SYNTHESIS OF $\text{La}_{1-x}\text{Nd}_x\text{NiO}_3$ NANOSYSTEM FOR MATERIALS AND CATALYTIC CO OXIDATION STUDIES

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ABSTRACT

Crystalline Lanthanum and Neodymium nickelate perovskites and their intermediate compositions $\text{La}_{1-x}\text{Nd}_x\text{NiO}_3$ ($x = 0.0, 0.3, 0.5, 0.7$, and 1.0) were successfully prepared via co-precipitation precursor technique. The crystal structure and phase formation were confirmed by powdered X-ray diffraction. LaNiO_3 and NdNiO_3 were identified to be single-phase and are indexed to rhombohedral and orthorhombic structures, respectively. The intermediate $x=0.3$, showed rhombohedral whereas $x=0.5$ and 0.7 showed orthorhombic phase. The bonding characteristics were studied by FTIR spectroscopy. Magnetic susceptibility measurements and Electron Spin Resonance study provide an insight into the paramagnetic catalytically active species. This investigation was an attempt to understand the influence of A-site substitution in LaNiO_3 with Nd^{+3} ions and their possible impact on the solid-state properties. Being thermally stable materials, they were tested for a model catalytic CO oxidation for pollution control strategy. They showed an increase in the activity of CO oxidation to CO_2 .

Keywords: Crystalline, Rare-earth Perovskites, Electron Spin Resonance, Catalytic CO Oxidation.

RASAYAN J. Chem., Vol. 14, No.4, 2021

INTRODUCTION

The perovskite-type rare earth nickelates of the general form ANiO_3 ($A = \text{Lanthanide ion}$) present very interesting physical properties. They exhibit a variety of applications in microelectronics, conductive electrodes, micro-actuators, piezoelectric energy harvesters, magneto electronics, sensors, magnetic memory devices, and catalysts.¹⁻⁵ The Ln ions support the framework, stabilize the system, and hence the size of these ions defines the octahedral structural transformations, which in turn decide the physical properties, govern the electronic state and the phase transition. Unlike many other rare earth nickelates, LaNiO_3 does not show a metal-insulator transition (T_{M-I}) and exhibits metallic nature down to 1.5 K, and shows a paramagnetic - metallic state. The evolution of T_{M-I} and temperature can be linked with the degree of divergence of the ideal perovskite structure, which increases with the substituted smaller-sized Nd ions in the La- site.^{1,2,5-8} Although it is not easy to synthesize these materials in their pure bulk form, due to the stabilization of Ni(III) and either oxygen pressure and/or high temperatures of $\sim 950^\circ\text{C}$ are necessary^{1, 2, 6-8}, it is possible to prepare these perovskite materials comparatively in the pure form either by modified conventional ceramic, co-precipitation, sol-gel, hydrothermal, auto-combustion and also by other modern techniques like pulse laser, spray pyrolysis techniques for thin films. With the exception that NdNiO_3 is reported to be rhombohedral⁹, the structures of LaNiO_3 and NdNiO_3 were found to be paramagnetic metal with R-3c rhombohedral and orthorhombic respectively, at room temperatures.^{3-4,10-13}

The rare earth-transition metal perovskite oxides provide an excellent base for correlating catalytic and solid-state properties because they can be well characterized by different techniques.¹⁴ These compounds are considered as active catalyst materials replacing noble metals, particularly for environmental catalysis like treatment of exhaust gases and oxidation of Carbon Monoxide (CO). The catalytic activity of these perovskites can be suitably modified by incorporating different

metal ions in the lattice to improve the quality of materials. The oxidation of CO with the aim of reducing air pollutants is obviously an important model reaction to check the efficacy of perovskite materials as catalysts.¹⁴⁻¹⁹

In this investigation, we present an understanding of the effect of A-progressive site substitution of Nd in the lattice of LaNiO_3 on their physical properties prepared by co-precipitation precursor technique and their correlation with the spectroscopic and solid-state properties. Also, these compositions are known for their excellent thermal stability and therefore, we explore their potential as candidates for CO conversion as a model reaction.

EXPERIMENTAL

Co-precipitation Precursor Synthesis

The $\text{La}_{1-x}\text{Nd}_x\text{NiO}_3$ ($x = 0.0, 0.3, 0.5, 0.7$ and 1.0) compositions were synthesized by co-precipitation precursor technique as discussed earlier.^{10,16} Stoichiometric quantities of hydrated $\text{La}(\text{NO}_3)_3$, $\text{Ni}(\text{NO}_3)_3$ (AR) were dissolved in 100 mL of pure water, and /or Nd_2O_3 was dissolved in a minimum quantity of 1:1 nitric acid. Both solutions were mixed on a magnetic stirrer and precipitated using 5% sodium hydroxide solution. The resultant precursor hydroxide precipitate was digested and the mixture was subjected to oxidation using 6% H_2O_2 . The precipitate was then washed, filtered, and dried in an oven at 120°C . It was homogenized well and then further heated in stages at $300, 600$, and finally 800°C in the air for a total time of 10-12 h. A purity improvement check was done by heating further the mid composition $x = 0.5, 0.7$, and NdNiO_3 at 900°C for 4 h.

Characterization of Catalyst Materials

The commonly used characterization techniques for the perovskite nanomaterials are Thermogravimetry, BET Surface area, X-ray Diffraction, SEM, AFM, Electrical conductivity, Dielectric constant etc.²⁰⁻²² The prepared materials were characterized by X-ray powder diffraction technique with Rigaku Miniflex benchtop instrument, using Cu K_α , filtered through Ni absorber. Shimadzu FTIR instrument (model 8101A) was used to record FTIR spectra. Atomic Absorption Spectroscopy (AAS) technique was employed to estimate the sodium contamination in the compounds prepared by the co-precipitation method using sodium hydroxide. The BET nitrogen adsorption method with QUANTACHROME NOVA 1200 version 3.70 instrument was used for the total specific surface area measurements. Temperature dependence of electrical conductivity measurements was carried out by a two-probe conductivity cell in the temperature range of room temperature (r. t.) to 525°C . The magnetic susceptibility χ_g in the air was determined by the Gouy method at r. t. they were employing a field of the order of 10,000 gauss and using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as standard materials. The perovskite materials were ESR analyzed for paramagnetic and for identifying the catalytically active species for the oxidation reaction. The Varian E-112 spectrophotometer at the X- band was employed at liquid nitrogen temperature to record the ESR spectra. A field calibrant TCNE material was used considering its g-value as 2.00277 and mounting the sample on a quartz tube for the analysis. The hysteresis behavior was studied to interpret the saturation magnetization capacity of the materials. A high field hysteresis loop tracer was used to measure the selected magnetic samples. The saturation magnetization values, σ_s in emu/g, of only magnetic perovskite materials were measured.

Catalytic CO Oxidation Reaction

The prepared materials were tested for a model reaction of catalytic CO oxidation, with a continuous flow using oxygen in nitrogen, fixed bed quartz reactor. For the catalytic studies, 1 g of powdered catalyst was placed in between glass wool plugs. A feed gas composition of 5% CO, 5% O_2 in nitrogen was used consistently for CO oxidation catalyst activity. The precision needle valves and flow meters were used to control the individual gas flow rates. An online gas chromatograph with a molecular sieve 13X and Porapak Q columns was employed to analyze the feed gases and the products. Hydrogen was used as a carrier gas. The standardized procedure was used to prepare CO

gas in the laboratory, purified of undesired minor impurities by passing through alkali and molecular sieve traps.¹⁶ Pure commercial cylinders of oxygen and nitrogen gases were used.

RESULTS AND DISCUSSION

Phase Formation Checks by XRD

X-ray powder diffractograms characterized the prepared compositions. The d_{hkl} and 2θ values obtained were compared with the values reported in the literature and found to be in good agreement. Since the d_{hkl} value of the intermediate $x = 0.3, 0.5$, and 0.7 compositions are not reported in the literature, the values were compared with the end compositions. Figure-1 shows the XRD plots of $\text{La}_{1-x}\text{Nd}_x\text{NiO}_3$ system materials. Our results of X-ray analysis of the materials calcined at 800°C showed that LaNiO_3 and $x = 0.3$ compositions could be clearly indexed to rhombohedral (JCPDS data file 34-1181). The diffraction pattern of $x = 0.5, 0.7$, and NdNiO_3 compounds structure is indexed to the GdFeO_3 type orthorhombically distorted perovskite structure, in accordance with other published work.^{10,11} The observed characteristic splitting in the diffraction peaks at 2θ of $32.9, 40.66, 58.87$, and 68.87 values is the evidence of the rhombohedral distortion of the perovskite structure in LaNiO_3 .⁷ Inset illustrates the perovskite phase growth studies by evaluating diffraction patterns recorded on selected LaNiO_3 , $\text{La}_{0.5}\text{Nd}_{0.5}\text{NiO}_3$, and NdNiO_3 calcined at 600°C , 800°C and 900°C respectively. The plots reveal that only LaNiO_3 compound shows the emergence of characteristic perovskite peaks at 600°C for above 2θ values and perovskite phase formation was achieved at 800°C For $\text{La}_{0.5}\text{Nd}_{0.5}\text{NiO}_3$ and NdNiO_3 compounds, the no characteristic peaks are observed at 600°C , but perovskite phase formation was achieved at 800°C . Additional heat treatment for $x = 0.5, 0.7$, and NdNiO_3 compounds at 900°C has revealed sharpening and the enhancement of the intensity of all reflections. For the practical purpose, all the compositions heated at 800°C were studied, in order to preserve higher specific surface areas of the materials for the catalytic application. The crystallite size was calculated using the Debye-Scherrer formula, which estimates the size of smaller crystals from their diffraction peaks and was found to be in the range of 133 to 161 nm.

Fig.-1: XRD Patterns of (a) LaNiO_3 , (b) $\text{La}_{0.7}\text{Nd}_{0.3}\text{NiO}_3$, (c) $\text{La}_{0.5}\text{Nd}_{0.5}\text{NiO}_3$, (d) $\text{La}_{0.3}\text{Nd}_{0.7}\text{NiO}_3$, and (e) NdNiO_3 calcined at 800°C . Inset shows evolution of perovskite phase for representative A1) LaNiO_3 , C1) $\text{La}_{0.5}\text{Nd}_{0.5}\text{NiO}_3$, and E1) NdNiO_3 .

AAS Techniques

As the materials were prepared using NaOH solution to form the precursor mixture of hydrated $\text{La}(\text{OH})_3$, $\text{Ni}(\text{OH})_3$, and or $\text{Nd}(\text{OH})_3$, it was expected the presence of trace amounts of Na contamination. It was estimated using an AAS and found to be in the range of 0.2 to 0.4% by weight.

Perovskite Characteristic Absorptions by FTIR

The perovskite structure is known to be characterized by IR spectra in the region 1000 to 300 cm^{-1} . The two strong absorption bands corresponding to the stretching vibration of the metal-oxygen bond were observed in the 700 to 390 cm^{-1} region. A deformation mode of NiO_6 octahedral, i.e. the Ni-O-Ni bond angles, characteristics of the perovskite structure were observed in the lower frequency bands, which relates to the strength of metal-oxygen covalency. The FTIR of the LaNiO_3 compound shows no feature characteristic of localized vibration modes, which is typical of the LaNiO_3 . The vibrational modes disappear for the compounds having very low resistivity as in the case of LaNiO_3 , which can be qualitatively attributed to the force constant, dominated by the ionic component of the bonding and further independent to changes in the transfer of electrons or covalent mixing.²³ With the substitution of Nd^{+3} in the lattice LaNiO_3 at $x = 0.3$, a broad absorption peak is observed at 420 cm^{-1} . For $x = 0.5$ the band broadening is observed and for NdNiO_3 a broad-shouldered band with peaks at 553 cm^{-1} , 495 cm^{-1} , 471 cm^{-1} and 420 cm^{-1} were observed. The rhombohedral distortion in LaNiO_3 has R-3c symmetry, which arises from a rotation of the NiO_6 octahedra about the threefold axis of the ideal cubic perovskite. The NiO_6 octahedra, on account of the atomic size difference with the incorporation of Nd^{+3} ions in the lattice of LaNiO_3 , causes the unit cell to be smaller and more distorted in order to fill the extra interstitial space. The tilting angle in LaNiO_3 is 9.0 whereas, in NdNiO_3 , it is 14.7 degrees, making the unit cell of NdNiO_3 to be smaller and slightly more distorted. Since the magnitude of distortion is related to the relative distances $d_{\text{Ni-O}}$ and $d_{\text{R-O}}$ ($\text{R}=\text{La}$ or Nd), it can be explained in terms of tolerance factor 't'. Experimentally, when t value ≤ 1 , the NiO_6 octahedra are rotated around the [111] cubic axis as in the case of LaNiO_3 . For smaller t value, the NiO_6 octahedra tilt around the [110] and [001] cubic directions, resulting in the orthorhombic GdFeO_3 structure as found in NdNiO_3 .^{1,24} This may be the probable reason for the observed vibration bands for the spectra c, d, and e as seen in Fig.-2.

Fig.-2: FTIR Absorption Bands of (a) LaNiO_3 , (b) $\text{La}_{0.7}\text{Nd}_{0.3}\text{NiO}_3$ (c) $\text{La}_{0.5}\text{Nd}_{0.5}\text{NiO}_3$ (d) $\text{La}_{0.3}\text{Nd}_{0.7}\text{NiO}_3$, and (e) NdNiO_3

Electrical Behaviour

Figure-3 shows the trend of the temperature dependence of resistivity for room temperature (r. t.) to 525 $^{\circ}\text{C}$. The resistivity decreases with an increase in the temperature and all compositions show more or less similar resistivity behavior. For LaNiO_3 , the resistivity decreases slowly in the range from r. t. to 200 $^{\circ}\text{C}$, followed by a linear decrease in resistivity in the range of 200 to 400 $^{\circ}\text{C}$ indicating typical

semiconductor behavior. A very small change in resistivity was observed for the further rise in temperature beyond 400 °C. The resistivity curves show the extrinsic to intrinsic behavior, typical of the semiconductor materials. There is no phase transition in this compound above r. t. Intermediate compositions show similar trends of resistivity behavior in the same range, with the exception of $\text{La}_{0.5}\text{Nd}_{0.5}\text{NiO}_3$, which shows comparatively higher resistivity behavior. As the Ni content practically remains the same throughout the different compositions, the slight difference in the trend of resistivity behavior may be linked to distortion in the crystal structure with the increased substitution by Nd^{+3} ions. To our knowledge, there are scanty literature reports available for dc resistivity measurements above r. t. for these rare earth nickelates under study.

Fig.-3: Variation of Electrical Resistivity of $\text{La}_x\text{Nd}_{1-x}\text{NiO}_3$ System

Electron Spin Resonance Spectroscopy

ESR spectroscopy, also referred to as electron paramagnetic resonance (EPR) spectroscopy, is a versatile, non-destructive analytical technique that can only be applied to samples having one or more unpaired electrons. The technique was carried out, to get an insight into the catalytically active and paramagnetic species and used as a qualitative tool to ascertain the changes occurring with the A-site substitution of La^{+3} with Nd^{+3} ions. Figure-4 illustrates the ESR spectra and the data of different compositions at liquid nitrogen temperature are presented in Table 1. It is observed that a signal with a broad line-width for all the compositions at liquid nitrogen temperature. At the same time, these compounds did not show any ESR spectra at r. t. For heavier atoms like La^{+3} ions, the spin-orbit coupling is strongly coupled to lattice vibrations and spin relaxation time; therefore, it is very small at high temperatures. This means that ESR spectra are too broad to be detected at r. t. The broad line spectra observed at liquid nitrogen temperature may be due to the presence of paramagnetic Nd^{+3} ions having a nuclear moment and a short lifetime of the excited state. Thus, the line width depends on the relaxation time of the spin state through either or both of the processes spin-lattice and spin-spin relaxation. The interaction of paramagnetic ions with the thermal vibrations of the lattice leads to short spin-lattice relaxation time. At low temperatures, the spin-lattice relaxation becomes less efficient as the violence in the inter-atomic motion decreases, thus increasing the relaxation time.²⁵ As the La^{+3} and Ni^{+3} ions are ESR inactive, throughout the material compositions under study, the observed variation of the line-width and the g-values are due to increased substituted paramagnetic Nd^{+3} ions, as the x values go up. A very weak ESR signal is recorded for $x = 0.5$ with a g-value of 2.15, which becomes sharp for $x = 0.7$ and end compound NdNiO_3 with a corresponding g-value of 2.5.

Fig.-4: ESR Spectra of (a) LaNiO_3 , (b) $\text{La}_{0.7}\text{Nd}_{0.3}\text{NiO}_3$, (c) $\text{La}_{0.5}\text{Nd}_{0.5}\text{NiO}_3$, (d) $\text{La}_{0.3}\text{Nd}_{0.7}\text{NiO}_3$ and (e) NdNiO_3

Table-1: Crystallite Size, Gram Susceptibility (χ_g), Magnetic Moment (μ_{eff}), Saturation Magnetization and ESR Data of Nanoperovskites

Compound	Crystallite Size (nm)	χ_g at r.t. (emu/g)	μ_{eff} (B.M.)	g-value at liq. N_2 temp	Line Width (gauss)
LaNiO_3	144	0.50×10^{-5}	1.76	3.8	860
$\text{La}_{0.7}\text{Nd}_{0.3}\text{NiO}_3$	152	1.64×10^{-5}	3.13	1.9	1200
$\text{La}_{0.5}\text{Nd}_{0.5}\text{NiO}_3$	161	1.79×10^{-5}	3.28	2.1	1940
$\text{La}_{0.7}\text{Nd}_{0.3}\text{NiO}_3$	149	2.18×10^{-5}	3.67	2.4	1880
NdNiO_3	133	2.33×10^{-5}	3.76	2.5	1260

BET Surface Area Analysis

The rare earth-transition metal perovskites provide an excellent base for correlating catalytic and solid-state properties because such materials can be easily characterized by different techniques. So, the prepared compositions were tested for a model reaction of catalytic CO oxidation. The surface areas of prepared compositions were measured by BET nitrogen adsorption at boiling liquid nitrogen temperatures, employing high-speed gas sorption analyzer. The surface areas are summarised in Table-2. The low surface areas of some of these compositions are low, which may be due to sintering.

Table-2: Kinetic Parameters of CO Oxidation over $\text{La}_{1-x}\text{Nd}_x\text{NiO}_3$ Catalyst at 225 °C

Catalyst	Surface area (m^2/g)	Rate (molec./ $\text{m}^2.\text{s}$)	E_a (Kcal/mole)	Frequency factor (molecules/ $\text{m}^2.\text{s}$)
LaNiO_3	3.9	1.531×10^{18}	42.30	6.38×10^{19}
$\text{La}_{0.7}\text{Nd}_{0.3}\text{NiO}_3$	4.3	1.702×10^{18}	13.74	7.39×10^{19}
$\text{La}_{0.5}\text{Nd}_{0.5}\text{NiO}_3$	7.6	4.997×10^{17}	15.10	1.97×10^{19}
$\text{La}_{0.3}\text{Nd}_{0.7}\text{NiO}_3$	3.8	2.352×10^{17}	17.16	0.11×10^{19}
NdNiO_3	3.5	1.988×10^{17}	20.97	5.65×10^{18}

Catalytic CO Oxidation as a Model Reaction

The temperature dependence of CO conversion studies for different materials of $\text{La}_{1-x}\text{Nd}_x\text{NiO}_3$ system is shown in Fig.-5. The rate of CO oxidation decreases with the increased substitution with Nd^{+3} ions. For the compositions $x = 0.0, 0.3$ and 0.5 , showed almost similar activity with little difference. The $\text{La}_{0.7}\text{Nd}_{0.3}\text{NiO}_3$ compound exhibit a slightly better CO oxidation efficiency. The induction temperature for the NdNiO_3 compound is higher and shows a lower efficiency. The CO conversion pattern reveals that with the increased substitution of Nd ions in the lattice of LaNiO_3 , the conversion rate gradually decreases. The surface areas of these materials do not appear to be the criteria for the displayed catalytic activity.

Fig.-5: Catalytic CO Oxidation on $\text{La}_x\text{Nd}_{1-x}\text{NiO}_3$ System

ABO_3 perovskites, in which the A = Lanthanide ions are essentially inactive in catalysis and B- site active transition metal ions are placed at relatively large distances from each other, are excellent catalytic models for the study of interactions of CO and O_2 on a single surface site. Since in our study, B- site Nickel metal, being present in the same amount in all compositions, the observed differences in a catalytic activity needs to be explained with respect to increasing substitution of A- site by Nd^{+3} ions and its effect on LaNiO_3 crystal structure. The catalytic activity for CO oxidation is closely related to the electronic structure of the surface oxide ions.¹⁴ Further, the oxidation of CO has been widely studied for the surface characterization of perovskite-type materials, which has shown a suggestive correlation between the oxidation efficiency and the electronic configuration of B-site transition metal ions. It was seen that maximum activity is attained for an occupation of e_g level of less than one electron and the t_{2g} levels being half-filled or totally filled.¹⁴

The observed catalytic behavior of CO oxidation can be explained by the ionic size effect. LaNiO_3 has a distorted rhombohedral structure with optimized Ni-O bond length having the tolerance factor (t) of 0.96 and the large size La^{+3} ions occupy 12 - coordinated A-site. The binding energy of oxygen is an important factor in the determination of the activity of CO oxidation. The high t value lowers the interactions of the Ni-O-Ni bond and thus decreases binding energy, which facilitates the release of lattice oxygen at the surface of the catalyst. Since CO is reducing gas, having a tendency to reduce the lattice oxygen from the catalyst surface creating oxygen vacancies, which are later filled by oxygen supplied during the catalytic reaction. Thus, lower binding energy for the surface oxygen species is favorable for the LaNiO_3 compound to be more active for CO Oxidation. As La^{+3} ions are increasingly substituted by Nd^{+3} ions in the lattice of LaNiO_3 , due to the substituted Nd^{+3} size difference, the NiO_6 octahedra get tilted. The average value of the Ni-O-

Ni angle in NdNiO_3 is 157.09° as compared to 165.2° in LaNiO_3 . There is also a decrease in tolerance factor ($t = 0.85$) for NdNiO_3 , resulting in enhanced interaction of Ni-O-Ni bond and increased binding energy. As a consequence, there may be a reduction in the formation of oxygen vacancies at the surface of the lattice, which may be a probable reason for the lesser CO oxidation capacity of NdNiO_3 .^{1,2,24}

For arriving at any correlation between catalytic behavior and other properties, the kinetic measurements of different compositions were carried out at low conversion rates and at fixed temperatures. Fractional conversion of CO (x_{CO}) versus W/F_{CO} , where 'W' is the mass of the catalyst taken and F_{CO} is the moles of CO flowing per hour at different temperatures. A linear variation of the conversion was observed with decreasing flow rate. The total flow rate used during the studies was between 5000 to 8000 mL with 5% CO and 5% O_2 with GHSV of 5×10^3 . The kinetic parameters such as the reaction rates, activation energy (E_a), and the frequency factor (A) were calculated from the Arrhenius plots and are summarised in Table-2. From the kinetic studies, it is observed that the energy of activation (E_a) increases with the substitution of La^{+3} with Nd^{+3} ions, with the exception of $\text{La}_{0.7}\text{Nd}_{0.3}\text{NiO}_3$, where the observed E_a is 13.74 Kcal/mole, thus showing slightly enhanced catalytic activity. The E_a values are in the range of 13.74 to 20.97 Kcal/mole. The highest value of the frequency factor also explains the exposure of a large number of active sites on the surface of the catalytic material. The lowest frequency factor value i.e. 5.65×10^{18} molec./ $\text{m}^2\cdot\text{s}$ for NdNiO_3 with its lowest activity, is attributed to Nd^{+3} ions and with its increased substitution for La^{+3} ions in the A- site of lattice, it is seen that the rate and frequency factor gradually decreases.

CONCLUSION

Crystalline LaNiO_3 and NdNiO_3 perovskite compounds and their selected intermediates were successfully prepared by stabilizing Ni^{+3} state with H_2O_2 by a comparatively low-temperature technique. Systematic La^{+3} substitution by Nd^{+3} ions in the LaNiO_3 lattice and their impact on electrical resistivity, magnetic properties, and catalytic CO oxidation as model reactions are the highlights of this investigation. A significant decline in the catalytic activity is observed by the A-site substitution of Ni^{+3} with Nd^{+3} in the LaNiO_3 perovskite system. $\text{La}_{0.7}\text{Nd}_{0.3}\text{NiO}_3$ shows higher activity and 100% CO oxidation efficiency at much lower temperatures, whereas NdNiO_3 shows the least. The intermediate compositions show in between catalytic activity. These materials under study show paramagnetic behavior. For the intermediate compositions, the saturation magnetization values are almost constant with 6.6 emu/g recorded for $x = 0.5$. These compounds are ESR inactive at room temperature but showed broad peaks at liquid nitrogen temperature due to spin-orbit coupling.

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[RJC-6541/2021]