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Fabrication and characterization of Ru-doped LiCuFe₂O₄ nanoparticles and their capacitive and resistive humidity sensor applications



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ABSTRACT

Polycrystalline ruthenium-doped lithium-copper-ferrite (Ru – LiCuFe₂O₄)nanoparticles (NPs) are synthesized using a simple and cost-effective chemical co-precipitation method and annealed at different temperatures for increasing the crystallinity. The transmission and scanning electron microscopy images have confirmed the presence of soft agglomerations and cuboids for the samples annealed at 1100 °C. X-ray photoelectron results along with Raman spectra have collectively demonstrated the presence of Ru in the structure of Ru – LiCuFe₂O₄ NPs. The dielectric properties of as-synthesized Ru – LiCuFe₂O₄ NPs are investigated using LCR meter where the smaller NPs demonstrates a higher dielectric constant. Also, the results of magnetic measurements of annealed Ru – LiCuFe₂O₄ NPs have corroborated a soft magnetic nature due to the pinning sites that endow lower coercivity, remanence and saturation magnetization than that of the pristine one. The variation of permittivity and electrical resistivity with respect to frequency under humidity conditions suggested that this material has a potential to use as capacitive and resistive humidity sensor. The results of this study open the doors for utilization of metal-doped magnetic ferrites for humidity sensing applications.

1. Introduction

Lithium-copper ferrites (LiCuFe₂O₄) have received considerable attention due to their unique electrical, dielectric and ferromagnetic properties which, basically, are dependent on the substitution of ions, preparation methods and annealing temperatures [1,2]. Structural and morphological properties of LiCuFe₂O₄ can be tuned for improving the permeability and density [3] which are essential to realize data storage devices, gas and humidity sensors, microwave devices and cancer cell treatment etc. [4–6]. Furthermore, elemental substitutions can greatly influence the performance of ferrites on enhancing the electromagnetic performance. In this regards, LiCuFe₂O₄ as a well-known ferrite has very interesting properties [7–9]. It is found that the substitution of divalent metallic ions or rare earth ions significantly alters the magnetic properties [10–11]. The rare earth elements were doped in Mn, Mg-Zn, Ni-Zn and Mn-Zn ferrites to induce the soft magnetism [12–14] which eventually demonstrated special and desired physical properties. Among different metals, ruthenium (Ru) has been enormously used as a dopant to improve the magnetic performance. For example, Hoque et al. reported the enhanced magnetic properties of lithium-doped copper ferrite nanoparticles (NPs) as a hard magnetic material with higher coercivity and retentivity than that of undoped one [1]. Wenwei et al. reported the magnetic properties of copper-manganese lithium ferrite with highest specific saturation magnetization and retentivity values close to zero, suggesting a soft magnetic behavior [15]. Lithium-copper ferrite, reported by us previously, also revealed an inferior soft magnetic nature [9]. Raveau et al. reported that Ru doping can effectively induce the ferromagnetism. Arash et al. has reported magnetes

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Received 14 September 2018; Received in revised form 9 November 2018; Accepted 11 November 2018 Available online 12 November 2018 0304-8853/ © 2018 Elsevier B.V. All rights reserved. doped zinc ferrite as dynamic adsorbents [16,17]. Comparing to other elements like samarium, terbium, gadolinium etc., Ru has a strong stabilized ferromagnetic nature because of its 4*d* metal character. Therefore, it is expected that inRu – doped LiCuFe₂O₄ NPs, soft magnetic properties along with high magnetization can be easily achieved.

In this work, we unveil a facile wet chemical synthesis, characterization and a highly soft magnetic nature of $Ru - doped LiCuFe_2O_4$ NPs. The effects of doping and annealing temperature on the structure, morphology, dielectric and magnetic properties are explored. Generally, the ferrite material surfaces exhibit a myriads of open pores, making them as proof of concept research for humidity sensor device assembly [18]. Accordingly, $Ru - doped LiCuFe_2O_4$ samples are used to fabricate humidity sensor. The main use of humidity sensor is to monitor the relative humidity of environment [19]. Therefore, we also attempted to explore our material as humidity sensor.

2. Experimental procedure

2.1. Synthesis of Ru - doped LiCuFe₂O₄NPs

Polycrystalline $Ru_x Cu_{0.5-x} Li_{0.5} Fe_2 O_4$ samples where x = 0.1 was synthesized by a simple chemical co-precipitation method using phase pureRuCl₃. 2H₂O, CuCl₂. 6H₂O, FeCl₃. 9H₂O and LiCl as starting chemicals. According to stoichiometry, the starting materials were dissolved in 100 mL distilled water while continuous stirring till the solution turned to be light green in color. Subsequently, 100 mL of sodium chloride solution was slowly poured which caused to change the color of the solution to brown. The final solution was kept at 60 °C for 2 h to complete the formation Ru - doped LiCuFe₂O₄ NPs, which were then washed thoroughly with de-ionized water to remove chloride content, if there could any, dried in hot-air oven overnight. As dried powders were transformed into a mortar agate for grinding process which was operated for 1 h to produce a fine NPs with narrow size distribution. Finally, the NPs were annealed at muffle furnace for 5 h to eliminate an organic residue. For electrical characterization, the samples were uniaxially pressed into disks of 6 mm diameter and of 1-1.5 mm thickness using a hydraulic pressure meter gauge.

2.2. Characterization details

The crystallinity and phase formation of the Ru – doped LiCuFe₂O₄NPs were examined by using X-ray diffractometer (XRD) with Rigaku Ultima III. The morphology was captured through JEOL 5600 SEM scanning electron microscopy (SEM) images. Transmission electron microscopy and selected area diffraction measurements were performed on Tecnai G2 F30S-TWIN to study the lattice spacing and crystallinity. Chemical compositions were studied using EPSRC X-ray photoelectron (XPS) spectroscopy. Raman spectroconfirm scopy was operated to the formation of Ru - doped LiCuFe2O4NPs. The disk-shaped samples were polished and painted with silver contact electrodes on both sides. The dielectric measurements of the pressed samples were studied using LCR meter (Wayner Kerr 6500P). Magnetic measurements were conducted on vibrational sample magnetometer (VSM), Microsense Inc. USA (EZ9 model), equipped with a field of 2.2 T. Humidity sensor analysis was done with help of LCR meter.

3. Results and discussion

3.1. Structural analysis

Fig. 1 presents the XRD patterns of Ru – doped LiCuFe₂O₄NPs annealed in three different temperatures *viz*. for 5 h where the reflections at (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) reflection planes of LiCuFe₂O₄ were obtained. All reflection peaks were indexed in accordance with cubic phase of the LiCuFe₂O₄. From the XRD patterns,



Fig. 1. The XRD patterns of $Ru-doped\ LiCuFe_2O_4\ NPs$ at different annealing temperatures.

secondary phases were evolved in all samples. In ferrites evolution, formation of secondary phases one of the common practices can be assigned to the presence of iron vacancies in the sub-lattices which decreases with annealing temperatures [20]. With annealing temperatures, the peaks were broadening, implying an increase of the crystal-linity. The average particle size was 5–41 nm.

3.2. Microstructural analysis

Fig. 2(a-b)depicts the SEM images of the Ru – doped LiCuFe₂O₄NPs annealed at 1100 °C at two different magnifications. The SEM images of the Ru - doped LiCuFe2O4was composed of corroborated cuboids and nanorods. Also, the formation of soft agglomerated NPs was confirmed. Such kind of features would ensure high dielectric properties and moderate humidity sensing. Fig. 2(c-d) highlights the TEM image of Ru - doped LiCuFe2O4NPs annealed at 1100 °C which was desirable annealed temperature for ferrite NPs preparation. Fig. 2c shows the inhomogeneous particle formation with soft agglomeration, where the NPs with cuboids in shape were evidenced. Fig. 2d describes the selected area electron diffraction (SAED) pattern of the Ru - doped LiCuFe₂O₄ NPs. Slightly less concentric rings and bright spots were seen, suggesting the formation of well-crystalline microstructure at elevated annealing temperatures [21].

3.3. Binding energy analysis

Fig. 3(a–f) describes the high resolution XPS spectra of Ru – doped LiCuFe₂O₄NPs annealed at 1100 °C scanned for knowing the elements and their binding energies. The carbon signal located at 284.63 eV was due to the presence of air carbon species (Fig. 3a). Fig. 3b depicts O 1s core-level region with two peaks; the peak around



Fig. 2. (a–b) SEM, (c) TEM and (d) SAED pattern images of Ru – doped $LiCuFe_2O_4$ NPs annealed at 1100 $^\circ C.$



Fig. 3. The XPS spectra of the Ru – doped LiCuFe $_2O_4$ NPs annealed at 1100 °C.



Fig. 4. Raman spectra of Ru – doped LiCuFe₂O₄ NPs for various annealing temperatures.

529.67 eV was accredited to lattice oxygen and the one located at 531.70 eV was attributed to the surface hydroxyl group [22]. Fig. 3c displays strong spectrum of Fe 2p around 710.70 eV for Fe2p_{3/2} and 724.14 eV forFe2p_{1/2} [23,24]. Fig. 3d supplies three peaks of Cu around 933.41 eV forCu2p_{3/2}and 941.69 eV for Cu²⁺ satellite [25,26]. The third peak at 953.17 eV was from Cu2p_{1/2}. Fig. 3e displays Li 1s core level at 55.30 eV [25]. Finally, Fig. 3f reveals the Ru 3p core-level region with a peak located at 497.05 eV, suggesting effective doping of Ru in LiCuFe₂O₄ as Ru – doped LiCuFe₂O₄ [27].

3.4. Raman spectroscopy analysis

To confirm the formation of the Ru - doped LiCuFe₂O₄NPs, Raman spectroscopy measurement was carried out at room-temperature and the obtained results are elucidated in Fig. 4. Raman spectra of 900-1100 °C temperature annealed samples were almost similar and bands were relatively broad. The synthesized ferrite NPs belonged to the cubic space group with first-order Raman active modes $(E_g + T_{2g} + 2A_g)$. Usually, ~785 cm⁻¹ mode demonstrates the motion of oxygen in tetrahedral sub-lattice that of lower modes demonstrate the vibrational mode of octahedral sublattice [28]. In Fig. 1, four Raman modes are obtained at 280, 777, 1534 and 1724 cm⁻¹ which were assigned to Eg, T2g and 2Ag, respectively. Raman intensity was reduced on increasing of the annealing temperature from 1000 to 1100 °C. This behavior was due to the formation of ion vacancies and lattice defects at octahedral sites. Additionally, the modes at 1534 and 1724 were noted on account of the cation redistribution at tetrahedral sites, suggesting an effective Ru doping [29].

3.5. Dielectric properties

The variation of dielectric constant with respect to frequency at room-temperature for the Ru – doped LiCuFe₂O₄disc shaped pellets annealed at different temperatures is shown in Fig. 5a. In all samples, dielectric constant increased and then decreased with respect to frequency. At high frequency, dielectric constant decreased which is one of the common behaviors in ferrite structures [30,31]. The variation in dielectric constant with respect to frequency demonstrated the dispersion, in agreement with Koop's theory, which was characterized through a space charge polarization method. According to Koop's theory, from conductivity point of view, as-obtained ferrites were composed of two layers namely conducting and poor conducting [32]. The well-conducting grains belonged to high frequency region and a poor conducting grains were of low frequency region [33]. High dielectric constant was achieved at low frequency because the number electrons could be piled or displaced at poor conducting grains which led to maximize the space charge of polarization. Likewise, low dielectric constant was achieved at high frequency due to interruption of electron displacement, leading to decrease of the space charge polarization. However, electron displacement between the well and poor conducting grains might be interrupted on localizing the charge accumulation at the interface. Also, the electron displacement betweenFe²⁺ and Fe³⁺ ions cannot follow alternate field, resulting a low space-charge polarization [34]. Dielectric constant depends on the particle size, where small-sized particles offer large surface grain boundaries and reveal a high dielectric constant. On the other hand, large sized particles demonstrate lower surface grain boundaries, revealing a low dielectric constant. Fig. 5b shows the variation of dielectric loss with respect to frequency. At high frequency, as the jumping frequency of electric charge carriers cannot follow the alternate field, dielectric loss decreases. The variation of dielectric loss with respect to frequency, initially, showed relaxation peak which due to relaxation in dipole was shifted to higher frequency side. Such dipoles occur due to electronic, space charge, molecular polarization etc., relaxing at different frequencies [35].

3.6. Magnetic properties

describes loop 6(a-c) the hysteresis of Fig. Ru - doped LiCuFe₂O₄NPs annealed at different temperatures. The measurement was carried out at room-temperature. Under the influence of applied field, the Ru - doped LiCuFe₂O₄NPs confirmed a clear soft magnetic hysteresis behavior. Due to the elements occupied sites, the synthesized NPs demonstrated ferrimagnetic nature [36]. Based on the literature survey, the elements like lithium, copper and ruthenium occupy in octahedral sites whereas, the iron occupies in tetrahedral sites. According to ferrimagnetic nature of ferrites, the magnetic moments in octahedral and tetrahedral sites were aligned antiparallel. Likewise, magnetic moment of rare earth elements originated from 4d electrons is characterized by a low magnetic ordering temperature (below 60 K) and exhibits disorder magnetic dipolar orientation. Therefore, ruthenium is considered to be non-magnetic [36]. From Fig. 6, the magnetization increased with annealing temperature as the particle size increases with annealing temperature, resulting in development of wellcrystallized microstructure. Correspondingly, the number of grain boundaries increased and then the amounts of surface and interfaces also increased, supplying more pinning sites for domain wall motions [37,38]. Also, the domain walls might coincide with the grain boundaries [39], suggesting Ru - doped LiCuFe₂O₄NPs were in soft magnetic character. Refereeing to our previous report on Li - CuFe₂O₄ NPs, the contribution of domain wall displacement was high on magnetization process, implying an increase of both high magnetization and soft magnetic behaviors on doping process [9,36]. Likewise, in this study, the saturation magnetization values increased due to Ru doping, suggesting the growth of magnetization process. The obtained high magnetization in Ru - doped LiCuFe₂O₄ NPs was a result antiparallel sublattice magnetization of Fe3+balancing[46]. Hence, the effect of ruthenium substitution was entirely different from other non-magnetic elements in octahedral sites. The Ru - doped LiCuFe2O4NPs revealed superior paramagnetic behavior at 900 and 1000 °C where, coercivity and remnance magnetization values were zero. At 1100 °C, Ru - doped LiCuFe2O4 NPs showed smaller values of coercively and remanence magnetization. It has been reported that high coercivity, saturation magnetization and low remanence are essential for data storage device applications [40]. The magnetic parameters were tabulated in Table 1.



Fig. 5. (a) Dielectric constant, and (b) dielectric loss of $Ru - doped LiCuFe_2O_4$ NPs annealed at different temperatures.



Fig. 6. Hysteresis loops of Ru – doped LiCuFe₂O₄ NPs annealed at various temperatures.

Table 1 Shows the XRD, dielectric and Magnetic parameters of $Ru - doped LiCuFe_2O_4$ NPs.

| Parameters | Ru – LiCuFe ₂ O ₄ | $(Ru_{0.1}Cu_{0.4}Li_{0.5}Fe_2O_4)$ | |
|--|---|--|---|
| Temperature (°C) | 900 | 1000 | 1100 |
| Particle size (nm) Dielectric constant (ε) Dielectric loss (D) Coercivity (Oe) Remanence (emu/g) Saturation (emu/g) | 5 617.39 3.85 - - - | 27 261.22 1.93 - - 7.91 | 41 37.96 1.30 388.71 10.73 21.08 |

3.7. Humidity sensing properties

For humidity sensing applications, the electrical permittivity and electrical resistance measurements were performed in the range of 20 Hz–20 MHz at room-temperature, in an enclosure box with a known relative humidity (RH) in 0–97% RH range. From the investigation, the relative permittivity and electrical resistivity of annealed samples showed frequency dependence. From Figs. 7 and 8, the electrical resistivity and relative permittivity were respectively obtained as a function of frequency which was in accordance with Koop's phenomenological theory. The obtained dielectric dispersion was explained on the basis of Maxwell-Wagner-type of interfacial or space-charge

polarization [41,42]. The relative permittivity demonstrated a higher relative change in the range from 0 to 97%RH than the relative change of electrical resistivity, which in fact was more informative. The relative permittivity values were high even at low frequency range (Fig. 7). In this range, maximum conductivity across the grain boundaries led to high permittivity. Also, the high sensitivity of electrical resistivity to RH change was appeared in low frequency. The relative permittivity decreased at high frequency owing to the $Fe^{3+} \leftrightarrow Fe^{2+}$ electronic displacement and because of predominance species like oxygen vacancy, lattice defects and Fe²⁺ ions, it was free from the alternate field [43,45]. The sample annealed at 1100 °C showed a maximum relative permittivity as compared to 900 and 1000 °C samples, which was attributed to maximum space charge polarization. The relative permittivity is influenced by number of parameters like frequency, crystallinity, pore size and pore-size distribution [43]. Based on Figs. 7 and 8, increase in the relative permittivity and decrease in the electrical resistivity could be The appreciated in the humidity sensor application. Ru – doped LiCuFe₂O₄NPs exhibited increasing nature of the relative permittivity and decreasing nature of the electrical resistivity which could be due to Maxwell-Debye relaxation where, the open pores are filled with water vapors pores [44,45]. The variation of electrical resistivity and permittivity with respect to frequency under humidity suggested that this material was of potential candidate to be used as humidity sensor. As it can be seen in Fig. 7, under different humidity conditions, the permittivity response showed maximum variations for the Ru - doped LiCuFe2O4NPs annealed at 1000 °C, demonstrating



Fig. 7. Variation of relative electrical permittivity vs. frequency for different relative humidity levels.



Fig. 8. Variation of relative electrical resistivity vs. frequency for different relative humidity levels.

suitability for application in capacitive humidity sensors. The electrical resistance measurements suggested that the Ru – doped LiCuFe₂O₄NPs annealed at 900 °C revealed smaller particles and showed a maximum variation of electrical resistivity at different humidity levels (Fig. 8). Consequently, at lower frequencies, this material could act as active material for realization of resistive humidity sensors.

4. Conclusion

In brief, Ru - doped LiCuFe2O4NPs were successfully synthesized by a facile chemical co-precipitation method followed by annealing treatment at various temperatures (900-1100 °C). XRD results confirmed the formation of well-crystalline ferrites and the morphology studies by SEM and TEM microscopes demonstrated the presence of soft agglomerations of cuboids and nanorods. Also based on the XPS and Raman analyses, the presence of Ru was in the synthesized products was confirmed. According to magnetic studies, upon substitution of Ru, a soft magnetic behavior was induced in all samples. Dielectric constant and dielectric loss of as-fabricated pellets of Ru - doped LiCuFe2O4 annealed at different temperatures were studied as a function of frequency, where in agreement with Koop's theory, they demonstrates the dispersion which can be characterized by space charge polarization. Finally, the study of the variations of dielectric constant and electrical resistance in the presence of various RH (0-97%), demonstrated the possibility of using of Ru - doped LiCuFe₂O₄as a humidity sensor, in which, the resistance values decreased, while dielectric constants were increased. These results suggests the search for finding of more sensitive ferrite samples for practical applications such as humidity and gas sensors.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jmmm.2018.11.072.

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