Chelating Agents Assisted Rapid Synthesis of High Purity BiFeO₃: Remarkable Optical, Electrical, and Magnetic Characteristics

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Abstract
In this study, we presented two reliable methods, the sol–gel and autocombustion, to synthesis a high purity BiFeO₃ single phase with low calcination time using glycine as chelating agent. The glycine-autocombustion method produced a high purity BiFeO₃ phase using either low or high concentrations of the reactants (Bi(NO₃)₃ + Fe(NO₃)₃), while the glycine-sol–gel method delivered a high purity BiFeO₃ phase using low concentrations of reactants. In the case of using tartaric acid and urea as chelating agents, mixtures of BiFeO₃ and Bi₂₅FeO₄₀ phases were formed. The morphology, size, and porosity of the particles were obviously changed by varying the synthesis method and chelating agents. The high purity BiFeO₃ samples exhibit a visible light band gap of 2.05 eV with long absorption tail extending to the infrared region, suggesting the suitability of the synthesized powders in the solar photocatalytic applications. A weak hysteresis ferromagnetic loop was observed for BiFeO₃ (glycine method) and BiFeO₃/Bi₂₅FeO₄₀ (urea method) with large contribution from the paramagnetic behavior. On contrast, robust ferromagnetic loops were found for BiFeO₃/Bi₂₅FeO₄₀ sample synthesized by tartaric acid with saturation magnetization reaching to 2.5 emu/g. Remarkably, the pure single phase BiFeO₃ powders synthesized by sol–gel and auto-combustion methods using glycine possess room temperature dielectric constant values of 622 and 845 respectively at a frequency of 42 Hz. In the case of BiFeO₃ powders prepared by using tartaric acid, the dielectric constant exhibits values of 401 and 1118 for sol–gel and auto-combustion assisted samples, at the same frequency, respectively. At low frequency, the values of the real part of the complex permittivity tend to be zero which confirms a negligibly small contribution of the electrode effect.

Keywords Pure BiFeO₃ · Single phase · Sol–gel · Autocombustion · Glycine · Tartaric acid · Urea

1 Introduction
Developing the magnetoelectric properties of multiferroic BiFeO₃ is one of the reliable ways to commercialize spin-based devices like memory chips [1–3]. Magnetic and ferroelectric random access memories (M-RAM, Fe-RAM) are new separated classes of commercial memory devices which operate based on ferromagnetic and ferroelectric properties, respectively [4–6]. Although each of the magnetic and the ferroelectric random access memories has separated advanced properties, they, unfortunately, have some defects [4–6]. Combined of M-RAM and Fe-RAM in a single memory is a world challenge issue, leading to innovative and ultimate memory devices [4–6]. One of the basic requirements for attaining this step is to produce materials that can pair the advanced room temperature ferromagnetic-ferroelectric properties in a single structure [4–6]. For this purpose, BiFeO₃ is a strong candidate for combining these properties at room temperature [4–6]. Multiferroic BiFeO₃ has ferroelectric properties under Curie temperature (TC) of ~830 °C and G-type anti-ferromagnetic order below Néel temperature (TN) of ~370 °C [7–9]. In the recent decade, BiFeO₃ is considered as one of the top-investigated single-phase multiferroic materials [4]. These condensed investigations aimed to overcome the synthesis obstacles and enhance the BiFeO₃ properties to meet the spin-based application requirements [4]. One of the basic obstacles related to BiFeO₃ is to obtain a pure single-phase structure without the generation of impurities.
such as Bi$_2$Fe$_3$O$_9$, Bi$_2$O$_3$, and Bi$_{25}$FeO$_{39}$ [10–12]. Synthesizing of bulk or nanoparticle powders or thin-film of pure single phase BiFeO$_3$ is a challenging task [13]. Scientists investigated various physical and chemical pathways to achieve this purpose [14]. Numerous research attempts were employed to develop efficient, simple, and inexpensive chemical methods to synthesize a high purity BiFeO$_3$ [15]. Chien et al. reported the influences of numerous synthesis routes on photoelectrochemical and photocatalytic characteristics of single-phase perovskite BiFeO$_3$ [16]. The authors found the formation of single phase BiFeO$_3$ structure with remarkable magnetic and sunlight photocatalytic properties. Other studies on the synthesis and characterization of pure single phase BiFeO$_3$ for biological and wastewater treatment were carried out by different authors [17–19]. Sol–gel and autocombustion are two easy synthesis methods with low requirements, and preparation of BiFeO$_3$ by both techniques is favorable due to low-cost production. The sol–gel and auto-combustion techniques offer several advantages including the homogenous mixing of metal cations of the required composition at a molecular scale, high crystallinity and purity of the products, and small and narrow particle size distribution. Also, stoichiometry controlling and the introduction of dopants into the final product are convenient. Furthermore, the two techniques involve simple preparation processes, low consumption of external energy, and no complicated handling is involved. Ortiz-Quíñonez et al. [20] reported a successful synthesis of pure BiFeO$_3$ nanoparticles using a glycine-assisted route. However, the authors stated that the formation of the pure phase of BiFeO$_3$ needed calcination time for the as-synthesized powder for a long period (1 h at 350 °C, 6 h at 500 °C, and 1 h at 600 °C) [20]. In the present study, the authors successfully and powerfully reduced the calcination time for synthesized single BiFeO$_3$ powder (glycine route) to only 2 h to attain a high purity BiFeO$_3$ (1 h at 500 °C and 1 h at 600 °C). For saving time and energy, the total calcination time was reduced from 8 [20] to 2 h only in the present work. Besides, the authors prepared a single phase BiFeO$_3$ using low and high reactant concentrations for large amount production. Herein, we study the synthesis of pure BiFeO$_3$ phase by two methods including sol–gel and autocombustion using three chelating agents (glycine, tartaric acid, and urea). The structure, morphology, optical, magnetic, and electrical properties of the synthesized samples were investigated and discussed. The obtained results show that glycine-autocombustion method produced a high purity BiFeO$_3$ phase using either low or high concentrations of the reactants (Bi(NO$_3$)$_3$ + Fe(NO$_3$)$_3$), while the glycine-sol–gel method delivered a high purity BiFeO$_3$ phase using low concentrations of reactants. In the case of sol–gel and autocombustion using tartaric acid and urea as chelating agents, mixed phases of BiFeO$_3$ and Bi$_{25}$FeO$_{40}$ were formed.

2 Experimental

2.1 Chemicals

The reagents used in the synthesis were (Fe(NO$_3$)$_3$·9H$_2$O, J.T. Baker, 99.6%), (Bi(NO$_3$)$_3$·5H$_2$O, Aldrich, >98%), glycine (H$_2$NCH$_2$COOH, Aldrich, 99%), urea, tartaric acid (CH$_3$N$_2$O, C$_2$H$_6$O$_6$, Alfa Aesar, 99%), and diluted nitric acid (HNO$_3$, J.T. Baker, 70%). Figure 1 shows a diagram of the synthesis methods and the label of each sample.

2.2 Synthesis of Bismuth Ferrite Using Sol–Gel Technique

Ferric nitrate (Fe(NO$_3$)$_3$·9H$_2$O, 99%) and bismuth nitrate (Bi(NO$_3$)$_3$·5H$_2$O, 98%) were used as the metal salt precursors while glycine, urea, and tartaric acid were used as chelating agents and as fuels. To prepare BiFeO$_3$ using glycine, 0.004 mol of Bi(NO$_3$)$_3$·5H$_2$O and 0.004 mol of Fe(NO$_3$)$_3$·9H$_2$O were dissolved in 10 mL of 5 M HNO$_3$. This mixture was stirred for 10 min then added drop-wise to 8 mmol a stirred 250-mL aqueous solution of the glycine chelating agent. The obtained solution was then vaporized at 70–80 °C under continuous magnetic stirring for 6 h until a xerogel was formed. The obtained xerogel was slightly ground and calcined in air atmosphere at 500 °C for 1 h, then, further calcined at 600 °C for another 1 h, and naturally cooled to room temperature. The synthesized BiFeO$_3$ sample was coded G1. The same procedures were repeated to prepare BiFeO$_3$ using the other two chelating agents, urea and tartaric acid, and were coded U1 and T1 respectively. The same procedures were also followed to synthesize BiFeO$_3$ using higher concentrations of the starting reagents: 0.008 mol of Bi(NO$_3$)$_3$·5H$_2$O, 0.008 mol of Fe(NO$_3$)$_3$·9H$_2$O, and 0.016 mol of glycine; the synthesized material was coded G1H.

2.3 Synthesis of Bismuth Ferrite Using the Autocombustion Technique

Ferric nitrate and bismuth nitrate were used as the metal salt precursors. BiFeO$_3$ nanoparticles were prepared by combustion method using three separate different organic fuels: glycine, urea, and tartaric acid. The organic materials acted as organic fuels and run as a platform for the redox reactions to arise between the reactants during the process of combustion. 0.008 mol of Bi(NO$_3$)$_3$·5H$_2$O, 0.008 mol of Fe(NO$_3$)$_3$·9H$_2$O, and 0.016 mol of organic fuel were mixed and put on a hotplate at 80 °C. Slurry
mixtures were formed when the hygroscopic metal nitrates were mixed with the carboxylic organic fuel. The high oxygen content of the reactants and the role of the metal nitrates as oxidants make the combustion process occurred efficiently. The mixture was further heated for 10 min to initiate and achieve dehydration and the combustion process. The obtained brown powders were heated in a furnace at 500 °C in the air for 1 h, and then it was further calcined at 600 °C for another 1 h. The obtained powder samples using glycine, urea, and tartaric acid were coded G2, U2, and T2 respectively.

2.4 Characterization and Measurements

The phase structure, lattice constant, and crystallite size of the synthesized BiFeO₃ samples were estimated via X-ray diffraction analysis (XRD, PANalytical X-ray diffraction equipment model X’Pert PRO). The optical characteristics and the band gap of the synthesized BiFeO₃ samples were determined by using a double beam spectrophotometer-JASCO (model V-570 UV–Vis-NIR). The morphological structure of BiFeO₃ powders was determined by using a scanning electron microscope (SEM, model Quanta 250 FEG) attached with EDX unit. The magnetic characteristics of BiFeO₃ samples at room temperature were measured by using a vibrating sample magnetometer (VSM, LakeShore Model 7410). Electrical conductivity and dielectric constant properties of the prepared pellets were carried out by using LCR meter (Hitester, model Hioki 3532–50, made in Japan).

3 Results and Discussion

3.1 Phase Purity: XRD and Rietveld Refinement Analysis

Figure 2 demonstrates the X-ray diffraction pattern of BiFeO₃ powders synthesized by sol–gel and auto-combustion methods in the presence of glycine, tartaric acid, and urea. Interestingly, the synthesized powders through the sol–gel method (low concentrations of reactants, Fig. 2b) and auto-combustion (high concentrations of reactants, Fig. 2c) exhibited only the crystallographic planes of BiFeO₃ without any impurities, indicating high purity phase formation. In this pattern, all the XRD planes of (012), (104), (110), (113), (006), (202), (024), (116), (122), (018), (214), (300), (208), (220), (036), (131), (312), (128), and (134) are indexed to rhombohedral structure of BiFeO₃ without any impurities, indicating high purity phase formation. In this pattern, all the XRD planes of (012), (104), (110), (113), (006), (202), (024), (116), (122), (018), (214), (300), (208), (220), (036), (131), (312), (128), and (134) are indexed to rhombohedral structure of BiFeO₃ structure (JCPDS No. 86–1518, R3c space group). The XRD pattern of BiFeO₃ powder synthesized by sol–gel using high concentrations of reactants in presence of glycine (Fig. 2a) showed a very small impurity peak located at 2θ = 27.8° which is probably related to the presence of small impurity of Bi₁₂₅Fe₂₄O₄₀ phase along with the basic BiFeO₃ structure. These results clearly show that two reliable methods (glycine-sol–gel and glycine-auto-combustion) can lead to high purity phase of BiFeO₃ (Fig. 2a and c). Ortiz-Quinonez et al. [20] reported a successful synthesis of pure BiFeO₃ nanoparticles using a glycine-assisted route. However, the authors stated that the formation of the pure phase of BiFeO₃ needed a calcination for the as-synthesized powder for a long period (1 h at 350 °C, 6 h at 500 °C, and 1 h at 600 °C) [20]. In the present study,
Fig. 2 XRD pattern of BiFeO₃ synthesized using (a) glycine-sol–gel (high reactants concentration), (b) glycine-sol–gel (low reactants concentration), (c) glycine-autocombustion, (d) tartaric-sol–gel, (e) tartaric-autocombustion, (f) urea-sol–gel, and (g) urea-autocombustion

The synthesized powders need only 2 h to attain a high purity BiFeO₃ (1 h at 500 °C and another 1 h at 600 °C). For saving time and energy, the total calcination time was reduced from 8 [20] to 2 h only in the present work. The high flame temperature exceeds 1200 °C of glycine which results in an extremely violent combustion reaction [21]. Furthermore, the swift release of massive amounts of heat and gases may be improved the growth of the crystals and the formation of pure phase. Concerning BiFeO₃ powders synthesized by sol–gel and auto-combustion methods in the presence of tartaric acid, the XRD patterns show the formation of BiFeO₃ with high content of Bi₂FeO₄₀ phase reached to 44% and 38%, respectively (Fig. 2d and e). In the same context, the XRD patterns of BiFeO₃ powders synthesized by sol–gel and auto-combustion methods in the presence of urea also revealed the existence of Bi₂FeO₄₀ phase with contents of 44% and 24% (Fig. 2f and g), respectively. It can be noticed that the using of the auto-combustion method yield less content of impurities compared to the sol–gel method. The formation of such bismuth oxide impurity phase (Bi₂FeO₄₀) could be explained by the tendency of hydrated Bi(III) cations to undergo polycondensation process and forming intramolecular polycondensation species. This polycondensation process could lead to the formation of poly-nuclear cationic species: [Bi₆(μ₃-O)₆(μ₃-OH)₆]⁶⁺, [Bi₅(OH)₄]⁶⁺, and [Bi₉O₅(OH)₁₅]⁶⁺ [22, 23], which upon the thermal treatment could decompose into the α- and β-Bi₂O₃ phases. Thus, the formation of bismuth oxides (α and/or β) impurities during the synthesis of BiFeO₃ could be related to the presence of these poly-nuclear moieties which largely depends on the availability of hydrated Bi(III) cations. This suggestion is further supported by our findings. In the case of glycine-assisted samples, both the combustion and the sol–gel route using a low molar concentration of the reactants led to the formation of pure BiFeO₃ with no secondary phase products. This could be attributed to no presence or low number of hydrated Bi(III) cations in the combustion synthesis and the sol–gel synthesis (low concentration of reactants), respectively. On the other hand, using high concentrations of the reactants in the synthesis process resulted in the formation of more hydrated Bi(III) cations that are so enough to polycondense and produce undesirable secondary poly-nuclear cationic species. The presence of impurities in the case of BiFeO₃ synthesized by using tartaric acid or urea, either via sol–gel or autocombustion routs, could be further explained based on the affinity of urea and tartaric acid anions to coordinate with Bi³⁺ and Fe³⁺. In contrary to glycinate ions which possess equivalent affinity constant for both Fe³⁺ and Bi³⁺ (log K = 10) [24], both the urea and tartrate anions have different coordination affinities for Bi³⁺ and Fe³⁺ [24, 25]. Consequently, the dispersion of bismuth and ferric cations in polymeric chains of the precursor solutions is not homogenous and results in creating separate α- and/or β-Bi₂O₃ and Bi₂FeO₄ byproducts. As a result, glycine as a chelating agent under different synthesis methods induces a pure phase formation compared to tartaric...
acid or urea. The least square Rietveld refinement analysis was carried out by using FullProf software to investigate the phase purity as well as to obtain the lattice parameter, unit cell volume, space group, and crystal system as shown in Fig. 3 and tabulated in Table 1. The refinement of the BiFeO₃ powders synthesized using glycine-assisted route following the standard cards JPCDS No. 86–1518 revealed that both samples possess rhombohedral structure of the BiFeO₃. The crystallite size of the prepared BiFeO₃ samples was found by using Williamson-Hall equation:

\[ \beta \cos \theta = (K \lambda / D) + 4 \epsilon \sin \theta \]

By plotting \( \beta \cos \theta \) as a function of \( 4 \sin \theta \), the crystallite size was found from the intercept (\( D = K \lambda / \text{intercept} \)) as shown in Fig. 4 and Table 1. The refinement of the BiFeO₃ powders synthesized using glycine-assisted route following the standard cards JPCDS No. 86–1518 revealed that both samples possess rhombohedral structure of the BiFeO₃. The crystallite size was 60.5 nm, 57.8 nm, and 46 nm for G1, G2, and G1H samples, respectively. The crystallite size is significantly influenced by the type of chelating (Table 1). The average crystallite size was 44.5, 39.7, 45.6, and 47.7 nm for T1, T2, U1, and U2 samples, respectively. The observed low crystallite size of the tartaric-assisted sample prepared using auto-combustion method (T2) compared to glycine- and urea-assisted samples could be related to the combustion process occurs in different ways depending on the fuel/chelating agent. Tartaric acid has a relatively lower flame temperature (505 °C) compared to glycine and urea that have flame temperatures of 1200 °C and 600 °C respectively [21]. Subsequently, in the case of tartaric-assisted auto-combustion, the rate of the combustion process is slower and the process occurs over a longer period and permits the cations to arrange more slowly within the spinel lattice. On the other hand, the more rapid release of a large volume of heat and gases through the combustion course in the case of glycine and urea favors crystallite growth. Also, the energy released from the reaction between ammonia (released from glycine or urea decomposition) and nitrogen oxides (NOₓ) from the decomposition of metal nitrates is much higher than that released from the reaction between oxygen and hydrocarbonaceous fragments in the

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**Table 1** The crystallite size \( D \) (nm), lattice parameters \( (a, c) \), unit cell volume \( V \), band gap \( (eV) \), coercivity \( (Hc) \), and retentivity \( (R) \) of BiFeO₃ samples

| Samples   | \( D \) (nm) | \( a \) (Å) | \( c \) (Å) | \( V \) (Å³) | Band gap (eV) | \( Hc \) (Oe) | \( R \) (emu/g) |
|-----------|--------------|-------------|-------------|--------------|--------------|--------------|--------------|
| BiFeO₃-G1 | 60.5         | 5.5790      | 13.8698     | 373.8639     | 2.05         | 1.53         | 63.3         | 0.0011       |
| BiFeO₃-G2 | 57.8         | 5.5777      | 13.8656     | 373.5765     | 2.05         | 1.46         | 108.7        | 0.0013       |
| BiFeO₃-T1 | 44.5         | 5.5766      | 13.8625     | 373.3471     | 2.25         | 1.57         | 188.7        | 0.67         |
| BiFeO₃-T2 | 39.7         | 5.5736      | 13.8580     | 373.8230     | 2.19         | 1.57         | 57.4         | 0.0056       |
| BiFeO₃-U1 | 45.6         | 5.5757      | 13.8660     | 373.3261     | 2.17         | 1.56         | 45           | 0.00090      |
| BiFeO₃-U2 | 47.7         | 5.5765      | 13.8621     | 373.3229     | 2.14         | 1.55         | 34.3         | 0.00065      |
case of tartaric acid [26] which also provides preferability for growth of crystallite. Figure 5 shows the polyhedral and packing structure of BiFeO₃ synthesized by the glycine-assisted method.

### 3.2 Morphological Analysis

The SEM micrographs of the synthesized BiFeO₃ powders using sol–gel and autocombustion methods in the presence of glycine, tartaric acid, and urea are shown in Fig. 6. The image of the BiFeO₃ powder obtained by sol–gel method using glycine shows large irregular connected particles with clear boundary between them (Fig. 6a). The BiFeO₃ powder synthesized by autocombustion using glycine exhibits irregular connected particles shape but with a smaller grain size compared to the sol–gel method (Fig. 6b). The two images reveal the presence of remarkable porous networks. The formation of such large pores is highly connected to the vast and fast release of combustion gases due to using of glycine as a chelating agent. Several reports showed that the combustion course of glycine and metal nitrates results in increasing the flame temperature to reach to 1100–1450 °C [20, 27, 28]. Such abruptly raising, in a very short time, leads to a sudden release of several gases such as CO, CO₂, NH₃, NO, NO₂, and H₂O; the coupling effect of such highly released energy and gases leads to the formation of such microporous structures. In the case of BiFeO₃ powders prepared by using tartaric acid, the sol–gel method yields small
size particles with non-uniform shapes related to BiFeO₃ and Bi₂₅FeO₄₀ phases (Fig. 6c) while the autocombustion method produces smaller grains (Fig. 6d). The micrograph of the BiFeO₃ prepared by sol–gel in presence of urea (Fig. 6e) has a similar morphology to that prepared by tartaric acid (Fig. 6c) while the BiFeO₃ powder synthesized by the autocombustion in presence of urea (Fig. 6f) revealed the formation of elongated particles like rods (major) besides non-uniform or irregular particles (minor). The EDX spectra of the synthesized BiFeO₃ powders are shown in Fig. 7. The presence of the peaks which related only to the Bi, Fe, and O elements in the EDX spectra confirms the high purity for the synthesized powders. The Bi/Fe ratio was determined by the SEM–EDX technique. These ratios were measured in two different zones of an area of about 1 μm² each. In the case of the glycine-assisted sample G1, the experimental atomic percentages of Bi, Fe, and O in BiFeO₃ are about 19.26, 20.35, and 60.4 respectively. These percentage values are very close to the theoretical values of BiFeO₃ (20, 20, and 60).

### 3.3 Optical Properties

Figure 8 depicts the diffuse reflectance spectra for the different synthesized BiFeO₃ powders within wavelengths of 200–2000 nm. Pure BiFeO₃ powders prepared using glycine exhibit the lowest intensity of diffuse reflectance in the visible and near infrared spectrum, indicating high absorption ability. These nanostructures powders are the purest and the most crystalline among all the synthesized samples, so the highest crystalline order at the inter-particles contact could be responsible for such high absorption property. In contrast, the powders obtained by using tartaric acid have the highest diffuse reflectance intensity while the synthesized powders by urea have moderate intensity. A clear red shift in the absorption edge was seen for BiFeO₃ prepared by glycine compared to other samples (Fig. 8). The precise band gap value of the synthesized BiFeO₃ powders was measured using the Kubelka–Munk function as shown in Fig. 9. Wang et al. showed that the strong hybridization of Fe-3d, Bi-6p, and O-2p states form the top of the valence band.
while Fe-3d states form the bottom of the conduction band [29]. The synthesized pure BiFeO3 particles (glycine as a chelating agent) showed a visible band gap of 2.05 eV with strong long tails extending from the visible to the infrared region which is an important factor in the photocatalytic applications. The synthesized powders by using sol–gel and autocombustion methods in the presence of urea possess band gap energy of 2.17 eV and 2.14 eV, respectively. All samples showed an additional band gap energies related to indirect inter-band transition; these bands were detected in the range of 1.46–1.57 eV using the Tauc’s plot fit in the long tail-like part of the absorption spectrum, around 600 nm. Several reports demonstrated the attendance of both direct and indirect band gaps, with different energy values in BiFeO3. In these cases, the indirect transitions are situated about 0.4–1.0 eV lower than that the direct transitions [20, 30, 31]. These reports as well as our findings are consistent with some theoretical studies that predicted the presence of both indirect and direct gaps in BiFeO3 structure, and the indirect band gap is of lower energy than the direct ones [29, 32]. The calculated direct and indirect band gap values for the BiFeO3 synthesized using glycine, urea, and tartaric acid are depicted in Table 1.

### 3.4 Room Temperature Ferromagnetism

Figure 10 shows the room temperature ferromagnetic properties of BiFeO3 synthesized by sol–gel and autocombustion methods in the presence of glycine and urea. All samples synthesized using glycine and urea exhibit small ferromagnetic hysteresis shapes at the low applied magnetic field with paramagnetic contribution at the high magnetic field. The ferro-hysteresis behavior of the samples was established based on the presence of positive coercivity and retentivity as reported in Table 1. The magnetic properties of the BiFeO3 powders obtained by sol–gel and autocombustion from the tartaric-assisted method are shown in Fig. 11. BiFeO3 samples formed by tartaric sol–gel and autocombustion methods revealed complete room temperature ferromagnetism with saturation magnetization of 2.4 emu/g and 1.01 emu/g and coercivity (Hc) of 188.7 Oe and 57.4 Oe, respectively. Interestingly, impurities like Bi2Fe4O9 and Bi24FeO40 are paramagnetic, which do not contribute to the magnetic properties in our BiFeO3 ceramic samples. These results confirm the hypothesis that the observed ferromagnetism can be related to BiFeO3 in the powders. This behavior is consistent with previous
reports of nanosized BiFeO₃ particles with a mean diameter below 62 nm, whose enhanced ferromagnetism can be ascribed to the effect of breaking periodicity (62 nm) of the spin cycloid structure which is characteristic of bulk BiFeO₃ [33–35]. Thus, the existence of apparent remanence and coercivity in the tartaric-assisted samples could be explained in terms of disturbance in the period of the spin cycloid. The particle size of BiFeO₃ is lesser than the period of the incommensurate spin cycloid; thus, the antiferromagnetic order is interrupted and the spiral of BiFeO₃ is partially destroyed. At the nano-size scale, the surface to volume ratio is large; thus, the surface generated uncompensated spins highly participate in the net magnetization. Wang et al. [36] have synthesized BiFeO₃ nanoparticles of 60–90 nm using tartaric acid with saturation magnetization (M) value of 0.34 emu/g at 15,000 Oe which is lower than the measured value in the present work. Although BiFeO₃ synthesized from urea contain the same phases as that obtained from tartaric acid, it demonstrated different magnetism behaviors. This ruled out that the Bi₂Fe₄O₉ and Bi₃FeO₄₀ impurities are responsible for room temperature ferromagnetism. The difference in magnetic behavior may be assigned to the differences in morphology and size of the particles produced using tartaric and urea. For glycine-assisted samples, a clear ferro/antiferromagnetic behavior is established in the corresponding M–H curve (Fig. 10). The observed magnetization value at 20,000 Oe was 0.136 emu g⁻¹ which nearly seventy times lower than that obtained using tartaric acid (2.4 emu/g). This result is consistent with XRD results and demonstrated that no undesirable secondary magnetic phases were detected. In addition, the SEM images of glycine-assisted nanocrystals demonstrated the formation of a highly porous BiFeO₃ network (Fig. 6) which may induce a fractional assembly and spin cycloid discontinuation. This could result in magnetic moment dilution and consequently a significant reduction in magnetization.

### 3.5 Dielectric Properties

Figure 12 illustrates the change of the dielectric constant ($\varepsilon'$) with frequency for BiFeO₃ nanopowders synthesized by sol–gel and auto combustion methods using different chelating agents at room temperature. All the synthesized BiFeO₃ powders display a decreasing trend in the dielectric constant with increasing the applied frequency in similar performance with that found for metal oxides as explained by Maxwell–Wagner model [37, 38]. Remarkably, pure single phase BiFeO₃ powders synthesized by sol–gel and auto combustion methods using glycine possess room temperature dielectric constant values of 622 and 845 at a frequency of 42 Hz, respectively. In the case of BiFeO₃ powders prepared using tartaric acid, the dielectric constant exhibits values of 401 and 1118 at the same frequency,
respectively. The obtained BiFeO₃ samples by the urea method reveal dielectric constant values of 655 and 1587. At low frequency, all types of polarization can contribute and the quick increase in the dielectric constant is essentially due to the space charge and dielectric polarization. At low frequencies, the high dielectric constant values of the
synthesized BiFeO₃ powders can be attributed to the influence of the relaxation polarization including space charge or orientational and also to the deformational polarization [37, 38]. It is recognized that the relaxation polarization is mainly linked to the interfacial or orientational effects which is related to the electronic and ionic polarization.

Fig. 11 Room temperature magnetism of the synthesized BiFeO₃ by using tartaric methods (T1, T2)

![Figure 11](image1)

Fig. 12 Variation of dielectric constant with frequency of BiFeO₃ prepared by using sol–gel and auto combustion using different chelating agents

![Figure 12](image2)
while the deformational polarization is related to the displacement of electrons or ions. With increasing the applied field, a decrease in the orientational polarization takes place, and accordingly the molecular dipoles require much time to change their orientation, leading to a decrease in the dielectric constant. Figure 13 displays the change of the imaginary part (dielectric loss, $\varepsilon''$) of dielectric constant as a function of frequency for all samples. The dielectric loss shows a decreasing trend with increasing the frequency for all samples due to the decrease in the electrical resistivity \[37, 38\].

3.6 Electric Modulus

The analysis of complex electric modulus ($M^*$) was used to study the frequency and temperature dependence of the conductivity of many polycrystalline oxides and ceramics materials. The complex electric modulus ($M^*$) methodology gives a clear vision about the bulk response which can separate the local behavior of defects from the electrode effect. The complex dielectric modulus, $M^*$ ($\omega$), can be defined as the reciprocal of the complex dielectric permittivity:

$$M^* = \frac{1}{\varepsilon^*} = M' + j M'' = \frac{\varepsilon'}{[\varepsilon' + (\varepsilon'')^2]} + \frac{j\varepsilon}{[\varepsilon' + (\varepsilon'')^2]}$$

Moreover, it can also be expressed in terms of a derivative of complex impedance $Z^*$.

$$M^* = \frac{1}{\varepsilon^*} = M' + j M'' = j\varepsilon_0 Z^* = j\varepsilon_0 Z' - = j\varepsilon_0 Z''$$

where $M'$ and $M''$ are the real and imaginary parts of the complex electric modulus respectively, $j = (-1)^{1/2}$ and $\omega = 2\pi f$ is a radial.

Figure 14 illustrates the frequency dependence of the real part of electric modulus ($M'$) for BiFeO$_3$ powders prepared by sol–gel and auto combustion using different chelating agents at room temperature. It can be seen that at low frequency, the values of $M'$ tend to be zero and coincide with each other, which confirms a negligibly small contribution of electrode effect \[39\]. With increasing the frequency, the values of $M'$ of all samples were strongly increased and tend to saturate at high frequency which can be assigned to the conduction phenomena due to short-range mobility of charge carriers \[39\]. At fixed frequency, it is also clear that the values of $M'$ have the highest values in the following order:

![Figure 13](image_url)
The change of the imaginary parts of electric modulus spectra ($M''$) of BiFeO$_3$ powders prepared using sol–gel and autocombustion using different chelating agents at room temperature is shown in Fig. 15. The $M''$ values of the synthesized powders increase with frequency and show recurring declines and increase at high frequencies.

G2 > G1 > U1 > T1 > U2 > T2. The change of the imaginary parts of electric modulus spectra ($M''$) of BiFeO$_3$ powders prepared using sol–gel and autocombustion using different chelating agents at room temperature is shown in Fig. 15. The $M''$ values of the synthesized powders increase with frequency and show recurring declines and increase at high frequencies.

**Fig. 14** Variation of the real part of the complex electric modulus, $M'$, with frequency of BiFeO$_3$ prepared by using sol–gel and autocombustion using different chelating agents.

**Fig. 15** Variation of the imaginary part of the complex electric modulus, $M''$, with frequency of BiFeO$_3$ prepared by using sol–gel and autocombustion using different chelating agents.
3.7 Electrical Conductivity

The change of the electrical conductivity with frequency for BiFeO$_3$ powders prepared by using sol–gel and autocombustion methods using different chelating agents at room temperature is shown in Fig. 16. It can be seen that the electrical conductivity was increased with increasing the applied frequency for all BiFeO$_3$ samples, which could be assigned to the decreases in the dielectric constant or due to the charge-hopping mechanism. The BiFeO$_3$ powders prepared by using urea revealed the highest electrical conductivity values compared to other samples.

4 Conclusions

In this study, two dependable methods to synthesize high purity single phase BiFeO$_3$ powders were realized. The sol–gel and autocombustion techniques using three different chelating agents, glycine, tartaric acid, and urea, were investigated. The X-ray diffraction data confirmed that the glycine-autocombustion method produced a high purity single phase of BiFeO$_3$ using either low or high concentrations of reactants (Bi(NO$_3$)$_3$ + Fe(NO$_3$)$_3$), while the glycine-sol–gel method produced a high purity single phase of BiFeO$_3$ using low concentrations of reactants only. In case of using tartaric acid and urea as chelating agents, mixtures of BiFeO$_3$ and Bi$_{25}$FeO$_{40}$ phases were formed. The particle size, morphology, and porosity were changed by altering the chelating agent and the synthesis method. The highest purity BiFeO$_3$ sample exhibits a visible light band gap of 2.05 eV with a long absorption tail extending to the infrared region, suggesting the suitability of this material in solar photocatalytic applications. Weak hysteresis ferromagnetic behavior was observed for glycine- and urea-assisted BiFeO$_3$ powders with a large contribution from the paramagnetic behavior. On the other hand, tartaric-assisted samples demonstrated remarkable ferromagnetic loops with saturation magnetization reaching to 2.5 emu/g for sol–gel-assisted sample. All the synthesized samples exhibit high dielectric constant values at low frequency and follow the Maxwell–Wagner model.

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Declarations

Conflict of Interest The authors declare no competing interests.
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