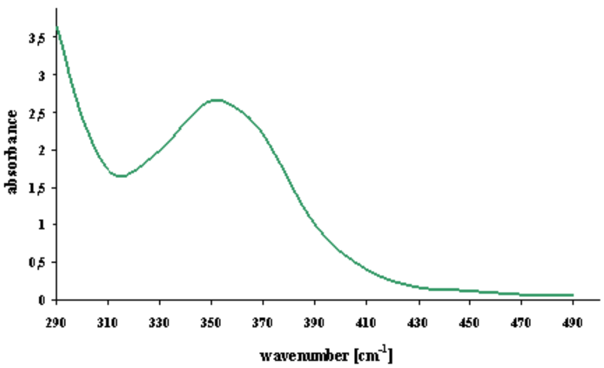

Fig. 4. UV-VIS spectrum of $CoFe_2O_4$ powder

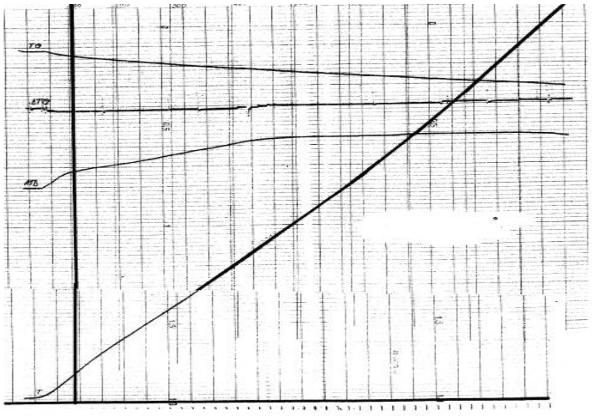

Fig. 5. The thermal analysis of $CoFe_2O_4$

The thermal analysis (TG) determines the temperature - and time - dependent changes in the mass of $CoFe_2O_4$ samples. Mass loss curves (Fig. 5) confirm that the structure of cobalt ferrite is a unitary one, without impurities and reagents not reacted.

Mössbauer spectroscopy is concerned with transitions that occur inside atomic nuclei. The technique measures the resonant absorption of γ-rays by a nucleus held rigidly within a crystal. Mössbauer data confirmed that the appearance at 500 °C a partial inverse spinelic structure appears, with the following structure: $[Co^{2+}_{0.57}Fe^{3+}_{0.43}]_{tetra}$ $[Co^{2+}_{0.43}Fe^{3+}_{1.57}]_{octa}$ O^{2-}_4.

The hyperfine parameters (e.g. isomer shift IS, quadruple splitting QS, and effective magnetic field Heff as well as line width and relative weight of partial element of spectra, G, were determinate. These parameters are shown in the Table 1.

The Mössbauer spectrum recorded on ferrite powder has the same shape and parameters with $CoFe_2O_4$ described on the literature. Mössbauer data confirmed that at 500 °C was obtained an inverse spinel structure. The Mössbauer parameters show that we have obtained the monophasic powder with magnetic properties.

Table 1. Mössbauer data on ferrite powder obtained at 500 °C.

Coordination	IS (mm/s)	QS (mm/s)	H_{eff} (kOe)	G (%)
Fe^{3+} tetrahedral	0.24	0	484	41.6
Fe^{3+} octahedral	0.36	0	512	30.7
			496	14.8
			478	14.8
			442	14.8

This powder has been analyzed by electronic microscopy. As shown in Fig. 6, most $CoFe_2O_4$ particles are well crystallized. $CoFe_2O_4$ particle size falls in the size range 0.01 - 3 μm.

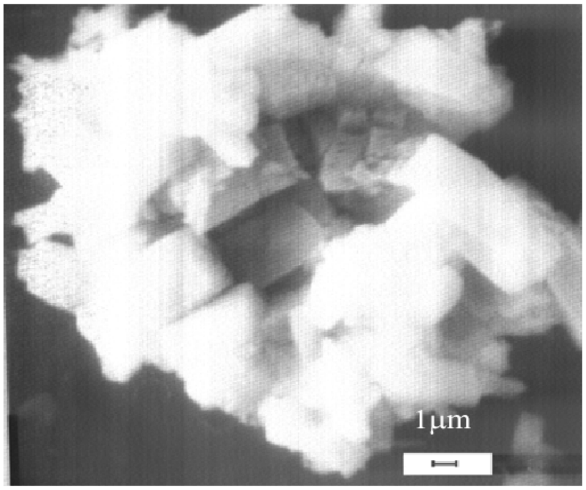

Fig. 6. The morphology of cobalt ferrite using electron microscopy

The spectral analysis of sample FeMnZn at 6h and respectively 24h are presented in Fig. 7 and 8:

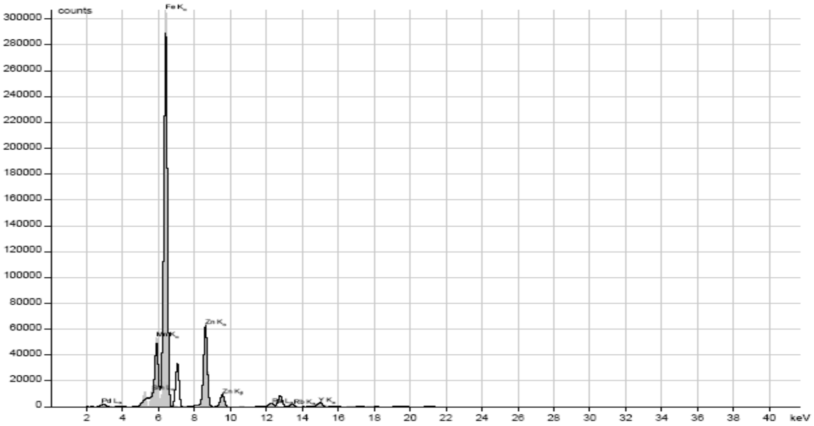

Fig. 7. Spectrum analysis of sample FeMnZn at 6h.

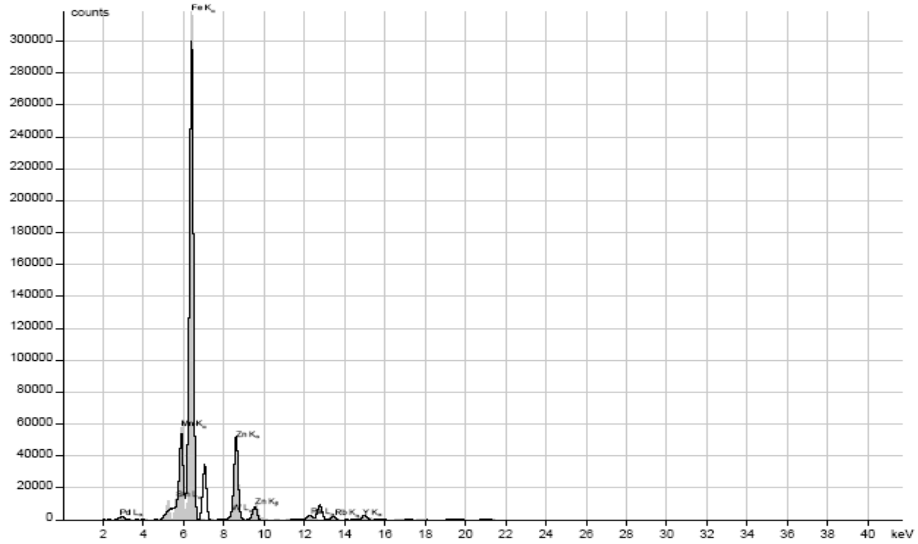

Fig. 8. Spectrum analysis of sample FeMnZn at 24h.

Spectrum Analysis of sample FeNiZn at 6h and respectively 24h are presented in Fig. 9 and 10:

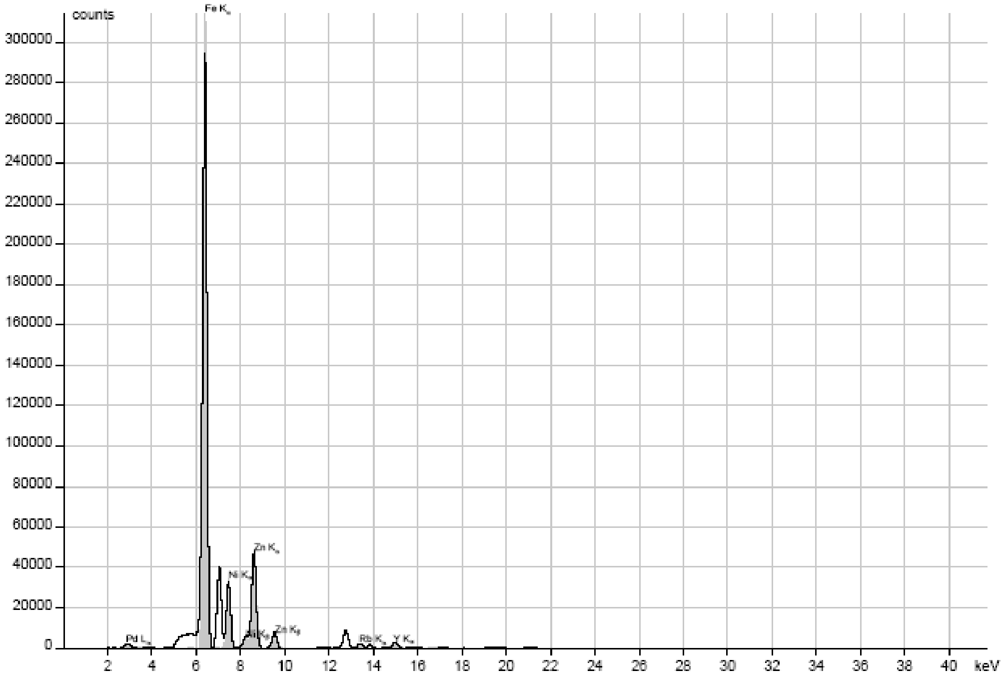

Fig. 9. Spectrum analysis of sample FeNinZn at 6h.

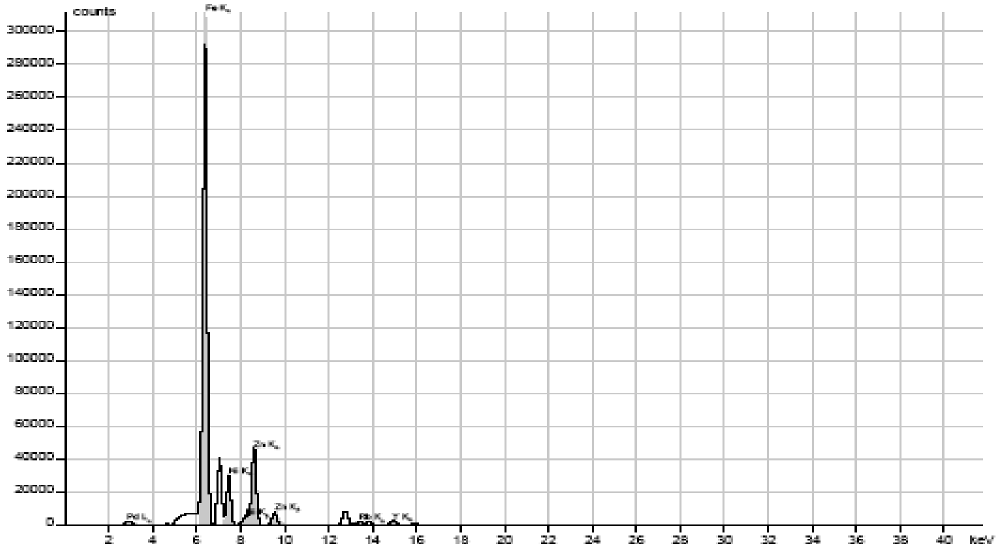

Fig. 10. Spectrum analysis of sample FeNiZn at 24h.

Is important to mention that an optimum time for ferite synthesis was 6 hours, because the composion and spinel structure were formed and the reaction time was shorter

4. Conclusions

Co-Fe oxalate hydrazinate complex with the chemical formula: $CoFe_2 \cdot 3N_2H_4 \cdot 6H_2O$ a very good precursor for $CoFe_2O_4$ ferrite was obtained. The optimum composition of oxalate hydrazinate precursors from the point of view of the number of hydrazine molecules is the results of the compromise between the decomposition temperature and the violence of the decomposition. It is desired a low decomposition temperature, but also a control of the decomposition reaction is necessary. The presence of water is necessary because it is a moderator for thermal decomposition and it favors the yielding of oxide ceramics. The analyses show the presence of a crystalline compound with characteristic properties. IR spectrum of Co-Fe oxalate hydrazinate has demonstrated that hydrazine is present into complex structure. There was demonstrated the formation of cobalt ferrite at low temperatures. Homogeneous and well crystallized ferrite powder ($CoFe_2O_4$), at 500 °C has been obtained.

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References

[1] ***, Nanotehnologia, Military Observaters, Nr. 8 (27 februarie - 4 martie 2008), www.presamil.ro.
[2] R. M. Ion, Materiale Nanocristaline, Ed.FMR, Buc. (2003).
[3] R. Zavaglia, N. Sbirrazzuoli, A. Mija, L. Vincent, N. Guigo, Congres GFP 2008, Lyon, 25-27 Nov. (2008).
[4] K. K. Patankar, V. L. Mathe, R. P. Mahajan, S. A. Patil, Ram Manohar Reddy, K. V. SivaKumar, Materials Chemistry and Physics, **72**(1), 23 (2001).
[5] S. Roy, J. Ghose, Journal of Magnetism and Magnetic Materials, **307**(1), 32 (2006).
[6] Muhammad Javed Iqbal, http://www.ncp.edu.pk.
[7] M Shinkai, J. Biosci. Bioeng. **94**(6), 606 (2002).
[8] B. Parvatheeswara Rao, K. H. Rao, Journal of Materials Science Letters **22**, 1607 (2003).
[9] A. Braibanti, F. Dallavalle, M. A. Pellinghelli, E. Leporati, Inorg. Chem. **7**(7), 1430 (1968).
[10] R. H. Kodama, A. E. Berkowitz, E. J. Mcniff, S. Foner, Phys. Rev. Lett. 77, 394 (1996).
[11] P. Ravindranathan, G. V. Kashinath, K. C. Patil, Journal Solid State Chemistry, **66**, 20 (1987).
[12] I. Mindru, L. Patron, M. Brezeanu, Romanian Chemical Quarterly Review **4**(3-4), 167 (1996).
[13] Longo, H. S. Horowits, L. R. Clavena, Solid state chemistry, Edited by S. L. Holt, J. B. Milstein, M. Robins, American Chemical Society, Washington DC, 139 (1980).
[14] E. W. Schmidth, Hydrazine and its derivatives, Wiley, (1984).
[15] V. Borker, K. S. Rane, V. N. Kamat Dalal, J. Mat. Sci.: Mat. in Electr. **4**, 241 (1993).
[16] R. M. Ion, E. Chirtop, C. Bercu, Rev. Chim, **42**(10), 34 (1996).
[17] ***, Portable X-ray Fluorescence Spectrometer (user's manual), Elvatech Ltd.

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