Metal–Organic Precursor Synthesis, Structural Characterization, and Multiferroic Properties of GdFeO₃ Nanoparticles

Irfan H. Lone, Huma Khan, Arvind K. Jain, Jahangeer Ahmed, Kandalam V. Ramanujachary, and Tokeer Ahmad

ABSTRACT: GdFeO₃ nanoparticles were fabricated by a facile metal–organic precursor method using citric acid as a complexing agent. The phase purity and structural analysis by powder X-ray diffraction and FTIR studies indicates that the material is highly crystalline with an orthorhombic structure. Electron microscopic (TEM and SEM) studies of rare earth ferrites reveal worm-shaped nanoparticles with an average grain size of 95 nm. The high-resolution TEM study provides an insightful image, which shows an interplanar spacing of approximately 0.12 nm that corresponds to the (112) crystalline plane. A high surface area of 231.5 m² g⁻¹ has been achieved with a mesoporous texture, which in turn gives a high dielectric constant. Well-defined hysteresis is obtained with a saturation magnetization of 17.5 emu g⁻¹. Room-temperature ferroelectricity in GdFeO₃ nanoparticles has been found for the first time with no leaky current and hence may be used in multistate memory devices.

1. INTRODUCTION

Ternary perovskite-type oxides have gained growing interest at the nanoscale due to their special properties and applications such as a high dielectric constant and surface area, photocatalysis, electrocatalysis, optical properties, and magnetic and ferroelectric interactions.¹⁻² Multiferroic materials exhibit multifunctional properties and depict enormous applications, such as memories, hydrogen evolution, sensors, and actuators, as a result of the coexistence of at least two ferroic orders.³⁻⁸ These ferroic properties may be ferroelasticity or ferromagnetism.⁹ The main focus of technological devices demands the fabrication of innovative materials at the nanoscale so that their multiferroic properties must allow the fine-tuning of new applications.⁸ Particular attention has been given to the synthesis of nanocrystalline orthoferrite oxides due to the huge diversity of their functional properties, which make them ideal candidates for electrical and magnetic properties.⁶,¹⁰ Earlier reports have shown strong magnetoelectric coupling by the single crystals of DyFeO₃ and GdFeO₃, but the multiferroic nature appears only at very low temperatures.¹¹ The synthesis strategy of multiferroic GdFeO₃ has attracted the attention of researchers in order to obtain the ultrapure powders using low-temperature chemical routes with room-temperature ferroelectricity. The low-temperature method includes solvothermal,¹²,¹³ hydrothermal,¹⁴ reverse micelle,¹⁵,¹⁶ polymeric citrate precursor,¹⁷ and sonochemical¹⁸ methods used for the fabrication of various metal oxide nanoparticles. Though several reports are available on hydrothermal, sol–gel, colloidal, co-precipitation, and combustion synthesis of GdFeO₃,¹⁹⁻²² there are less reports that discuss the perceptible room-temperature ferroelectricity in GdFeO₃ nanoparticles. GdFeO₃ has a perovskite distorted ABO₃-type structure, and there exists tilting of the rigid FeO₆ octahedral symmetry. When the A-site cation is too small for its 12-coordinate cavity in the cubic perovskite structure, it breaks the symmetry of GdFeO₃ and through the exchange interaction between Gd and Fe, spin ferroelectric polarization is generated in GdFeO₃ nanoparticles. Recently, room-temperature ferroelectricity was observed in nanocrystalline YMnO₃ and YCrO₃ prepared by an organic precursor route.²³,²⁴ In earlier reports, room-temperature ferroelectricity was reported in GdFeO₃ nanoparticles prepared by a chemical co-precipitation method but a large leakage current was a major drawback.²⁵ While in the single crystal of GdFeO₃, the ferroelectric property was found at 2 K.²⁶ In this paper, we report the synthesis of pure nanocrystalline GdFeO₃ by a low-temperature facile polymeric

Received: May 7, 2022  
Accepted: September 2, 2022  
Published: September 13, 2022

© 2022 The Authors. Published by American Chemical Society

http://pubs.acs.org/journal/acsodf  
ACS Omega 2022, 7, 33908−33915
2. EXPERIMENTAL SECTION

The chemical reagents used in the work were Gd(NO$_3$)$_3$.6H$_2$O (Alfa Aesar, 99.9%), Fe(NO$_3$)$_3$.9H$_2$O (Rankem, 98%), citric acid (Spectrochem, 99%), and ethylene glycol (SD Fine-Chem Ltd., 99%). All the chemicals were of analytical grade purity and used without any further purification. For the synthesis of GdFeO$_3$, an as-prepared 0.1 M solution of ferric salt was added in the beaker containing 1.4 mL of ethylene glycol followed by addition of 21 g of citric acid. Then, the mixture was left for 2 h under stirring at room temperature to obtain a clear solution. Further, 25 mL of 0.1 M aqueous solution of Gd$^{3+}$ salt was added followed by continuous stirring for 2 h. The solution was further heated at 70 °C for 2 h to accelerate the polyesterification reaction between ethylene glycol and citric acid. The formed viscous gel was heated in muffle furnace at 135 °C for 20 h to evaporate the excess of solvent. The resin was then charred at 300 °C for 2 h in the same muffle furnace wherein it turned into a black mass precursor, which was frivolously ground to finely ground powder using a Teflon stick. Based on the existence of crystallization peaks and weight loss, the GdFeO$_3$ was calcined at 900 °C in a programmable furnace for 12 h in order to achieve a good crystalline structure. Powder GdFeO$_3$ thus obtained was brownish red in color. The stabilization of nanoparticles happens at the expense of a decrease in availability of the grain size area. Since the volume to surface area ratio decreases, the particle size increases and thus the surface energy also decreases. The increase in the sintering temperature increases the stability of nanoparticles at the cost of a decrease in the specific surface area. A schematic representation of the reaction between ethylene glycol, citric acid, and metal ions (Gd$^{3+}$ and Fe$^{3+}$) is shown in Figure 1.

Powder X-ray diffraction studies have been carried out using a Bruker D8 Advance X-ray diffractometer, which was fitted with Ni-filtered Cu Kα radiation of wavelength 1.54056 Å. The diffraction data was recorded in the 2θ range of 20° to 70° with a step size of 0.05° at an interval of 1 s. The Cu Kα reflections were removed by a stripping procedure to obtain accurate lattice constants. Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer spectrometer of Model 1750. Transmission electron microscopic (TEM) studies were carried out using an FEI TEM 200 kV (model Tecnai G2 20) electron microscope equipped with digital imaging and a 35 mm photography system. TEM specimens have been prepared by using a small amount of the powder sample and dispersed in ethanol on an ultrasonicator (UP-500, Ultrasonic Processor) and sonicated for 30 min at the optimized intensity. An approximately 100 μL volume of the sonicated sample was placed on a carbon-coated copper grid. Scanning electron microscopic (SEM) measurements have been carried out on a new versatile series ZEISS EVO 50 equipped with 0.2 to 30 kV acceleration voltages having a magnification range from 15× to 200,000× and a resolution of 5 nanometers.

The surface area of GdFeO$_3$ nanoparticles was determined at 77 K using a BET surface area analyzer (model: Nova 2000e, Quantachrome Instruments Limited, USA) with the help of a multipoint BET method. Nearly 0.08 g of the sample was placed in the cell and allowed to degas in vacuum at 250 °C for 3 h, which removes the contaminants such as moisture and adsorbed gases from the sample. The degassed powder was then analyzed for data collection by allowing the known quantities of the adsorbed dry N$_2$ gas into the sample cell containing the solid adsorbate. For dielectric and ferroelectric studies, a pellet of 8 mm in diameter was prepared by mixing 100 mg of GdFeO$_3$ nanoparticles with 2–3 drops of 5% aqueous solution of polyvinyl alcohol. The slurry was allowed to dry and the dried material was then reground and pressed with an applied 5 tons of pressure. The pellet was then sintered in air at 1000 °C for 8 h for further measurements. Silver paste (Ted Pella, Inc.) was applied to both faces before drying the pellet at 100 °C in an oven. Dielectric properties were measured on the as-prepared sample using a high-frequency LCR meter (model: 6505P, Wayne Kerr, UK) in a 100 kHz to 1 MHz frequency range and a temperature range of 25–430 °C. The room temperature ferroelectric measurements were carried out on the sintered pellet at a 50 kHz frequency and varying applied voltages on the P−E loop tracer (M/S Radiant Instruments, USA). Magnetic properties have been studied using MPMS with a SQUID magnetometer at an external magnetic field of ±60 kOe in the temperature range of 5–300 K.

3. RESULTS AND DISCUSSION

The X-ray diffraction pattern of the GdFeO$_3$ sample is shown in Figure 2. All the reflections could be satisfactorily indexed in an orthorhombic structure of GdFeO$_3$ (JCPDS: 74-1900). Note that no extra peak due to any other impurity phase such as room-temperature ferroelectricity with better results was achieved.
as α-Fe$_3$O$_4$ and Gd$_2$O$_3$ has been found that attributes to the monophasic formation of GdFeO$_3$ at 900 °C. The significantly high intensity and appearance of distinct reflections may be associated to the good crystallinity in as-prepared biferroic nanoparticles. The average particle size of GdFeO$_3$ nanopowder was calculated from the diffraction pattern using Scherrer’s formula$^{27}$ given by
\[ D = \frac{K\lambda}{\beta \cos \theta} \]
where $D$, $\lambda$ = 1.5418 Å, $\beta$, $K = 0.91$, and $\theta$ are the crystallite size, wavelength of X-ray, full width at half-maximum (FWHM) of the diffraction pattern, Scherrer’s constant, and the diffraction angle, respectively. The values of $\beta$ are extracted from fitting the peak to Gaussian distribution. The calculated average grain size is found to be 92 nm.

FTIR investigation further supports the formation of the as-prepared GdFeO$_3$. Figure 3a,b shows the FTIR spectra of the GdFeO$_3$ precursor after charring and calcination at 300 and 900 °C, respectively. Before calcination, the vibrations at 1623 and 1383 cm$^{-1}$ are seen, which are attributed to the carbonyl stretching peak (esterification between citric acid, ethylene glycol, and metal ions).$^{28,29}$ On the other hand, the characteristic band at 3437.8 cm$^{-1}$ is associated to the atmospheric water vapor vibrations, while the band at 2354 cm$^{-1}$ is attributed to the carbon dioxide stretching mode. After calcination at 900 °C, the carbonyl peak diminishes, indicating the removal of organic species. In Figure 3b of the FTIR spectra after calcination, the bands obtained in the range of 560–590 cm$^{-1}$ are assigned to $\nu$(Fe–O) and $\nu$(Gd–O) in Fe–O–Fe and Gd–O–Fe systems, respectively, confirming the formation of GdFeO$_3$. The band at 592.4 cm$^{-1}$ could be assigned to this characteristic stretching.$^{30,31}$ The appearance of the IR band at 395 cm$^{-1}$ corresponds to the O–Fe–O deformation vibration. At a lower wave number, the prominent bands are characteristic of oxygen–metal stretching modes that confirm the formation of GdFeO$_3$ after 900 °C calcination.

SEM, TEM, and HRTEM studies have been investigated to examine the morphology, size, and lattice spacing of the as-prepared samples. SEM and TEM images at different resolutions showed the formation of a roughly undefined morphology of nanoparticles having an average particle size of 95 nm with a narrow size distribution as shown in Figure 4a,b. The average TEM particle size is found to be slightly larger than the XRD crystallite size of 92 nm as obtained by the Scherrer’s studies. The GdFeO$_3$ nanoparticles are highly magnetized and hence could not well disperse; thus, the particles were in an agglomerated form as shown in the TEM/SEM micrographs. The high-resolution TEM image of GdFeO$_3$ nanoparticles shows the presence of lattice fringes (interlayer fringes $\approx$ 12 Å) as shown in Figure 4c. This lattice fringe spacing matches with the interplanar ‘d’ spacing of GdFeO$_3$ nanoparticles in the [112] direction. The corresponding selected area electron diffraction (SAED) image of GdFeO$_3$ nanoparticles is shown in Figure 4d. The appearance of sharp diffraction spots in a circular pattern confirms the nanocrystalline nature and indexes with orthorhombic GdFeO$_3$. The elemental mapping of the GdFeO$_3$ nanoparticles is shown in Figure 4e, which confirms the presence of Gd, Fe, and O in the as-prepared sample. Note that the experimentally loaded composition was found to have a very close agreement with the EDAX spectra as shown in Figure 4f. The proportions of the constituents obtained from the weight percentages as seen in the table of the EDAX spectrum indicates that the molar ratio of two metal ions (Gd$^{3+}$:Fe$^{3+}$) are approximately close to a 1:1 ratio and they have good stoichiometry and pure chemical compositions. The table further displays the experimental composition, which shows the 1:1 mole ratio, confirming the Gd:Fe nearly equal mole ratio.

The nitrogen adsorption isotherm and the BET plot of GdFeO$_3$ nanoparticles (Figure 5a,b) shows the prominent hysteresis loop of the type-IV isotherm, which could be associated with the capillary condensation in mesopores.$^{32}$ The specific surface area of GdFeO$_3$ nanoparticles is found to be 231.5 m$^2$g$^{-1}$, which has been found to be comparatively much higher than earlier reports.$^{19,33}$ The pore size calculation of the nanoparticles for the mesopore size distribution has been carried out by the Barrett–Joyner–Halenda (BJH) method. Figure 5c,d shows the Barrett–Joyner–Halenda (BJH) and

Figure 2. Powder X-ray diffraction pattern of GdFeO$_3$ nanoparticles.

Figure 3. FTIR (a) before and (b) after calcination of GdFeO$_3$. 
Figure 4. (a) SEM, (b) TEM, (c) HRTEM, (d) SAED and (e) elemental mapping of Gd, Fe, and O, and (f) EDAX spectra; the inset shows table of elemental compositions of GdFeO$_3$ nanoparticles.

Figure 5. (a) Nitrogen adsorption isotherm, (b) BET plot, and (c) BJH and (d) DA plots for the pore size distribution of as-prepared GdFeO$_3$ nanoparticles.
Dubinin–Astakhov (DA) plots of GdFeO$_3$ nanoparticles with the later displayed pore radius of 15 Å. As shown in Figure 5c, the BJH pore size distribution curve confirmed the predominance of mesopores of a radius of 18.3 Å for GdFeO$_3$ nanoparticles. The positive BET constant value from the BET surface area studies of GdFeO$_3$ was found to be as high as 3.34. This shows the high affinity of solid GdFeO$_3$ with the adsorbate (the N$_2$ molecules), which may lead to the high heat of adsorption.

The variation of dielectric constant ($\varepsilon$) and dielectric loss ($D$) of GdFeO$_3$ nanoparticles with the frequency and temperature is shown in Figure 6. The dielectric constant and dielectric loss were found to decrease with the increase in frequency (Figure 6a), which might be associated to the failure of electric dipoles to follow the alternating applied field, and this can be justified on the basis of Maxwell–Wagner interfacial polarization. The temperature dependence of the dielectric constant shows a slight increase below 300 °C; however, beyond which, a rapid increase of the dielectric constant with the temperature could be seen as shown in Figure 6b and was corroborated to the reports of other ferrites. This may be attributed to the fact that the temperature enhances the orientation of dipoles; however a low-frequency dielectric constant is strongly dependent due to the interfacial and dipolar polarizations. The accumulation of charges on the grain boundaries and more charge carriers get excitation from their trapping centers, which contribute to the polarization carrier and lead to the high dielectric constant. The dielectric loss decreases with the increase in frequency and achieve saturation in the higher frequency range. The high dielectric loss of GdFeO$_3$ nanoparticles originates from electron hopping and local structural distortions. With the increase in frequency, the electron hopping decreases and thus the dielectric loss decreases at a higher frequency range. The high dielectric constant and low dielectric loss of as-prepared nanoparticles could be attributed to large amounts of nano-size porosities with distinct grain and grain boundary structures. Dielectric properties increase at high temperatures, which is due to increase in thermally activated drift mobility of electric charges. The dc conductivity ($\sigma_{dc}$) is plotted as a function of reciprocal temperature (Figure 6c) and it well obeys the Arrhenius relation, $\sigma = \sigma_0 \exp \left( - \frac{E_{\text{cond}}}{kT} \right)$, where $\sigma_0$ is the pre-exponential term and $E_{\text{cond}}$ is abbreviated for the conduction activation energy. $E_{\text{cond}}$ was calculated from the slope of the straight line of log$\sigma_{dc}$ versus the 1000/$T$ plot and was found to be 0.28 eV, which shows that the grain boundary defects and ionic charges are the main carriers of thermal conductivity in as-prepared GdFeO$_3$ nanoparticles.

Temperature and magnetic field dependent dc magnetization measurements were carried out using a superconducting quantum interference device magnetometer under an external magnetic field of ±60 kOe at temperatures ranging from 5 to 300 K (Figure 7). The susceptibility of GdFeO$_3$ nanoparticles was studied as a function of temperature at a constant magnetic field of 1 kOe as shown in Figure 7a. The molar magnetic susceptibility ($\chi_m$) decreases with the increasing temperature; however, the susceptibility anomaly could be seen at 13.5 K, which is associated to the magnetic ordering in the nanoparticles. The result is found to be consistent with Curie–Weiss law in the paramagnetic region. According to the Curie–Weiss law, the temperature dependence of the inverse susceptibility ($\chi^{-1}$) was fitted with a positive extrapolated Weiss temperature ($\theta_p \approx 175$ K) as shown in Figure 7a, which implies the ferromagnetic interaction. The ferromagnetic hysteresis loop at 5 K of GdFeO$_3$ nanoparticles is shown in Figure 7b, which has a coercive field ($H_c$) of approximately ~446 Oe and saturation ($M_s$) and remanent ($M_r$) magnetizations of ~17.5 and 3.9 emu g$^{-1}$, respectively. The weak ferromagnetic behavior shown by GdFeO$_3$ may be due to the distortion from the ideal perovskite structure, resulting in the alignment of Fe$^{3+}$ ions slightly canted, which gives the small net magnetization. The total magnetization in the temperature range 5–300 K corresponds to the sum of iron containing sublattices and the paramagnetic gadolinium sub lattices. The enhanced magnetic properties were observed in this study as compared to the previous reports. Hence, we conclude that this method is able to prepare nanocrystalline orthoferrite powders with improved ferromagnetic characteristics. Polarization–electric field (P–E) hysteresis measurements of GdFeO$_3$ nanoparticles at different applied electric fields are

Figure 6. Variation of $\varepsilon$ and $D$ with the (a) frequency and (b) temperature and (c) showing the temperature dependence of dc conductivity of GdFeO$_3$ nanoparticles.
shown in Figure 8 at a 50 kHz frequency. The appearance of prominent hysteresis at room temperature with a remanent polarization ($P_r$) of $0.014 \mu C/cm^2$, saturation polarization ($P_s$) of $0.052 \mu C/cm^2$, and coercive field ($E_c$) of $-2.001 \text{kV/cm}$ is attributed to the ferroelectric characteristics in GdFeO$_3$ nanoparticles. The ferroelectric loop of GdFeO$_3$ nanoparticles is found to be dependent on the applied electric field, where as the applied field increases, the area of loop increases. Both the saturated and remanent ferroelectric polarizations increase by the increase in the applied electric field, and this observation could be associated to the potential application of as-prepared GdFeO$_3$ nanoparticles in nonvolatile multistate memory devices. The ferroelectric property may be elaborated by the canted antiferromagnetic ordering with two non-equivalent spin pairs of GdFeO$_3$, which led the room-temperature ferroelectric hysteresis to be comparable to that of the SmFeO$_3$-type compound.

4. CONCLUSIONS

Monophasic and nanocrystalline GdFeO$_3$ (95 nm) has been prepared with a high surface area ($231.5 \text{ m}^2 \text{ g}^{-1}$) using a metal–organic precursor route. The nanoparticles were further extensively investigated by means of HRTEM, SAED, and EDSX studies. The appearance of well-established hysteresis in electrical and magnetic properties with enhanced parameters sets its multiferroic characteristics. The room-temperature ferroelectricity was found for the first time, for which we believe it may have potential applications in multistate memory devices.

- **Figure 7.** (a) Temperature dependence of molar and inverse molar susceptibility and (b) M-H curve at 5 K of as-prepared GdFeO$_3$ nanoparticles. Inset a shows a closer look of magnetic ordering and inset of b is a magnified version of the M-H graph.

- **Figure 8.** (a) Full and (b) closer view of P-E hysteresis loops of GdFeO$_3$ nanoparticles at different electric fields and measured at 50 kHz.

- **AUTHOR INFORMATION**

**Corresponding Author**

Tokeer Ahmad – Nanochemistry Laboratory, Department of Chemistry, Jamia Millia Islamia, New Delhi 110025, India; orcid.org/0000-0002-7807-315X; Phone: 91-11-26981717; Email: tahmad3@jmi.ac.in

**Authors**

Irfan H. Lone – Nanochemistry Laboratory, Department of Chemistry, Jamia Millia Islamia, New Delhi 110025, India;

https://doi.org/10.1021/acsomega.2c02809

ACS Omega 2022, 7, 33908–33915
Department of Chemistry, University of Kashmir, Srinagar 190006 Jammu and Kashmir, India

Huma Khan – Nanochemistry Laboratory, Department of Chemistry, Jamia Millia Islamia, New Delhi 110025, India

Arvind K. Jain – School of Basic and Applied Sciences, Galgotias University, Greater Noida 201306 UP, India

Jahangeer Ahmed – Department of Chemistry, College of Science, King Saud University, Riyadh 11451, Saudi Arabia; orcid.org/0000-0003-2331-6406

Kandalam V. Ramanujachary – Department of Chemistry and Biochemistry, Rowan University, Glassboro, New Jersey 08028, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c02809

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
T.A. thanks the SERB-DST research scheme (no. EMR/2016/001668) and SPARC scheme (no. SPARC/2018-2019/P843/SL) of Ministry of Education, Govt. of India, for financial support. I.H.L. thank the UGC New Delhi for research fellowship. Authors thank Dr. V. R. Reddy (UGC-DAE Indore) for P-E measurements and also acknowledge the measurement support provided through the DST PURSE program at CIF, Jamia Millia Islamia and AIIMS, New Delhi, for electron microscopic studies. The authors extend their sincere appreciation to Researchers Supporting project number RSP-2021/391, King Saud University, Riyadh, Saudi Arabia.

REFERENCES
(1) Ahmad, T.; Farooq, U.; Phul, R. Fabrication and Photocatalytic Applications of Perovskite Materials with Special Emphasis on Alkali Metal Based Niobates and Tantalates. Ind. Eng. Chem. Res. 2018, 57, 18–41.
(2) Farooq, U.; Phul, R.; Alshehri, S. M.; Ahmed, J.; Ahmad, T. Electrocatlytic and Enhanced Photocatalytic Applications of Sodium Niobate Nanoparticles Developed by Citrate Precursor Route. Sci. Rep. 2019, 9, 4488.
(3) Farooq, U.; Ahmed, J.; Alshehri, S. M.; Ahmed, T. High Surface Area Sodium Tantalate Nanoparticles with Enhanced Photocatalytic and Electrical Properties Prepared through Polymeric Citrate Precursor Route. ACS Omega 2019, 4, 19408–19419.
(4) Mehtab, A.; Ahmed, J.; Alshehri, S. M.; Mao, Y.; Ahmad, T. Rare Earth Doped Metal Oxide Nanoparticles for Photocatalysis: A Perspective. Nanotechnology 2022, 33, 142001.
(5) Vaz, C. A. F.; Hoffmann, J.; Anh, C. H.; Ramesh, R. Magnetoelectric Coupling Effects in Multiferroic Complex Oxide Composite Structures. Adv. Mater. 2010, 22, 2900–2918.
(6) Huang, A.; Handoko, A. D.; Goh, G. K. L.; Pallathadika, P. K.; Shannigrahi, S. Hydrothermal Synthesis of (001) Epitaxial BiFeO3 Films on SrTiO3 Substrate. CrystEngComm 2010, 12, 3806–3814.
(7) Spaldin, N. A.; Fiebig, M. The Renaissance of Magnetoelectric Multiferroics. Science 2005, 309, 391–392.
(8) Ahmad, T.; Lone, I. H.; Ansari, S. G.; Ahmed, J.; Ahamed, T.; Alshehri, S. Multifunctional Properties and Applications of Yttrium Ferrite Nanoparticles Prepared by Citrate Precursor Route. Mater. Des. 2017, 126, 331–338.
(9) Morkoc, H.; Izumyska, N.; Alivov, Y. Oxides, Oxides, and More Oxides: High-κ Oxides, Ferroelectric, Ferromagnetics, and Multiferroics. Crit. Rev. Solid State Mater. Sci. 2009, 34, 89–179.
(10) Lone, I. H.; Ahmed, J.; Ahmad, T. Reverse Micellar Synthesis, Characterization, Magnetic and Ferroelectric Properties of YFeO3 Nanoparticles. Mater. Today: Pro. 2018, 5, 15303–15310.
(11) Tokunaga, Y.; Iiguchi, S.; Arima, T.; Tokura, Y. Magnetic-Field-Induced Ferroelectric State in DyFeO3. Phys. Rev. Lett. 2008, 101, 097205–097204.
(12) Khatoon, S.; Ahmad, T. Synthesis, Optical and Magnetic Properties of Ni-Doped ZnO Nanoparticles. J. Mater. Sci. Eng. B 2012, 2, 325–333.
(13) Jain, S. K.; Fazil, M.; Pandit, N. A.; Ali, S. A.; Naaz, F.; Khan, H.; Mehtab, A.; Ahmed, J.; Ahmad, T. Modified, Solvothermally Derived Cr-doped SnO2 Nanostructures for Enhanced Photocatalytic and Electrochemical Water Splitting Applications. ACS Omega 2022, 7, 14138–14147.
(14) Jain, S. K.; Fazil, M.; Naaz, F.; Pandit, N. A.; Ahmad, J.; Alshehri, S. M.; Mao, Y.; Ahmad, T. Silver doped SnO2 Nanostructures for Photocatalytic Water Splitting and Catalytic Nitrogen Reduction. New J. Chem. 2022, 46, 2846–2857.
(15) Ahmad, T.; Ganguli, A. K. Synthesis of Nanometer-Sized Particles of Barium Orthotitanate Prepared through a Modified Reverse Micellar Route: Structural Characterization, Phase Stability and Dielectric Properties. J. Mater. Res. 2004, 19, 2905–2912.
(16) Ahmad, T.; Ganguly, A.; Ahmad, J.; Ganguli, A. K.; Al-Hartomy, O. A. Nanorods of Transition Metal Oxalates: A Versatile Route to the Oxide Nanoparticles. Arab. J. Chem. 2011, 4, 125–134.
(17) Ahmad, T.; Lone, I. H. Development of Multifunctional Lutetium Ferrite Nanoparticles: Structural Characterization and Properties. Mater. Chem. Phys. 2017, 202, 50–55.
(18) Ahmad, T.; Wani, I. A.; Al-Hartomy, O. A.; Al-Shihri, A. S.; Kalam, A. Low Temperature Chemical Synthesis and Comparative Studies of Silver Oxide Nanoparticles. J. Mol. Struct. 2015, 1084, 9–15.
(19) Li, L.; Wang, X.; Lan, Y.; Gu, W.; Zhang, S. Synthesis, Photocatalytic and Electrocatlytic Activities of Wormlike GdFeO3 Nanoparticles by a Glycol-Assisted Sol–Gel Process. Ind. Eng. Chem. Res. 2013, 52, 9130–9136.
(20) Zhang, Y.; Zheng, A.; Yang, X.; He, H.; Fan, Y.; Yao, C. Cubic GdFeO3 Particle by a Simple Hydrothermal Synthesis Route and its Photoluminescence and Magnetic Properties. CrystEngComm 2012, 14, 8432–8439.
(21) Bedekar, V.; Jayakumar, O. D.; Manjanna, J.; Tyagi, A. K. Synthesis and Magnetic Studies of Nano-Crystalline GdFeO3. Mater. Lett. 2008, 62, 3793–3795.
(22) Soderling, F.; Fortin, M. A.; Petoral, R. M.; Klasson, A.; Veres, T.; Engstrom, M.; Uvdal, K.; Kall, P. Colloidal Synthesis and Characterization of Ultra-small Perovskite GdFeO3 Nanocrystals. Nanotechnology 2008, 19, No. 085608.
(23) Ahmad, T.; Lone, I. H.; Ubaibullah, M. Structural Characterization and Multiferroic Properties of Hexagonal Nano-sized YMO3 Developed by Low Temperature Precursor Route. RSC Adv. 2015, 5, 58065–58071.
(24) Ahmad, T.; Lone, I. H. Citrate Precursor Synthesis and Multifunctional Properties of YCrO3 Nanoparticles. New J. Chem. 2016, 40, 3216–3224.
(25) Prakash, B. J.; Rudranadevi, B. H.; Buddhudu, S. Analysis of Ferroelectric, Dielectric and Magnetic Properties of GdFeO3 Nanoparticles. Ferroelectr., Lett. Sect. 2014, 41, 110–122.
(26) Tokunaga, Y.; Furukawa, N.; Sakai, H.; Taguchi, Y.; Arima, T.; Tokura, Y. Composite Domain Walls in a Multiferroic Perovskite Ferrite. Nat. Mater. 2009, 8, 558–562.
(27) Cullity, B.D.; Stock, S. Elements of X-Ray Diffraction, Prentice Hall. Upper Saddle River, NJ, 2001, 388.
(28) Nakamato, K. Infrared and Ramen spectra of Inorganic and Coordination Compound. 4th Ed., Wiley, New York, USA, 1986, 148.
(29) Bellamy, L. J. Infrared Spectra of Complex Molecules. 2nd Ed., London, England, 1958.
(30) Predoi, D.; Crisan, O.; Jitianu, A.; Valsangiacomo, M. C.; Raileanu, M.; Crisan, M.; Zaharescu, M. Iron Oxide in a Silica Matrix Prepared by the Sol–Gel Method. Thin Solid Films 2007, 515, 6319–6323.
(31) Gao, Q.; Chen, F. H.; Zhang, J. L.; Hong, G. Y.; Ni, J. Z.; Wei, X.; Wang, D. J. The Study of Novel Fe3O4@γ-Fe2O3 Core/Shell
Nanomaterials with Improved Properties. J. Magn. Magn. Mater. 2009, 321, 1052–1057.
(32) Brunauer, S.; Teller, D. Theory of the Vander Waals Adsorption of Gases. J. Am. Chem. Soc. 1940, 62, 1723–1732.
(33) Xu, H.; Hu, X.; Zhang, L. Generalized Low-Temperature Synthesis of Nanocrystalline Rare-Earth Orthoferrites LnFeO₃ (Ln=La, Pr, Nd, Sm, Eu, Gd). Cryst. Growth Des. 2008, 8, 2061–2065.
(34) Wagner, K. W. Dissipation of Energy Under AC. Ann. Phys. 1913, 40, 817–855.
(35) Koops, C. G. On the Dispersion of Resistivity and Dielectric Constant of Some Semiconductors at Audio Frequencies. Phys. Rev. 1951, 83, 121–124.
(36) Shaik, A. M.; Bellad, S. S.; Chougule, B. K. Temperature and Frequency-Dependent Dielectric Properties of Zn Substituted Li–Mg Ferrites. J. Magn. Magn. Mater. 1999, 195, 384–390.
(37) Vandana, C. S.; Rudramadevi, B. H. Structural, Magnetic and Dielectric properties of Cobalt doped GdFeO₃ Orthoferrites. Mater. Res. Express 2019, 6, 126126.
(38) Soderlind, F.; Selegard, L.; Nordblad, P.; Uvdal, K.; Käll, P. O. Sol–Gel Synthesis and Characterization of Polycrystalline GdFeO₃ and Gd₃Fe₅O₁₂ Thin Films. J. Sol-Gel Sci. Technol. 2009, 49, 253–259.
(39) Bozorth, R. M.; Williams, H. J.; Walsh, D. E. Magnetic Properties of some Orthoferrites and Cyanides at Low Temperatures. Phys. Rev. 1956, 103, 572–578.
(40) Lee, J.; Jeong, Y. K.; Park, J. H.; Oak, M.; Jang, H. M.; Son, J. Y.; Scott, J. F. Spin-Canting-Induced Improper Ferroelectricity and Spontaneous Magnetization Reversal in SmFeO₃. Phys. Rev. Lett. 2011, 107, 117201–117205.
(41) Ning, S.; Kumar, A.; Klyukin, K.; Cho, E.; Kim, J. H.; Su, T.; Kim, H. S.; LeBeau, J. M.; Yildiz, B.; Ross, C. A. An Antisite Defect Mechanism for Room Temperature Ferroelectricity in Orthoferrites. Nat. Commun. 2021, 12, 1–7.
(42) Prellier, W.; Singh, M. P.; Murugavel, P. The Single-phase Multiferroic Oxides: from Bulk to Thin Film. J. Phys.: Condens. Matter 2005, 17, R803–R832.
(43) Choi, E. M.; Maity, T.; Kursumovic, A.; Lu, P.; Bi, Z.; Yu, S.; Park, Y.; Zhu, B.; Wu, R.; Gopalan, V.; Wang, H.; MacManus-Driscoll, J. L. Nanoengineering Room Temperature Ferroelectricity into Orthorhombic SmMnO₃ films. Nat. Commun. 2020, 11, 1–9.