Role of Ruthenium in the Dielectric, Magnetic Properties of Nickel Ferrite (Ru–NiFe$_2$O$_4$) Nanoparticles and Their Application in Hydrogen Sensors

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ABSTRACT: In this work, Ru-doped nickel ferrites (NiFe$_2$O$_4$) were synthesized by a chemical co-precipitation method. Subsequently, they were annealed at different temperatures. The crystallinity of the samples was evaluated using X-ray diffraction and the morphology of the samples was investigated by scanning electron microscopy and transmission electron microscopy. Dielectric constants and dielectric loss were studied. Ru-doped nickel ferrite samples showed relatively low dielectric constant and loss. Also, the dielectric constant and loss decreased with increasing annealing temperature. Vibrational sample magnetometer analysis shows the hysteresis loop of a soft magnetic nature and the relevant parameters ($M_r$, $M_s$ and $H_c$) have low values that confirmed the nature of the material. Subsequently, gas sensors were fabricated to study hydrogen-sensing properties. The gas sensors showed a response to hydrogen gas at a low temperature (100 °C) with selective response in the presence of NH$_3$ and C$_2$H$_5$OH gases. The reasons for electrical, magnetic, and sensing behavior of the samples were discussed in detail.

1. INTRODUCTION

Electrical, magnetic, and gas-sensing properties of metal oxides majorly depend on the synthesis methods, nature and concentration of dopants, particle size, annealing temperature, and so forth. Among the available metal oxides, spinel ferrites demonstrate high magnetic permeability, electrical resistance, catalytic properties, and chemical stability. Spinel compounds of ABO$_4$ type, where different cations of A and B and could form a closely packed array of O$^{2-}$ ions as with A$^{2+}$ and B$^{3+}$ cations on occupying parts or all of the tetrahedral and octahedral sites. Being majorly used in microwave, electronic, magnetic, and electrochemical devices, nickel ferrite (NiFe$_2$O$_4$) is one of the most important spinel ferrites. Also, its low eddy and coercivity, and hysteresis loss are beneficial for electronic device applications including in telecommunication and high-frequency devices. Magnetic coupling in NiFe$_2$O$_4$ is due to super-exchange where the A–B interaction coupling is stronger than that of A–A and B–B couplings. The angles of B–O–B and A–O–A bonds are <180°, which eventually could form a strong super-exchange interaction of the A–B pair.

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avail good stability in reducing atmospheres.\textsuperscript{19,20} Among different gases, hydrogen gas is an alternative green energy resource replace a fossil fuel in future.\textsuperscript{21} However, it is highly flammable with a risk of explosion during its storage, transportation, and use.\textsuperscript{22} Unfortunately, hydrogen gas cannot be detected by human senses. Usually, gas chromatography and mass spectrometry techniques are used to monitor hydrogen gases, which are associated with large size, high cost, and time consumption.\textsuperscript{23} Metal oxide-based gas sensors with good sensing properties can be a good choice for hydrogen gas detection. In particular, nanoscale-sized metal oxides with good electrical properties are good enough in gas-sensing studies.\textsuperscript{24,25} However, generally sensing temperature for hydrogen gas sensors is often high (≥150 °C), which is not practically viable for commercial benefits. For example, Jayatissa et al. reported sensor response 4% H\textsubscript{2} at 175 °C.\textsuperscript{26} Also, Falsa et al. reported a hydrogen gas sensor based on Sm-doped cobalt ferrite at 200 °C.\textsuperscript{23} Also, the nickel ferrite has good gas-sensing ability as compared ferrite materials.\textsuperscript{66−68}

In this study, the Ru-doped nickel ferrite nanoparticles (Ru-NiFe\textsubscript{2}O\textsubscript{4} NPs) were synthesized by using a simple and cost-effective chemical co-precipitation method which was annealed at 300, 600, and 900 °C temperatures. The structure, magnetic, and sensing properties of Ru-NiFe\textsubscript{2}O\textsubscript{4} were studied and reported. The optimized Ru-NiFe\textsubscript{2}O\textsubscript{4} showed a lower dielectric constant and loss suitable for low-frequency and gas sensor applications. In particular, the response time of the Ru-NiFe\textsubscript{2}O\textsubscript{4} sensor toward selective hydrogen gas was very small at its appropriate concentration, holding the potential of commercialization.

2. RESULTS AND DISCUSSION

2.1. Structural Studies. Figure 1 illustrates the X-ray diffraction (XRD) patterns of Ru-NiFe\textsubscript{2}O\textsubscript{4} NPs annealed at different temperatures. The reflection planes of (111), (220), (311), (222), (400), (422), (511), (440), (620), and (622) are common in all sensors, which are of a cubic spinel structure. However, the intensity of peaks for the Ru-NiFe\textsubscript{2}O\textsubscript{4} NP sensor annealed at 300 °C is low, suggesting poor crystallinity. An additional peak related to α-Fe\textsubscript{2}O\textsubscript{3} is present in sensors annealed at 300 and 600 °C. Few low-intensity peaks owing to the presence of secondary phases located at grain-boundaries because of the high reactivity of Fe\textsuperscript{3+} and Ru\textsuperscript{3+} ions are noticed in the Ru-NiFe\textsubscript{2}O\textsubscript{4} sensor annealed at 300 °C.\textsuperscript{27} At higher annealing temperatures, iron ions could distribute evenly with secondary phases, warranting the formation of the Ru-NiFe\textsubscript{2}O\textsubscript{4}.\textsuperscript{28} The grain sizes were estimated on the (311) diffraction peak using the Scherrer equation.\textsuperscript{29} On air-annealing, the grain-size increases from 3 to ~48 nm, suggesting stimulation of the nucleation and growth, which eventually increases the size.\textsuperscript{30} The concerned XRD parameters are listed in Table 1.

2.2. Microstructure Studies. Figure 2 a−c illustrates scanning electron microscopy (SEM) surface images of Ru-NiFe\textsubscript{2}O\textsubscript{4} NPs annealed at different temperatures. NiFe\textsubscript{2}O\textsubscript{4} annealed at 300, 600, and 900 °C, respectively. As shown, small-sized rounded particles of Ru-NiFe\textsubscript{2}O\textsubscript{4} are evidenced at 300 °C, which are considerably large when annealed at 600 and 900 °C. At higher annealing temperatures (≥900 °C), a broad size distribution is confirmed. A change in the particle size with annealing temperature is a common, which is reported previously in several ferrite studies.\textsuperscript{31} In fact, because of temperature-dependence of diffusion, at higher temperatures, more matter can be diffused, resulting in the formation of large-sized particles. Figure 3 a−c illustrates typical energy-dispersive X-ray spectroscopy (EDXS) spectra

| temperature (°C) | particle size (nm) | dielectric constant | dielectric loss | coercivity $H_c$ (G) | retentivity $M_r$ (emu/g) | saturation $M_s$ (emu/g) |
|-----------------|-------------------|---------------------|----------------|------------------|-------------------------|-------------------------|
| 300             | 0.48              | 115.57              | 1.94           | 47.02            | 0.48                    | 3.25                    |
| 600             | 12.84             | 97.33               | 1.83           | 67.92            | 2.07                    | 12.50                   |
| 900             | 33.58             | 15.42               | 1.24           | 99.26            | 6.76                    | 34.92                   |
of Ru–NiFe₂O₄ NPs annealed at 300, 600, and 900 °C, respectively, suggesting an incorporation of a trace amount of Ru in the NiFe₂O₄ as Ru–NiFe₂O₄. In all cases, the peaks related to O, Fe, Ni, and Ru are noted. The atomic percent of Ru in the Ru–NiFe₂O₄ NP sensor annealed at 300, 600, and 900 °C are 0.66, 0.36, and 0.29 %, respectively. Accordingly, there is no significant difference between Ru-contents of the samples. The variation Ru content in different samples can be due to local variation in homogeneity. Figure 4a–d shows typical transmission electron microscopy (TEM) images of Ru–NiFe₂O₄ NPs annealed at 300, 600, and 900 °C. Increasing annealing temperature and the Ru–NiFe₂O₄ NPs annealed at 900 °C endow the highest crystallite size. The corresponding selected area electron diffraction patterns of Ru–NiFe₂O₄ NPs are shown in Figure 4b–e. The continuous rings, in accordance with the nanocrystalline signature, are sharply appearing, supporting the structural change in Ru–NiFe₂O₄ NPs from amorphous to nanocrystalline with increasing the annealing temperature from 300 to 900 °C.32

2.3. Dielectric Studies. The dielectric properties of spinel ferrites depend on annealing temperature and applied frequency.33 Figure 5a illustrates the variation of the dielectric constant of Ru–NiFe₂O₄ NPs obtained at different annealing temperatures with frequency. In general, dielectric properties of ferrites alter with dopants, annealing temperature, preparation method, distribution of metal cations between A and B sites, and so forth.34 In the presence of Ru, the obtained dielectric constants are smaller than those reported in the literature for NiFe₂O₄.35–38 The substitution of Ru could result in lattice distortion and change of bond length between Fe–O and Ru–O at the B site, producing a change in atomic polarizability and dielectric constant.39,40 From Figure 5a it is inferred that the dielectric constant is high at small frequencies and is low at higher frequencies. Also, with increasing frequency, the dielectric constant decreases at the beginning very rapidly, which then remains almost constant. The variation in the dielectric constant of Ru–NiFe₂O₄ NPs at different frequencies can be explained on the basis of interfacial polarization, ionic and electronic polarization effect. The dielectric constant decreases, reaches constant value at high frequency because of the electronic polarization effect as dipoles cannot follow the electric field, and charges get spread with a low dielectric constant. On the other hand, the dielectric constant increases at low frequencies because of the interfacial polarization effect as electric dipoles follow the electric field and charges can be accumulated at the interface of grain boundaries with high dielectric constant.41 Usually, the dielectric constant increases with annealing temperature. However, in our case, a reverse trend is noticed. The dielectric constant decreases because of a variation of valence sites at octahedral sites, that is, Fe²⁺ and Fe³⁺ or electron hopping. The ferrous ions could be trapped continuously at high temperatures by generating a low dielectric constant. Also, lattice distortion is another factor that decreases the dielectric constant as the distance among neighboring oxygen sites changes with annealing temperature.42 Figure 5b provides dielectric loss at different temperatures that is, 300, 600, and
900 °C. The resonance optimums are at two frequencies, that is, 2.82 and 2.40 Hz, and are evidenced when the jumping frequency of electrons among ferrous and ferric ions is the same as that of the frequency of the applied electric field. Also, the presence of secondary phases, confirmed for Ru−NiFe₂O₄ NPs annealed at 300 and 600 °C temperatures, creates a resonance peak. Because of the involvement of phase pure spinel structure there is no resonance peak for Ru−NiFe₂O₄ NPs annealed at 900 °C, which can be explained by Koop’s phenomenological model where ion has more than one equilibrium position, namely, A and B with same potential energy and, second, the probability of jumping the ion from A to B and B to A is the same. Depending on this probability, the ion exchanges position between A and B with the same frequency as the natural frequency. When an external alternating electric field of the same frequency is applied, the maximum electrical energy can be transferred to the oscillation ions on shooting the power loss, resulting in resonance. The dielectric loss decreases suddenly with annealing temperature. The fall of dielectric loss can be assigned to different valence states of ions. In addition, both Ru and Ni ions occupy the positions of iron ions and the collective effect of these two ions deduces the hopping electrons a low dielectric loss.

2.4. Magnetic Studies. Figure 6a–c illustrates the hysteresis loops, obtained at room temperature (300 K), of Ru−NiFe₂O₄ NPs annealed at 300, 600, and 900 °C NPs. The narrow area of the hysteresis loop demonstrates a soft magnetic nature, which depends on the crystallinity, dopant, and particle size. In spinel ferrites, the configuration of Ni, Fe, and Ru ions at octahedral and tetrahedral sites changes the magnetization gesture. The magnetization increased with annealing temperature. The obtained data of coercivity, retentivity, and saturation magnetization (Table 1) are lower than those reported for Ru−NiFe₂O₄ NPs in the literature, suggesting that Ru-doping in NiFe₂O₄ has a favorable effect on its soft magnetic behavior. Also, the values of magnetic properties, that is, low saturation magnetization, are smaller on account of forming the magnetically dead layers on the surface of Ru−NiFe₂O₄ NPs, inducing canting and spin disorder because of broken superexchange bonds. The oscillation of saturation magnetization is defined by redistribution of cations on A and B sites and superexchange interaction between A and B sites using Neel’s ferromagnetic theory. On the basis of this theory, the magnetic moments of octahedral and tetrahedral sites confirm the magnetization of ferrites. The magnetic moments of Ru, Ni, and Fe ions are 4, 2, and 5 μB, respectively, which suggests that the Ni²⁺ cations are located in A sites and the trivalent cations (Ru³⁺ and Fe³⁺) are located in B sites which, eventually, increases the resulting magnetization. Because of a spin disorder, Figure 6 demonstrates an enhanced magnetization of Ru−NiFe₂O₄ NPs with annealing temperatures. In general, magnetic properties are particle size-dependent. The lower magnetization of Ru−NiFe₂O₄ NPs annealed at 300 °C is smaller particle size wherein a high surface disorder is expected. On further increasing of annealing temperature, the particle size increases on decreasing the surface disorder followed magnetization. Also, the coercivity rises with annealing temperatures. Generally, the coercivity increases with decrease of the particle size, but in this study, the reverse trend has been evidenced.
because of the fact that the grain boundaries can lead to increase pinning sites for spins, leading to increase in the coercivity. In addition, structural defects such as oxygen vacancies and lattice strains also increase the coercivity.55 The rise of coercivity depicts transition of the magnetic single-domain to the multidomain where the exchange coupling becomes strong, which results in a lesser disorder magnetic anisotropy among domains.56 The strong exchange coupling leads to an increase in retentivity with respect to annealing temperature, suggesting growth of anisotropic properties.

2.5. Sensing Studies. Figure 7 illustrates dynamic resistance hydrogen-sensing curves of Ru\textsuperscript{−}NiFe\textsubscript{2}O\textsubscript{4} NPs against 50 ppm hydrogen gas at different operating temperatures ranging from 25 to 150 °C. In all gas sensors, the electrical resistance increases upon exposure to hydrogen gas, demonstrating the p-type nature of the gas sensors. Also, the air resistance of gas sensors decreases upon increasing the operation temperature, indicating semiconducting behavior in Ru\textsuperscript{−}NiFe\textsubscript{2}O\textsubscript{4} NPs. The gas-sensing mechanism is based on the variation of resistance change of the gas sensor in the presence of hydrogen gas. First, when the sensor is in air, oxygen gas can be adsorbed on its surface. The amount of adsorbed oxygen species depends on the particle size, surface area, surface condition, and operating temperature. The relevant reactions are as follows:

\[
\begin{align*}
O_2(\text{gas}) & \rightarrow O_2(\text{ads}) \\
O_2(\text{ads}) + e^- & \rightarrow O_2^- \\
O_2^- + e^- & \rightarrow 2O^- 
\end{align*}
\]

The oxygen species capture electrons from the conduction band of the gas sensor, that is, Ru−NiFe\textsubscript{2}O\textsubscript{4} NPs, increasing the hole concentration. After injection of hydrogen gas, the following reaction takes place

\[
H_2 + \frac{1}{2}O^\cdot \rightarrow H_2O + e^- 
\] and released electrons return back to the surface of the gas sensor, leading to increase of the sensor resistance, which is a p-type material.55 Accordingly, a response is observed. In addition, because of the difference between work functions of the Ru and NiFe\textsubscript{2}O\textsubscript{4}, heterojunctions can be generated between the Ru and NiFe\textsubscript{2}O\textsubscript{4}. Upon exposure to hydrogen gas, the height of these heterojunctions changes, leading to modulation of electrical resistance of the gas sensor with a moderate sensor signal. In general, the electrical resistance of the gas sensor is higher in comparison to results reported for phase pure and doped NiFe\textsubscript{2}O\textsubscript{4} in the past.57 Accordingly, the presence of Ru in B-sites leads to increase of the sensor resistance.58 Because of transfer of electrons from Ru to NiFe\textsubscript{2}O\textsubscript{4} there may be change in the sensor resistance as Ru, with a large ionic radius, causes the lattice distortion.59 All Ru−NiFe\textsubscript{2}O\textsubscript{4} NP gas sensors showed a response of 1.1, which is slightly higher than that previously reported for NiFe\textsubscript{2}O\textsubscript{4}. Sapna et al. reported the sensitivity of the NiFe\textsubscript{2}O\textsubscript{4} thick film sensor with a response of 1.09−300 ppm hydrogen gas at 175 °C.60 In our previous Li−NiFe\textsubscript{2}O\textsubscript{4} gas sensor, a response of 1.08−100 ppm hydrogen gas at 200 °C was documented.57 The response increases from 25 to 100 °C and then decreases at 150 °C. Accordingly, the optimal sensing temperature is 100 °C. At this temperature, the response to 100 ppm hydrogen gas is 1.36. The thermally activated electrons can be increased during rise of operating temperature up to 100 °C, leading to increase in adsorption of gas molecules on the surface of the sensor.60 The response followed sensitivity decreases at 150 °C, which describes faster desorption than adsorption. The optimal sensing temperature is relatively small in comparison with temperatures reported for ferrite gas sensors. For example, Falsafi et al. demonstrated hydrogen gas sensing of Sm−
CoFe2O4 at an optimum sensing temperature of 200 °C.23 Mitra et al. reported hydrogen gas-sensing properties of ZnFe2O4 at 200 °C.62 Our previous report on Li−NiFe2O4 demonstrated an optimum sensing temperature at 200 °C.57 Among Ru−NiFe2O4 NP gas sensors, the gas sensor annealed at 300 °C showed the highest gas response, which is attributed to the presence of smaller-sized particles and the presence of the α-Fe2O3. In fact, the co-existence of Fe2O3 and NiFe2O4 phases can generate heterojunctions, which significantly can modulate the electrical resistance of the gas sensor. Even though gas sensors annealed at 300 and 600 °C have demonstrated the Fe2O3 phase, but amount of Fe2O3 in the previous sensor was higher than in the latter. Also, it should be noticed that after 300 °C the particle size increases drastically with decrease of specific surface area as a function of annealing temperature, producing a low response.63 In fact, smaller particles demonstrate higher surface area, which means adsorption of oxygen and hydrogen gases, leading to higher response of the gas sensor.64 Figure 8 illustrates long-term stability and reproducibility of Ru−NiFe2O4 NP sensors after a 6 month period. On the basis of these data, as-developed hydrogen sensors confirm nearly the same response. The slight declination in response is due to adsorption of humidity on the surface of the gas sensor.65 Also, the gas sensors reveal ∼85% reproducibility. The selectivity tests, performed on 50 ppm of ammonia, ethanol, and hydrogen gas, are shown in Figure 9. It can be seen that the Ru−NiFe2O4 NP gas sensor shows a response to hydrogen gas in comparison with NH3 and C2H5OH gases, demonstrating its selectivity to hydrogen gas.

3. CONCLUSIONS

In a nutshell, we report on the co-precipitate method-mediated synthesis and structural, magnetic, and sensing properties of annealed Ru−NiFe2O4 NPs. The samples were annealed at different temperatures. XRD, SEM, TEM and energy-dispersive X-ray analyses were performed to study the crystallinity, morphology, and chemical composition of the samples. Dielectric properties including dielectric constant and dielectric loss showed low value according to different annealing temperatures. Magnetic properties including hysteresis loops describe the soft behavior of NPs. Hydrogen gas sensing properties that contained sensitivity and response of Ru−NiFe2O4 NPs investigated. Changes in structure, magnetic, and gas-sensing performance are due to alteration in the particle of the Ru−NiFe2O4 NPs as a function of annealing temperature.

4. EXPERIMENTAL DETAILS

4.1. Synthesis of Ru−NiFe2O4 NPs. The chemical co-precipitation method was used for the synthesis of Ru−NiFe2O4 NPs. Analytical grade starting materials, that is, ruthenium chloride (RuCl3), nickel chloride (NiCl2), and ferric chloride (FeCl3), were used as received. Required proportions of precursor salts were mixed and the aqueous solutions were prepared under continuous magnetic stirring. The final homogenized solution was obtained by stirring at 60 °C, whose pH was adjusted to 11 using aqueous NaOH solution. This solution was washed several times to remove chloride and inorganic contaminants, if there could be any, and the precipitate was dried in an oven at 100 °C for 1 day. The dried powder was ground well using a mortar and pestle for 2 h and was annealed at 300, 600, and 900 °C annealing temperatures in a muffle furnace.

4.2. Measurement Details. The structure and crystallinity of Ru−NiFe2O4 NPs, annealed at different temperatures, were inspected using XRD spectra. Morphologies of the as-synthesized sensors were confirmed from the SEM and TEM digital photo images. Chemical compositions were identified using EDXS, which was in line with the SEM unit. Dielectric properties were investigated using an LCR meter. The hysteresis parameters were obtained from the hysteresis loop acquired from a vibrational sample magnetometer. Hydrogen-sensing properties were investigated using a gas-sensing system. The Ru−NiFe2O4 NPs were prepared in pellet form using a hydraulic pelletizer. The upper and lower surfaces of the pellets were painted with silver paste for better electrical connections, which, in reality, served as electrodes during gas-sensing tests.

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Notes
The authors declare no competing financial interest.

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