Synthesis, Characterization and Magnetic Study of
La_{0.33}Ca_{0.67}Mn_{0.99}Fe_{0.01}O_{3} Functionalised for Antimicrobial Therapy

Edobor-Osoh Abiola\(^1\), Ita Benedict I.\(^2\), de la Presa Patricia\(^3\), Ajanaku Kolawole O.\(^1\), Ajani Olawale O. \(^1\), Aladesuyi Olanrewaju\(^1\), Owolabi Fisayo E. \(^1\) and Olorunshola Shola J. \(^4\)

\(^1\)Department of Chemistry, Covenant University, Ota, Ogun State, Nigeria.
\(^2\)Department of Pure and Applied Chemistry, Calabar, Cross River State.
\(^3\)Instituto de MagnetismoAplicado, UCM-ADIF-CSIC, 28230, Las Rozas, Spain.
\(^4\)Department of Biological Sciences, Covenant University, Ota, Ogun State.

*corresponding author: abiola.edobor@covenantuniversity.edu.ng

Abstract. The structural, morphological and magnetic properties of La\(_{0.33}\)Ca\(_{0.67}\)Mn\(_{0.99}\)Fe\(_{0.01}\)O\(_3\) were studied using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Superconductive Quantum Interference Device (SQUID). The sample was synthesized using sol gel method and sintered at 700, 800 and 900 °C. The crystallite size of the sample was influenced by the increase in the sintering temperature. There was no significant difference in magnetisation as sintering temperature increased from 700 °C to 800 °C, however, the magnetic properties of La\(_{0.33}\)Ca\(_{0.67}\)Mn\(_{0.99}\)Fe\(_{0.01}\)O\(_3\) reduced drastically from 12.15 emu/g to 8.13 emu/g as sintering temperature increased from 800 °C to 900 °C. The surface of La\(_{0.33}\)Ca\(_{0.67}\)Mn\(_{0.99}\)Fe\(_{0.01}\)O\(_3\) sintered at 900 °C was functionalised using ethyl 4-nitrobenzoate. The wavelength of the functionalised manganite was monitored using ultraviolet-visible spectrophotometry. Antimicrobial properties of the complex formed was investigated against the bacteria and fungi strains, Staphylococcus aureus, Pseudomonas aeruginosa, Candida albicans, and Aspergillus niger, the zones of inhibition were 20, 40, 26 and 45 mm, respectively.

Keywords: Manganite, antimicrobial properties, Pseudomonas aeruginosa, ethyl 4-nitrobenzoate, La\(_{0.33}\)Ca\(_{0.67}\)Mn\(_{0.99}\)Fe\(_{0.01}\)O\(_3\)

1. Introduction

Manganites are perovskites with the transition element manganese (Mn) as a constituent in the compound; and it has a general notation AA’MnO\(_3\) [1 – 4]. The A and A’ are identified as the A-site, which constitutes a rare earth metal at the A-site and an alkaline earth metal at the A’-site, Mn is situated at the B-site of the manganite[4]. Manganites are doped at the A or/and B-sites [5, 6]. The alkaline earth metal at the A – site initiates some important intrinsic properties, such as: colossal magneto-resistance, magneto caloric effect, double exchange etc [7 – 9]. The intrinsic properties are exploited in various industries. The most interesting fact about doping of manganite is that the varying chemical properties and ionic radius of the dopant takes part in the structural, morphological, magnetic properties and applications of the manganite.
The emergence of multidrug resistant microbes is due to the accumulation of multiple genes encoded for resisting a single or multiple drugs in such microbes [10]. The lives of patients that have been infected with multidrug resistant microbes become threatened as the infectious diseases become difficult to cure. In recent time bacteria such as *E. coli*, *Staphylococcus aureus*, *Streptococcus pneumonia* and *Neisseria gonorrhoeae* have been found to be resistant towards the first – line drugs such as fluoroquinolone, oxacillin and azithromycin, which were hitherto effective against them [11].

Manganites have generally been applied in life science as antimicrobial agents [12 – 14], they have been functionalised with small ligands [15], photovoltaic and light polarisers [16]. In recent times, manganites have been used for cancer treatment by means of magnetic hyperthermia [17, 18].

There are only a few studies of the potentials of non-ferromagnetic manganites in nanobioscience. Manganese such as $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$, doped with europium have been utilized as an antibacterial agent against *Pseudomonas aeruginosa* ATCC 27853. It was observed that $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ had better antibacterial activities when compared to $\text{Eu}^{3+}$ doped $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ [12]. Nevertheless, the toxicity of manganites increased with the concentration of $\text{La}^{3+}$ in the compound [12]. The europium doped manganite was consequently the most appropriate as a potential antibacterial agent in terms of toxicity. In recent times paramagnetic nanoparticles such as iron oxide have been coated with human serum albumin and its surface functionalised with vancomycin. It was observed that the functionalised nanocomposite reduced the minimum inhibitory concentration (MIC) of the vancomycin from 250 – 400 µg/mL to 13 – 28 µg/mL [19, 20]. Giri et al [15] observed that the biocompatibility of manganites was determined by the environment of study and also the interacting species. It was observed that manganese ($\text{Mn}^{3+}$) was the interacting species in manganites in $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$. Manganites were citrate capped so that $\text{Mn}^{3+}$ would not dissolve into the solution. The $\text{Mn}^{3+}$ appeared at the surface of the nanoparticles and interacted with the ligand, 2-aminopurine and 4-nitrophenylanthralinate. Functionalisation of nanomaterials is paramount to its use in nanobiotechnology.

Iron nanoparticles ($\text{Fe}^{3+}$) have been observed to inhibit the growth of *E. coli*, *Pseudomonas aeruginosa* and *Staphylococcus aureus* [21]. The ratio of the Mn$^{3+}$ at the B – site decreases as Fe$^{3+}$ is doped into the structural matrix of the manganite [22]. Consequently, doping Fe$^{3+}$ into the matrix of the structural properties of $\text{La}_{0.33}\text{Ca}_{0.67}\text{MnO}_3$ will increase its potential as an antimicrobial agent. Iron oxides are also widely used in nano-bioscience due to their biocompatibility [23]. Stability, size of nanoparticles, methods of preparation of nanoparticles plays key roles in the use of nanoparticles as antimicrobial agents.

Therefore, in this report we describe the synthesis, morphological, structural and magnetic properties of iron doped manganites, the effect of the sintering temperature on the properties of the sample was also examined at 700°C, 800°C 900°C. The surface of the manganite $\text{La}_{0.33}\text{Ca}_{0.67}\text{Mn}_{0.99}\text{Fe}_{0.01}\text{O}_3$ prepared at 900°C was functionalised with ethyl 4-nitrobenzoate. Antimicrobial property of the functionalised manganite was investigated against the strains of *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Candida albicans* and *Aspergillus niger*.
2. EXPERIMENTAL PROCEDURES

2.1 Synthesis of La_{0.33}Ca_{0.67}Mn_{0.99}Fe_{0.01}O_3

Polycrystalline (manganite nanoparticles) MNPs were synthesized by sol gel method using analyte-grade precursors, La_2O_3, CaCO_3 and MnCO_3 and Fe_2O_3. Stoichiometric amount of the precursors of desired proportions were used according to the formula below,

\[ \frac{1}{3}La_2O_3 + \frac{2}{3}CaCO_3 + (1-x)MnCO_3 + \frac{x}{2}Fe_2O_3 \rightarrow La_{0.33}Ca_{0.67}Mn_{0.99}Fe_{0.01}O_3 + \delta CO_2 \]

Stoichiometric amount of La_2O_3 was dissolved in 250 ml acidified water, heated at 90°C for 5 minutes, after which 10 grams of citric acid is added. MnCO_3 was added with vigorous stirring until the sample became transparent. Again, CaCO_3 was introduced as well as an appropriate amount of Fe_2O_3 resulting to a brownish-red liquid and 10 grams of ethylene glycol were also incorporated as a gel-forming additive. Resulting solution was heated for several hours at 90°C until the solution evaporated forming a xerogel. Pyrolysis of the xerogel at 200°C further produced a dark brown powder. The powder was pulverised and sintered at 600°C for 24 hours. Furthermore, four different samples were prepared after subsequent heat treatment 700°C, 800°C, and 900°C for two hours. La_{0.33}Ca_{0.67}Mn_{0.99}Fe_{0.01}O_3 sintered at 700°C, 800°C, and 900°C are henceforth referred to as LCMF700, LCMF800 and LCMF900.

2.2 Synthesis of La_{0.33}Ca_{0.67}Mn_{0.99}Fe_{0.01}O_3-ethyl 4-nitrobenzoate

The complex was synthesized by a modified method used by [16]. LCMF900 was used as prepared and ethyl 4-nitrobenzoate (ENB) (98%) was used as purchased from Alfa Aesar. Stoichiometric amounts of the two precursors were dissolved in appropriate solvents. LCMF900 was dissolved in dilute 150mL of 1M hydrochloric acid (HCl) forming a greenish-yellow solution, whereas ENB was suspended in 150mL of analyte grade ethanol (99.7% purity) from Sigma-Aldrich, Germany.

The dissolved manganite was continuously stirred at room temperature to form a homogenous solution. 30 mL of the ENB solution was added every thirty minutes into the manganite solution while stirring. The mixture was stirred continuously once more for two hours to attain homogeneity. The reaction was monitored with thin layer chromatography (TLC). The solution was left undisturbed for approximately 14 days. The product was filtered out, air-dried.

2.3 Structural and Morphological Analyses of La_{0.33}Ca_{0.67}Mn_{0.99}Fe_{0.01}O_3

XRD (PANalytic X’pert Pro MPD diffractometre) was utilized in verifying the structural properties of the samples. The samples were indexed to a perovskite-like arrangement. Average crystallite size (\(\Delta D\)) of the samples were calculated using the Scherer’s formula [24],

\[ D = \frac{0.9A}{\beta_{FWM} \cos \theta} \]  

(1)

Properties of the surface of the sample were determined using JEOL JSM 6335F scanning electron microscope (SEM) operated at 30keV, the elemental composition of the samples were evaluated using energy dispersive spectroscopy (EDS).

2.4 Magnetic Properties of La_{0.33}Ca_{0.67}Mn_{0.99}Fe_{0.01}O_3

The magnetic measurements of the powdered samples were determined by means of Quantum Design SQUID (MPMS 5 Quantum Design cryo-magnet 5T; cryostat 2–400K). Zero-field
cooling (ZFC) curves were obtained from 5 to 300K at 1000 Oe applied magnetic field for all the samples.

2.5 Antimicrobial Analysis of the complex La$_{0.33}$Ca$_{0.67}$Mn$_{0.99}$Fe$_{0.01}$O$_3$-ENB

LCMF900 was screened for antimicrobial potentials against two bacteria- *Staphylococcus aureus* (ATCC 25923) and *Pseudomonas aeruginosa* (ATCC 15442)) and two fungi (*Candida albicans* (ATCC 10231) and *Aspergillus niger* (isolates)) using agar well diffusion method based on procedure employed by Geetha and Anita [25], with modifications. Streaks of the test organisms were put into the sub-cultured nutrient agar and labelled accordingly. The petri dish was left to set and incubated for 24 hours. Appropriate concentration of the sample was dissolved in dimethyl sulfoxide (DMSO) and pipetted into the well. The petri dish was kept warm for a day at 37 °C. Susceptibility study of the samples was determined. Gentamicin and nitrofurantoin were used as control for bacteria and fungi, respectively.

3. RESULT AND DISCUSSION

3.1 Structural analysis of La$_{0.33}$Ca$_{0.67}$Mn$_{0.99}$Fe$_{0.01}$O$_3$

XRD diffraction patterns of the manganite, La$_{0.33}$Ca$_{0.67}$Mn$_{0.99}$Fe$_{0.01}$O$_3$ synthesized using sol gel method is presented in Fig. 1. The powder x-ray diffraction study confirmed that the manganites had a single perovskite phase with identifiable peaks. Table 1 shows the crystallite size comparison of LCMF at different temperatures (700 °C, 800 °C and 900 °C). Average crystallite size determined reduced with increased in annealing temperature 800 °C, however, the crystallite size increased as annealing temperature increased to 900 °C [26]. The samples were all indexed to the Pbnm space group, orthorhombic crystallite structure indicating that the increase in sintering temperature did not influence the crystal structure of the samples. Comparison of the EDAX result showed that the product did not contain any impurities, the nominal composition La$_{0.30}$Ca$_{0.70}$Mn$_{1.02}$Fe$_{0.009}$O$_3$ was determined for LCMF700, LCMF800 and LCMF900.

| Sintering temperature (°C) | Crystallite size (nm) LCMF |
|---------------------------|---------------------------|
| LCMF700                   | 12.3                      |
| LCMF800                   | 11.1                      |
| LCMF900                   | 20.5                      |
3.2 Morphological Properties of $La_{0.33}Ca_{0.67}Mn_{0.99}Fe_{0.01}O_3$

SEM micrographs LCMF700, LCMF800 and LCMF900 represented in Figs. 2(a1) – (a3) were determined to show the effect of sintering temperature on the surface morphology of the sample. SEM images show that the grains on the surface of the samples were homogenous with the presence of highly porous spherical-like particles. This was due to the method of preparation (sol gel), which evolved a large amount of gases and ignition. A well-defined surface of the structure was observed as temperature increased.

Fig. 2: (a1) SEM images for LCMF700, (a2) SEM images for LCMF800 and (a3) SEM images for LCMF900
3.3 Magnetic properties of La$_{0.33}$Ca$_{0.67}$Mn$_{0.99}$Fe$_{0.01}$O$_3$

3.3.1 Magnetization of La$_{0.33}$Ca$_{0.67}$Mn$_{0.99}$Fe$_{0.01}$O$_3$

The zero-field cooling (ZFC) temperature dependent curves were measured at 5 – 300K under an external cooling field of 1000 Oe for each sample (Fig. 3). The samples show an antiferromagnetic (AFM) – ferromagnetic (FM) phase transition [5]. The replacement of Mn ions by Fe$^{3+}$ induced the anti-ferromagnetic interface that favours super-exchange over ferromagnetic double exchange [5]. Magnetization of La$_{0.33}$Ca$_{0.67}$Mn$_{0.99}$Fe$_{0.01}$O$_3$ was influenced by the increase in sintering temperature. Magnetization of the sample increased from 700 °C to 800 °C as 11.95 to 12.15 emu/g, this could be due to the reduction in the crystallite size from 12.3 nm to 11.1 nm for LCMF700 and LCMF800, respectively. The sharp drop in magnetization from 12.15 emu/g to 8.13 emu/g at 900 °C might be due to micro-structural defects incurred as crystallite size increased from 11.1 nm to 20.5 nm for LCMF800 and LCMF900, respectively. [25].

![Fig. 3: ZFC curves for LCMF700, LCMF800 and LCMF900](image)

3.3.2 Ferromagnetic properties of La$_{0.33}$Ca$_{0.67}$Mn$_{0.99}$Fe$_{0.01}$O$_3$

Fig.4 shows the relationship between the ferromagnetic content and sintering temperature for LCMF at 700 – 900 °C. It was noted that the ferromagnetic content of the sample reduced as sintering temperature reduced. The reduction observed may be due the increase in the anti-ferromagnetic properties of the sample as crystallite size of the sample increased. This follows the same trend as result observed by Iniama et al. [27] as magnetization also reduced when the sintering temperature increased.
3.4 Functionalisation of LCMF900 with ENB

3.4.1 Physical properties of the complex LCMF900-ENB

Table 2 shows the physical properties of the complex LCMF900-ethyl 4-nitrobenzoate as white feather-like which was distinctively different from the precursors LCMF900 and ENB. The melting point of the precursor, ENB was also different from the complex formed.

| Sample           | Colour      | Texture             | Melting point (°C) | State |
|------------------|-------------|---------------------|--------------------|-------|
| LCMF900 + ENB    | White       | Feather-like crystal| 60 - 62            | Solid |
| LCMF900          | Black       | Powdery substance   | ND                 | Solid |
| ENB              | White       | Spherical Crystal   | 56-59              | Solid |

3.4.2 Optical characterization of LCMF900, LCMF900-ENB and ENB

The reaction was monitored with UV-Vis spectrophotometer (Fig. 5 and Table 3). The adsorption spectrum showed peaks at \( \lambda_{\text{max}} = 208\text{nm} \) was observed for both LCMF900-ENB and ENB to the conjugated ring in the ENB. This therefore indicated that the reaction did not occur at the ring but at the other unsaturated bonds (O-C=O, O-N=O) or the \( \pi \rightarrow \pi^* \) transition associated with the presence of a benzenoid ring [28], while the bathochromic shift of the \( \lambda_{\text{max}} \) from 253nm to 256nm was due to the addition of a metallic substitute at the unsaturated bonds of O-C=O and/or O-N=O. Although ultraviolet-violet spectroscopy was used in studying the level of unsaturation in a compound, however the observed peaks for
LCMF was due to the variable oxidation state of the transition elements, also the chromophoric nature of the transition elements in the manganites [8].

Fig. 5: Ultraviolet-visible spectra of (a) LCMF900, (b) LCMF900-ENB and (c) ENB

Table 3: Assignment of wavelengths for ENB, LCMF900, LCMF900-ENB

| S/N | Sample                                      | $\lambda_{\text{max, \text{nm}}}$ | $\log \varepsilon_{\text{max}}$ |
|-----|---------------------------------------------|------------------------------------|----------------------------------|
| 1   | ENB                                         | 253 (4.049)                        | 208 (3.851)                      |
|     |                                             | 604 (2.8513)                       | 577 (2.8513)                     |
| 2   | $\text{La}_{0.33}\text{Ca}_{0.67}\text{Mn}_{0.99}\text{Fe}_{0.01}\text{O}_3$ (LCMF900) | 220 (3.300)                        | 334 (2.767)                      |
|     |                                             | 478 (-)*                           | 503 (-)*                         |
| 3   | LCMF900 + ENB                               | 256 (3.300)                        | 208 (2.945)                      |
|     |                                             | 877 (-)*                           | 892 (-)*                         |

*Values of absorbance were negative; therefore $\log \varepsilon_{\text{max}}$ could not be calculated.
3.4.3 Antimicrobial Analysis of LCMF900-ENB
From the result obtained, sensitivity test and activity of the complex against the test organisms were determined based on the zones of inhibition (Table 4). It was interestingly observed that the complex formed was active against all the organisms with zones of inhibitions, 20 mm, 40 mm, 26 mm and 35 mm for *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Candida albican* and *Aspergillus niger*, respectively. Gentamicin was used as the control for the bacteria (*Staphylococcus aureus* and *Pseudomonas aeruginosa*) and nitrofurantoin was used as the control for fungi (*Candida albican* and *Aspergillus niger*). The sample showed better zone of inhibition against *Pseudomonas aeruginosa*.

Table 4: Antimicrobial data of LCMF900-ENB

| Zone of inhibition (mm) | S. aureus | P. aeruginosa | C. albicans | A. niger |
|-------------------------|-----------|---------------|-------------|---------|
| LCMF900-ENB             | 20.0      | 40.0          | 26.0        | 35.0    |
| Nitrofurantoin (control)| -         | -             | 28          | 32      |
| Gentamicin (control)    | 25        | 24            | -           | -       |

4. CONCLUSION
The synthesis, structural, morphological and magnetic properties of \( \text{La}_{0.33}\text{Ca}_{0.67}\text{Mn}_{0.99}\text{Fe}_{0.01}\text{O}_3 \) at 700, 800 and 900°C was successfully accomplished by using sol gel method. The increase in sintering temperature influenced the properties the \( \text{La}_{0.33}\text{Ca}_{0.67}\text{Mn}_{0.99}\text{Fe}_{0.01}\text{O}_3 \). Ferromagnetic properties of the sample reduced as sintering temperature increased from 700 – 800 °C. The surface of the sample, LCMF900 was functionalised using a biologically active small ligand, ENB. The results obtained indicated that sample formed was effective against the gram-positive bacterium (*Staphylococcus aureus*), gram-negative bacterium (*Pseudomonas aeruginosa*) and fungi (*Candida albican* and *Aspergillus niger*). It was however more active against the gram negative *Pseudomonas aeruginosa* than all other microbes.

ACKNOWLEDGEMENTS
The authors would like to acknowledge Instituto de Magnetismo Applicado, UCM-ADIF-CSIC, 28230, Las Rozas, Spain, for allowing the utilisation of their instruments for this research and also Covenant University, Ota, Ogun State, for funding the research.

REFERENCES
[1] Konishi, Y., Fang, Z., Manaki, T., Kasai, M., Kuwahara, H., Kawasaki, M., Terakura, K. and Tokura, Y. (1999). Orbital state mediated control of manganites. *Journal of the Physical Society of Japan*, 68(102): 2790-3793.
[2] Majumder, D. D., Majumder, D. D., Karan, S. (2013). Magnetic properties of ceramic nanocomposite, In Ceramic nanoparticles, Ed. Banerjee R. and Manna I. Woodhead Publishing Series in Composites Science in Composite Science and Engineering, pp. 51-91. ISBN 978-0-85709-338-7.

[3] Cherif, W., Alonso, J. A. and Elhalouani, F. (2017). Evolution of the Fe-ion doped manganites synthesized by the ball milling method. European Physical Journal Plus, 132(48): 1-10.

[4] Venkataiah G., Y. Kalyana Lakshmi K. and Reddy P. V. (2012), Influence of sintering temperature on magnetotransport behavior of some nanocrystalline manganites, Sintering - Methods and Products, Dr. Volodymyr Shatokha (Ed.), ISBN: 978-953-51-0371-4, InTech.

[5] Hcini S., Boudard M., Zemni S. and Oumezzine M. (2014). Effect of Fe-doping on structural, magnetic and magnetocloric properties of Nd$_{0.67}$Ba$_{0.33}$Mn$_{1-x}$Fe$_x$O$_3$ manganites. Ceramic International, 40(10A): 16041-16050.

[6] Fertman, E., Syrkin, E., Lykah, V., Desnenko, V., Beznosov, A., Pal-Val, P., Pal-Val, L., Fedorchenko, A., Khalyavin, D. and Feher, A. (2015) Structural phase transition in La$_{2/3}$Ba$_{1/3}$MnO$_3$ perovskite: Elastic, magnetic, and lattice anomalies and microscopic mechanism, AIP Advances 5(7): 077189.

[7] Tokura, Y. and Tomioko, Y. (1999) Colossal magnetoresistive manganites, Journal of Magnetism and Magnetic Materials, 200(1-3): 1-23.

[8] Reddy, S. L., Endo, T. and Reddy, G. S. (2012). Electronic (adsorption) spectra of 3d transition metal complexes. Advanced Aspects of Spectroscopy, 1-48. http://dx.doi.10.5772/50128.

[9] Fatah, Z. A. (2016) Structural and transport properties of Te doped LaMnO$_3$. International Journal of Engineering Sciences and Research Technology, 5(9): 139-152.

[10] Nikaido, H. (2009). Multidrug resistance in bacteria. Annual Review of Biochemistry, 78: 119 – 146.

[11] Chang, H – H, Cohen, T., Grad, Y. H., Hanage, W. P., O’Brien T. F. and Lipsitch, M (2015). Microbiology and Molecular Biology Reviews, 79(1):101 – 116.

[12] De, D., Mandal, S. M., Gauri, S. S., Bhattacharya, R., Ram, S. and Roy, S. K. (2010). Antibacterial effect of lanthanum calcium manganite (La$_{0.67}$Ca$_{0.33}$MnO$_3$) nanoparticles against Pseudomonas aeruginosa (ATCC 27853). Journal of Biomedical Nanotechnology, 6: 1-7.
[13] Ehi-Eromosele, C. O., Olugbuyiro, J. A. O., Edobor-Osoh, A., Adebisi, A. A., Bamgboye, O. A and Ojeifo, J. (2018). Magneto-Structural and antimicrobial properties of sodium doped lanthanum manganite magnetic nanoparticles for biomedical applications: Influence of silica coatings. *Journal of Biomimetics. Biomaterial and Biomedical Engineering*, 7(2296-9845): 117-127.

[14] Edobor-Osoh, A., de la Presa, P., Ita, I. B., Ajanaku, K. O., Owolabi, F. E. and Olorunshola, S. J. (2019). Functionalization of La0.33Ca0.67MnO3 with biologically active small ligand at room temperature. *MethodsX*, 6(9):682 – 689.

[15] Giri, A., Makhal, A., Ghosh, B., Ravchaudhuri, A. K. and Pal, S. K. (2014) Functionalization of manganite nanoparticles and their interaction with biologically relevant small ligand: Picosecond time-resolved FRET studies. *Nanoscale*, 2: 2704-2709.

[16] Xin, H., Paudal, T., Dong, S. and Tsymbal, E. (2015). Hexagonal rare earth manganites as promising photovoltaic and light polarizers. *Physical Review B*, 92(12-15):1-8. doi:10.1103/PhyRev.92.125201.

[17] Tovstolytkin, A. I., Shlapa, Y. Y., Solopan, S. O., Bodnaruk, A. V., Kulyk, V. M., Zamorskyi, V. O et al., (2018). Manganite nanoparticles as promising heat mediators for magnetic hyperthermia: Comparison of different chemical substitution. *Acta Physica Polonica A*, 133(4): 1017 –1020.

[18] Ahmad, A., Bae, H., and Rhee, I. (2018). Silica coated gadolinium-doped lanthanum strontium manganite nanoparticles for self-controlled hyperthermia applications. *AIP Advances*, 8: 015108, doi: 10.1063/1.5011717.

[19] Hassan, M. M., Ranzoni, A., Phetsang, W., Blaskovich, M. A. and Cooper, M. A. (2016). Surface ligand density of antibiotic-nanoparticle conjugates enhances target avidity and membrane permeabilization of vancomycin – resistant bacteria. *Bioconjugate Chemistry*, 28, 353 – 361.

[20] Karmakar, P. And Gaitonde, V. (2019). Promising recent strategies with potential clinical translational value to combat antibacterial resistant surge. *Medicine*, 6(1), 2. doi: 10.3390/medicines6010021.

[21] Thukkaram, M., Sitaram, S., Kannaiyan, S. K. and Subbiahdoss, G. (2014). Antibacterial efficacy of iron oxide nanoparticles against biofilms on different biomaterial surfaces. *International Journal of Biomaterials*, 716080: 1-6. doi: http://dx.doi.org/10.1155/2014/716080.

[22] Fatnassi, D., Sbissi, K., Hill, E.K., Ellouze, M., Rehspringer J.L., and Elhalouani, F., (2015). Magnetic and magnetocaloric properties of nanosized
La$_{0.8}$Ca$_{0.2}$Mn$_{1-x}$Fe$_x$O$_3$ ($x = 0, 0.01, 0.15$ and $0.2$) manganites prepared by sol gel method. *Journal of Nanostructure in Chemistry*, 5(4):375-382.

[23] Ismail, R. A., Sulaiman, G. M., Abdulrahman, S. A. and Marzoog, T. R. (2015). Antibacterial activity of magnetic iron oxide nanoparticles synthesized by laser ablation in liquid. *Material Science and Engineering C*, 53: 286 – 297.

[24] Scherer, P. (1918). Determine of the size and internal structure of colloid particles by X-ray. *News from the Gesellschaft der Wissenschaften zu Göttingen*, 26:98-100.

[25] Geetha, R.V. and Anitha, R. (2013). In vitro evaluation of anti-bacterial activity of three herbal extracts on Methicillin resistant *Staphylococcus aureus* (MRSA). *Journal of Pharmaceutical Science and Research*, 5(10): 207-209.

[26] Ridha, S., Essebti, D. and Hlil, E. K. (2017). Impact of annealing temperature on the properties of the physical lanthanum deficiency manganites. *Crystals*, 7(307): 1-12. doi: 10.3390/cryst7100301.

[27] Iniama, G., de la Presa, P., Alonso, J.M., Multigner, M., Ita, B.I., Cortés-Gil, R., Ruiz-González, M.L., Hernando, A., and Gonzalez-Calbet,J.M. (2014). Unexpected ferromagnetic ordering enhancement with crystallite size growth observed in La$_{0.5}$Ca$_{0.5}$MnO$_3$ nanoparticles. *Journal of Applied Physics*, 116(11390): 1-8. doi: 10.1063/1.4895707.

[28] Ajani, O. O., Aderohunmu, D. V., Olorunshola, S. J., Ikpo, C. O. and Olanrewaju, I. O. (2016). Facile synthesis, characterization and antimicrobial activity of 2-alkanamino benzimidazole derivatives. *Oriental Journal of Chemistry*, 32(1): 109-120.