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Starch assisted sol gel synthesises and characterization of $NdFeO_3$

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Abstract: Neodymium orthoferrite ($NdFeO_3$) was synthesized by starch assisted sol-gel combustion method. The structural, phase conformation and chemical composition were studied and effectiveness of optical and magnetic properties were investigated. Fundamental expressions such as magnetic saturation, retentivity, and coercivity are accentuated because these characteristics strongly affect the magnetic properties of the ceramics.
Key words: Sol-gel combustion, Ferrite, optical band gap, magnetic property.

1. Introduction:

In current scenario rare-earth oxide based perovskite compounds are having superior spin nature and remarkable multiferroic and magentoelectric properties. Multiferroic materials are incredible in the current science and technology because of its potential applications in non-volatile memories, sensors and spintronic devices [1-3]. Recently, it was realized that rare earth orthoferrites ($RFeO_3$, R=Y, Gd, Sm, Nd) are having spin reorientation with respect to temperature, which evoke fascinating magnetic, optical, electrical, mechanical and other physical properties. Ortho-ferrites are particularly attractive to study the rare-earth relationship between structural, electronic and magnetic degrees of freedom which strongly depending upon the rare-earth element [4-6]. The crystal structure of the $NdFeO_3$ was first analyzed by R. L. White (1971), and they reported that it has orthorhombic structure with space group Pbnm. The orthorhombic distortion in orthoferrites increases with the size of the rare-earth ion which controls the magnetic properties, essentially due to the super exchange via Fe-O-Fe bonds [7-8].

The magnetic properties of $RFeO_3$ have two magnetic sublattices (R^{3+} and Fe^{3+}) which can be of varying magnetization dependences leading to complex magnetic phase illustration. In general, all types of rare earth orthoferrites, Fe^{3+} ions are having Neel temperature (T_N) that lies between 620K– 700K, but R^{3+} ions have T_N below 5K because its super exchange interaction lies between 3d- 4f electrons. Among all $RFeO_3$ (rare earth ferrite), $NdFeO_3$ has a significant magnetic property which has a relatively high magnetic order in Nd^{3+} at high temperature and also a clear spin reorientation in canted antiferromagnetic systems. Some of the researchers have recently reported the ferroelectric nature of $NdFeO_3$ at room temperature [9-11].

Ceramic orthoferrites are widely synthesized in various techniques but in general $NdFeO_3$ powders are synthesized by the solid-state reaction process at high temperature followed by repeated grinding [12–13]. But this process has few disadvantages like reaction at high temperatures, low chemical homogeneity and high in oxygen vacancies [14]. A simple method to overcome the drawback of solid state is sol–gel combustion method and it provides several advantages which are as follows: simple, economical in preparation, easy control of homogeneity and stoichiometric [15]. In supporting, the reports shows that $NdFeO_3$ samples synthesized by the

sol–gel method have a finer grain and uniform size distribution which are believed to be important key figures to improve electrical, magnetic and optical properties [12, 16].

In this article, we have described optimization of the sol gel synthesis of $NdFeO_3$ ceramics. Further the structural, composition, and particles were analysed by PXRD, EDAX and HRSEM respectively. The optical properties by UV-Visible Diffused Reflectance Spectrometer (UV-DRS) spectroscopy and the room temperature magnetic behaviour were investigated by Vibrating Sample Magnetometer (VSM).

2. Methodology

Polycrystalline samples of $NdFeO_3$ were synthesized by the sol–gel combustion method using starch as a gelling agent and also as combustion fuel. The starting materials are analytical-grade starch, $Nd(NO_3)_2.4H_2O$ and $Fe(NO_3)_2.6H_2O$. 50 ml of 1M of Neodymium nitrate and 50 ml of 1M of Ferrite nitrate are mixed using magnetic stirrer attached with hot plate (Magnetic stirrer–REMI–1MLH model) and 50 ml of 2M starch solution is added slowly into the mixed metal nitrate solution. The resulting transparent solution is heated from room temperature to 393 K with constant stirring to obtain a brown gel. The resultant gel is kept for 623 K for 30 min in a preheated silica carbide furnace (Indfur furnace heating rate 101°C/min), resulting in a large voluminous fluffy mass of brown precursor. This precursor is then heated for 2 h each at 873 K, 1123 K and 1400 K and subjected to PXRD. On further heating up to 1600 K for 12 h, the single phase carbonaceous free $NdFeO_3$ is obtained.

3. Powder X-Ray Diffraction

XRD pattern of the synthesized precursors at various temperatures were recorded using Rigaku Geiger-flex with Cu-K_α radiation source. The data was recorded over a range of 20° to 40° with a step size of 0.01° and the obtained pattern was plotted [Fig. 1]. The result of the sintered sample at 873 K shows the presence of the metal carbonates. $NdCO_3$ and $FeCO_4$ phases are prominently seen in the sample are sintered at 1123 K for 2 h. The decomposition of ferrite carbonate sintered at 1400 K seen in the XRD pattern. On further sintering the precursor at 1600 K, the XRD pattern confirms the single phase of $NdFeO_3$. The peaks were indexed using JPCDS file 88-0477. From PXRD, it was observed that the grown crystal belongs to orthorhombic system with the lattice parameters a= 5.587 Å, b=7.761 Å, c=5.450 Å, α=β=γ =90° which is in good agreement with the reported values [4-6, 12].

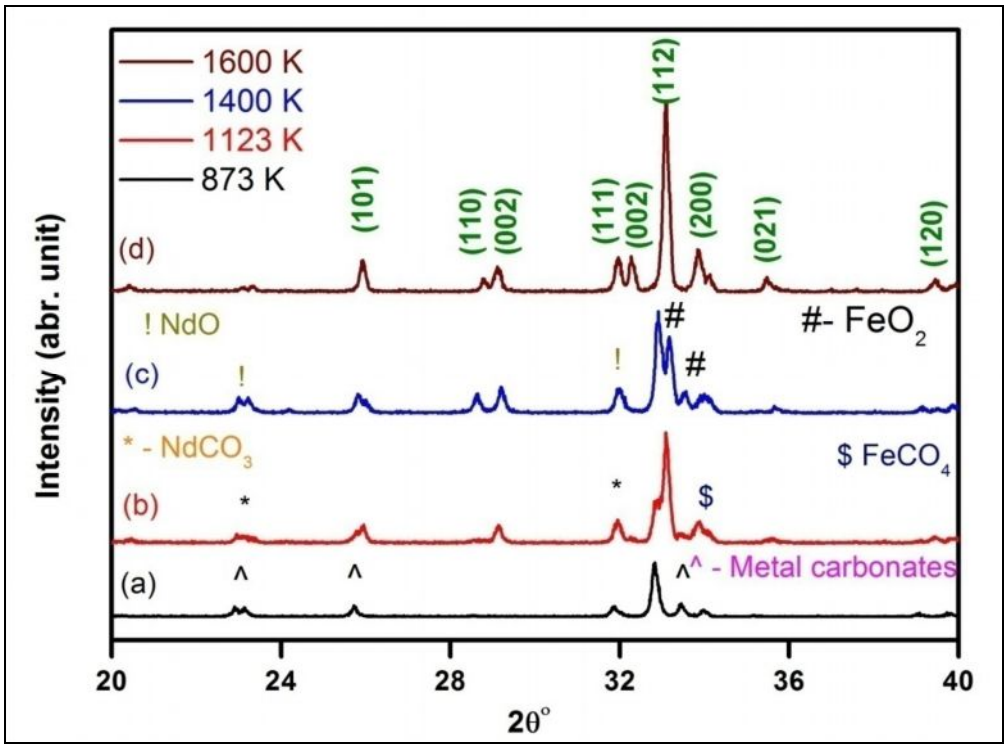

Fig. 1. Powder XRD for synthesized powder

4. SEM AND EDAX

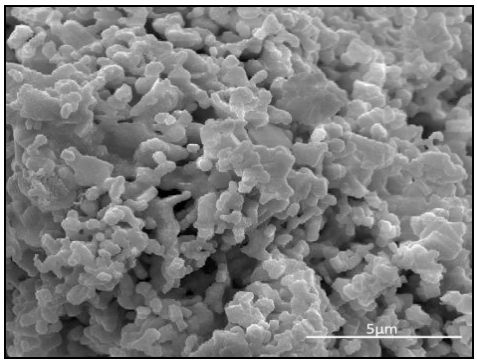

Fig.2. HRSEM image of $NdFeO_3$ ceramics

The structural morphology and chemical composition of crystalline phases were obtained using FEI Quanta FEG 200-High resolution scanning electron microscope (HRSEM). Fig. 2 shows the HRSEM and Fig. 3 shows EDAX image of $NdFeO_3$ compound. From the image, we observe an agglomerated cubic like morphology for various scale regions because $NdFeO_3$ belongs to canted pervoskite type structure in which FeO_6 octahedral are bonded with atoms through corner-sharing, so it leads to the formation of cubic morphology in the particles. Hence, it proves that each particle have small cubical shape, size of the order of 10^{-6} m and are arranged in an irregular pattern [11-12].

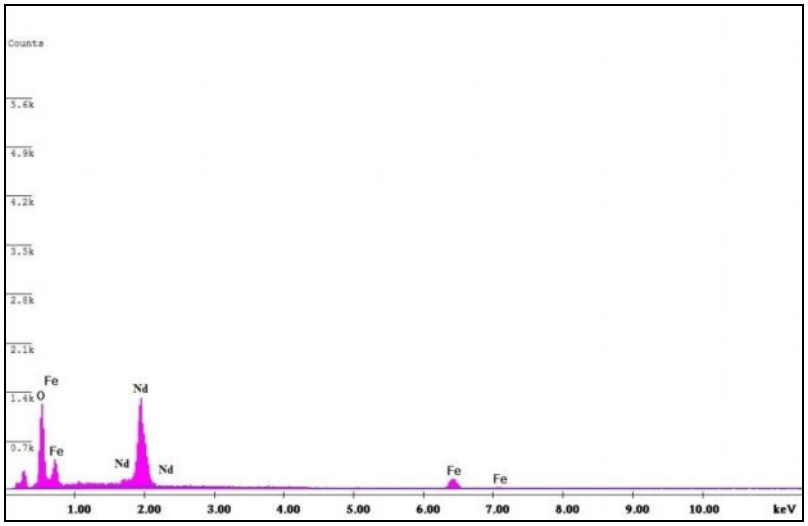

Fig. 3 EDAX spectra for $NdFeO_3$ ceramics

For confirming the composition of the synthesized powder EDAX analysis was carried out. The data was collected at three different locations on the sample. The variation of the composition was found to be within the experimental error of the instrument. Fig. 3 shows the EDAX spectra and the result is tabulated in Table 1. The results of EDAX analysis exhibit that the atomic ratio of Fe and Nd is as per the intended stoichiometric composition of the product $NdFeO_3$.

Table: 1 EDAX data

Element	Weight % (Experimental)	Weight % (Theoretical)
O_K	33.68	32.55
Fe_K	17.05	18.29
Nd_L	49.27	49.16
Total	100 %	100 %

5. DRS Spectroscopy

The optical absorption spectrum of $NdFeO_3$ powder was recorded in the range 200–1100 nm using an Jasco V-670-UV-Visible diffused reflectance spectrometer and optical band gap were determined using tauc's plot shown in Fig. 4(a) and inset Fig. 4(b).

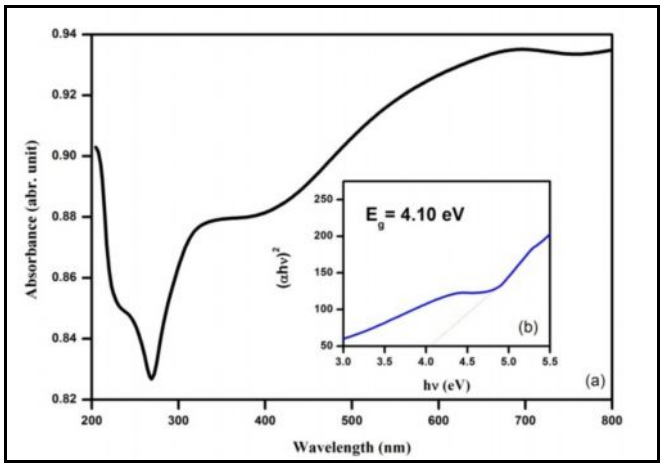

Fig. 4 (a) Optical absorption spectrum of $NdFeO_3$ powder, and inset graph (b) Optical band gap.

The absorbance is an important phenomenon to reveal the information about structural and oxidation state of the compound. In visible region most of the canted pervoskite inorganic systems involves promotion of the electrons in π-π, π* and n orbital from the ground state to higher excitation states. The graph gives clear information about high absorbance nature in visible region and after visible region sudden drop in graph due to very little absorbance in IR region after 845 nm. The optical band gap (Eg) of $NdFeO_3$ can be obtained in Tauc's relation.

$$(\alpha h\nu)^n = A(h\nu - Eg) \qquad (1)$$

Where, α–the absorption coefficient, A– constant, Eg - band gap and exponent n depends on the type of transition. For n is directly allowed transition, or indirect allowed transition or direct forbidden transition, it values are 1/2, or 2, or 3/2, respectively [12]. Inset Fig. 4(b) shows Tauc relation by plotting $(\alpha h\nu)^2$ against hν (eV), by extrapolating the curve to photon energy axis and the optical band gap was calculated using fit straight line near linear changes in the plot. The optical absorption plot shows energy band gap as 4.1eV because ligand to metal charge transfer ($NdFeO_3$) takes place from O^{2-} to Fe^{3+}. Hence d-d charge transfer takes place in the $NdFeO_3$ system behave as an insulator [12].

6. Magnetic Measurement

The magnetic measurement of $NdFeO_3$ ceramics were carried out using VSM (Lakeshore VSM 7410) at room temperature for MH loop measurement. The room temperature hysteresis loops are shown in Fig.5.

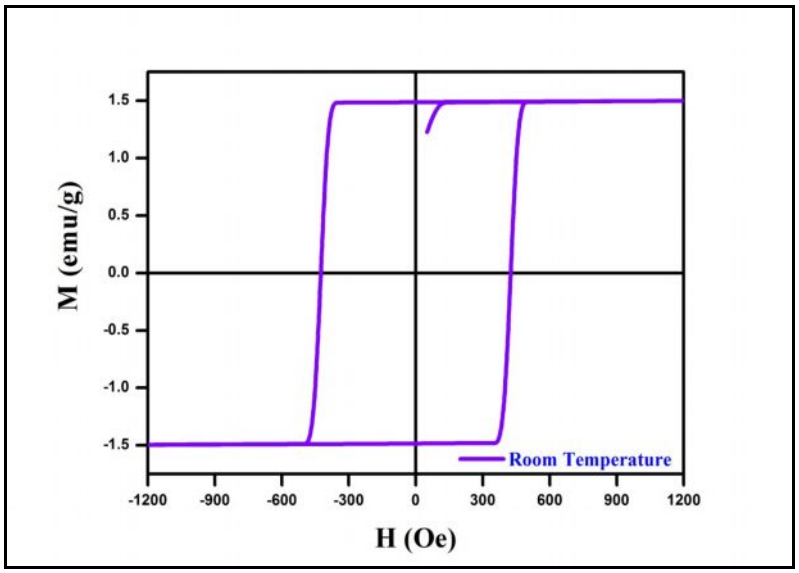

Fig. 5 MH loop for $NdFeO_3$ ceramics.

Most of the orthoferrites are distorted perovskite crystal structure in nature and hence it behaves as an antiferromagnet at room temperature. In general all the rare-earth Orthoferrites [$RFeO_3$] exhibits rectangular magnetic hysteresis loop below its neel-temperature [2-3]. A rectangular magnetic hysteresis is exhibited by rare-earth orthoferrites $RFeO_3$ (R- Y,Sm, Gd, Nd), which is also exhibited by $NdFeO_3$ at room temperature. The magnetic interactions between Nd-Nd, Nd-Fe, Fe-Fe and Fe-O-Fe in these distortions in $NdFeO_3$ perovskite crystal system were observed at low temperature ahead few interesting fact for these materials. G. Song et al. could achieve only less magnetization of < 1 emu/g in A axis and < 0.7 emu/g in C axis due to very less applied field (max field 200 Oe) but in our case we achieved greater than 1 emu/g due to high applied magnetic field 1200 Oe and it leads to high magnetic moment loop when compared to already reported [9-11].

7. Conclusion

$NdFeO_3$ was successfully synthesized by starch assisted sol-gel combustion method. The crystalline nature was confirmed by powder XRD pattern at every stage and chemical composition was confirmed through EDAX. . The optical absorption shows energy band gap as 4.1eV because ligand to metal charge transfer ($NdFeO_3$) takes place from O^{2-} to Fe^{3+}. Hence d-d charge transfer takes place in the $NdFeO_3$ and it lies in an insulator region. $NdFeO_3$ exhibit G-type weak ferromagnetic property at room temperature.

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