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Dielectric Studies of Bi₂MoO₆/Graphene Oxide and La-Doped Bi₂MoO₆/Graphene Oxide Nanocomposites

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Abstract: The mixed metal oxides Bi₂MoO₆ and La-doped Bi₂MoO₆ were prepared by the sol–gel method. Then, varying quantities of the as-prepared mixed metal oxides were blended with graphene oxide (GO), employing sonication, to obtain Bi₂MoO₆/GO (BM/GO) and La-Bi₂MoO₆/GO (LBM/GO) nanocomposites. These prepared materials were characterized by different techniques such as thermal gravimetric analysis (TGA), X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), and transmission electron microscopy (TEM). Dielectric properties were studied by using a precision impedance analyzer. Dielectric constant and loss tan of the synthesized composites were studied as a function of frequency by using a precision impedance analyzer. Overall, the dielectric constant (ϵ) observed for the LBM/GO composites was higher than that of BM/GO.

Keywords: dielectric studies; Bi2MoO6; lanthanum; graphene oxide

1. Introduction

A growing demand for electric charge storage devices, due to the invention of battery-powered automobiles and other devices, has led to the study of the preparation of materials with enhanced dielectric properties. A variety of nanocomposites such as Mnsubstituted ZnFe₂O₄; Co₂Y hexaferrites substituted by Mn-Ge, Ce-Nd₂Zr₂O₇, Co(II), Ni(II), Cu(II), and Mn(II)-oxaloyldihydrazone complexes; and ZnO microspheres with polyaniline (PANI) have been studied for their dielectric behaviors due to the fact that nanocomposites possess unique properties as compared to bulk material [1–3]. Nanocomposites have great importance due to their remarkable catalytic, dielectric, and luminescence properties, based on the morphology of the nanomaterials. The electrical conductance and thermal stability of the metal nanocomposites can be improved by the help of a carbonbased support, usually achieved with graphene oxides [4,5].

One such carbon-based support is graphene, a 2D material that has been found to be an excellent support for the enhancement of properties of the resulting nanocomposites [6–13]. Various reports of the use of graphene can be found in the literature, such as poly (p-phenylene benzobisoxazole/graphene, PVA/graphene composites graphene oxide (GO)/ZnxFe_{1-x}Fe₂O₄ composites, graphene/BaTiO nanocomposites rGO-Cu₂O, etc., for the creation of nanocomposites that display enhanced dielectric properties due to the inclusion of graphene [14–16].

Furthermore, the incorporation of metals and non-metals with metal oxides nanoparticles also enhances the functionality of the materials. One such metal that has been

Citation: Adil, S.F.; Latif, S.; Waqar, M.; Imran, M.; Noreen, S.; Khan, M.; Shaik, M.R.; Hatshan, M.R. Dielectric Studies of Bi2MoOs/Graphene Oxide and La-Doped Bi2MoOs/Graphene Oxide Nanocomposites. *Metals* **2021**, *11*, 559. https://doi.org/10.3390/ met11040559

Academic Editor: Peter Baumli

Received: 18 February 2021 Accepted: 26 March 2021 Published: 29 March 2021

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extensively studied is bismuth, and there are a series of nanocomposites (Bi₂WO₆, Ba-TiO₃Bi₂O₃, Bi₂S₃, BiVO₄, Bi₂Ti₂O₇, Bi₁₂TiO₂₀ and Bi₂InNbO₇) that show a variety of properties [17–21]. Bismuth molybdate (Bi₂MoO₆) is a versatile metal molybdate with photoelectric characteristics that has been widely used as a photocatalyst and as an anode material in lithium batteries. Some notable citations in this regard are available in the literature [22– 26].

Recently, bismuth molybdate (Bi2MoO₆) was employed as a photocatalyst, exhibiting increased performance among metal molybdates for the degradation of dyes and luminescence, and it has been synthesized by various methods: co-precipitation, hydrothermal, solid state reaction, and sol–gel [27]. In continuation of our efforts to prepare various graphene-based nanocomposites, we extended our previous work regarding synthesis and morphological studies of Bi2MoO₆ and La-doped Bi2MoO₆ [28–30], and herein we report on the graphene oxide nanocomposites of Bi2MoO₆ and La-doped Bi2MoO₆ and La-doped Bi2MoO₆, i.e., Bi2MoO₆/GO and La-Bi2MoO₆/GO composites, respectively, and their dielectric behavior.

2. Materials and Methods

2.1. Materials

All chemicals used for the synthesis, such as graphite powder, sodium molybdate (Na₂Mo₂O₄ × 2H₂O), bismuth chloride (BiCl₃), and lanthanum chloride (LaCl₃ × 7H₂O), were of analytical grade purchased from Sigma Aldrich and PubChem (Saint Louis, MO, USA). Bi₂MoO₆ and La-doped Bi₂MoO₆ were synthesized using a previously reported method [28].

2.2. Methods

Graphene oxide was synthesized by the modified Hummers method [31]. A variety of nanocomposites of bismuth molybdate and lanthanum-doped bismuth molybdate with graphene oxide were synthesized by depositing varying amounts by weight of Bi₂MoO₆ and La-BiMoO₆ on graphene oxide to yield 2, 3, and 4% of Bi₂MoO₆/GO (BM/GO) and La-Bi₂MoO₆/GO (LBM/GO). The mixed metal oxides and graphene oxide were dispersed in deionized water by applying sonication for 3 h. After sonication, the samples were dried in an electric oven at 90 °C for 48 h, and we obtained X% BM/GO (X wt.% Bi₂MoO₆/GO) and X% LBM/GO (X wt.% La-Bi₂MoO₆/GO) composites, where X = 2, 3, or 4, which denotes the wt.% of the mixed metal oxide in the GO nanocomposite.

2.3. Characterization

The crystalline structures of the as synthesized nanocomposites were characterized with XRD patterns on a Bruker D2 Phaser X-ray diffractometer with Cu K α radiation (λ = 1.5418 Å), having accelerating voltage and current of 30 kV and 10 mA, respectively (Bruker, Berlin, Germany). TGA was performed by heating the samples in an N₂ flow using a Perkin-Elmer Thermogravimetric Analyzer 7 with a heating rate of 10 °C/min (Perkin-Elmer, Waltham, MA, USA). BET surface area and BJH pore volume were measured by an N₂ adsorption-desorption isotherm with a liquid nitrogen temperature of –196 °C using Micromeritics (Gemini VII, 2390 surface area and porosity, Norcross, GA, USA). The samples were degassed at 120 °C for 3 h using N₂ gas. The surface morphology of the nanocomposites was determined by scanning electron microscopy (SEM, Jeol, JED-2200 series, Tokyo, Japan). Transmission electron microscopy (TEM) analysis of nanocomposite measurements was carried out using Jeol TEM model JEM-1011 (Jeol, Tokyo, Japan) at 100 keV. XPS spectra were measured on a PHI 5600 Multi-Technique XPS (Physical Electronics, Lake Drive East, Chanhassen, MN, USA) using monochromatized Al Ka at 1486.6 eV.

3. Results and Discussions

3.1. Thermal Gravimetric Analysis

A thermal gravimetric analysis (TGA, Perkin-Elmer, Waltham, MA, USA) was conducted to identify the thermal behavior of all the synthesized composites. The results of 4% BM/GO and 4% LBM/GO are compared in Figure 1, while the TGA curves of other compositions are given in the supplementary data (Figure S1). Among these composites, in general, a large weight loss was observed between 220 and 445 °C, which can be attributed to the thermal decomposition of rGO in these composites. Such a large loss is in agreement with similar degradation patterns of Bi2MoO6/rGO composites [22]. The TGA thermogram of Bi2MoO6 reveals that there was an 8% weight loss and that of La-Bi2MoO6 shows a weight loss of up to 16%, indicating that the later nanocomposite is thermally less stable than its precursor. However, when the GO nanocomposites of the mixed metal oxides BM and LBM, i.e., X% Bi2MoO6/GO and X% La-Bi2MoO6/GO, were subjected to similar studies wherein the samples were heated up to 800 °C starting from 25 °C at a heating rate of 10 °C/min under an inert atmosphere, a similar trend of thermal stability was observed, indicating the formation of composites. However, when the La-doped Bi2MoO₆ was subjected to a similar study, it was found that the weight loss was up to 16%, indicating that the later nanocomposite, i.e., 4% LBM/GO, is thermally less stable.



Figure 1. Comparative thermal degradation patterns of Bi2MoO₆ (BM), La-Bi2MoO₆ (LBM), graphene oxide (GO), 4% BM/GO, and 4% LBM/GO.

3.2. X-ray Diffraction

The XRD pattern of the prepared 4% BM/GO and 4% LBM/GO composites is given in Figure 2. The diffractogram obtained for the sample of 4% BM/GO revealed the presence of GO along with the pattern of Bi₂MoO₆ (JCPDS No. 76-2388), which yielded diffraction peaks at 2θ values 23.5° (111), 28.2° (131), 32.5° (002), 33.2° (060), 36.1° (151), 46.8° (202), 47.2° (260), 55.5° (133), 56.4° (191), and 58.4° (262) that were found in the original mixed metal oxide BM [32]. However, the XRD pattern of 4% LBM/GO revealed the presence of mixed phases of La₂Mo₂O₉ and Bi₂MoO₆ along with GO [32–34].



Figure 2. Comparative XRD patterns of BM, 4% BM/GO, and LBM, 4% LBM/GO composites.

3.3. BET Analysis

The nitrogen adsorption isotherms of 4% BM/GO and 4% LBM/GO composites measured at 333K are shown in Figure 3. From the isotherms obtained, it can be observed that the adsorption of N₂ was much higher in the composites than in their precursors, suggesting that the enormous alteration of structural characteristics takes place due to incorporation of GO in the system [35]. Moreover, the surface area of the 4% BM/GO and 4% LBM/GO composites was found to be 12 m²/g and 10.7 m²/g, respectively, which is several times greater than that of the precursors Bi₂MoO₆ (1.0277 m²/g) and La-doped Bi₂MoO₆ (3.4077 m²/g), respectively [28]. This difference in surface area can also be attributed to the GO incorporation with BM and LBM precursors [36].



Figure 3. Nitrogen adsorption isotherms of 4% BM/GO and 4% LBM/GO composites.

Furthermore, when comparing the pore distribution of the composites with the precursor metal oxides, i.e., BM and LBM, it was observed that the pore size of the composites ranged from 1.1 to 18.6×10^{-3} cm³/g and 2.8 to 19.7×10^{-3} cm³/g for the 4% BM/GO and 4% LBM/GO composites, respectively (Figure 4).



Figure 4. Pore distribution curves of 4% BM/GO and 4% LBM/GO composites.

3.4. Microscopic Analysis

The surface morphology of the prepared 4% BM/GO and 4% LBM/GO composites was examined by SEM, and the respective SEM micrograms are shown in Figure 5. The surface morphology of 4% BM/GO possesses irregular shining particles with small crystals of bismuth molybdate on a graphene oxide platform. The surface morphology of 4% LBM/GO exhibits a distribution of particles arranged as relatively large rod-like crystals of lanthanum molybdate embedded on a graphene oxide platform. The surface morphology of both composites is quite different than that of Bi2MoO₆ and La-Bi2MoO₆, which are dense rod-like and scattered granular, respectively [28].



Figure 5. Scanning electron micrograms of 4% BM/GO and 4% LBM/GO composites.

The prepared composites were subjected to TEM analysis by dispersing the prepared composites in hexane and using a sonicator water bath, then, the dispersed solution was dropped on the TEM grid to evaluate the dispersion of BM and LBM on the graphene oxide sheets. It was observed that the dispersion of LBM, i.e., La-Bi2MoO₆, on the graphene oxide sheets in the composite 4% LBM/GO was superior to that observed in the case of BM, i.e., Bi2MoO₆ in the 4% BM/GO composite, wherein agglomeration of the mixed metal oxides was seen on the surface of the GO. The TEM images obtained for both the composites, i.e., 4% BM/GO and 4% LBM/GO, are given in Figure 6.



Figure 6. Transmission electron microscopy analysis of 4% BM/GO and 4% LBM/GO composites.

3.5. X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy is one of the best tools to analyze the surface composition and particularly the valence state of elements in these composites. The scan of the 4% LBM/GO composite revealed the presence of Bi, Mo, O, and La elements in the prepared composites, and an additional signal corresponding to the element C revealed the successful doping of GO in the nanocomposite (Figure 7). The full spectrum for the 4% LBM/GO composite contains peaks for C 1s (287 eV), O 1s (537 eV), Mo 3d (235 eV), Bi 4f (158 eV), and La 3d. These results are in agreement with previous literature [22,28]. It was observed that there was no change in the binding energies of the respective elements of the mixed metal oxides, indicating that the formation of the composites is by physisorption of the mixed metal oxides, i.e., BM and LBM, on the surface of the employed GO, as confirmed by the TEM images.



Figure 7. XPS spectra of the 4% LBM/GO composite.

3.6. Dielectric Properties

Dielectric properties of Bi2MoO6/GO and La-Bi2MoO6/GO as a function of frequency were studied by using an impedance analyzer, and the values of the dielectric constants were plotted against the log of frequency, as shown in Figures 8a,b and 9a,b. Figure 8a,b shows the increase in dielectric constant from X% BM/GO (X = 2, 3, and 4). ε' decreases with an increase in frequency. High dielectric constants at low frequencies were attributed to the electrode polarization phenomenon, wherein an increase in of the electrode potential lags behind the frequency, and space charges have less time to be arranged according to the applied electric field [37]. An increase in ε' was observed with an increase in BM content from 2 to 4% in the GO nanocomposite. Values of ε' were 17.69, 76.67, and 142.33 for 2, 3 and 4%, respectively. A high dielectric constant was considered due to the electronic and ionic polarizability, and contribution by the oxide contents and Bi ions mainly contributed to the high ϵ' [38,39]. Moreover, existence of the oxygenated groups in the GO caused entrapment of Bi ions and reduced the interaction of Bi with molybdate ions, and hence, more available Bi caused a high ϵ' [40]. ϵ' observed for the LBM/GO composites was higher than that of the undoped nanocomposite, i.e., BM/GO, but overall, the value of the ε' was much lower than that of Bi₂MoO₆/GO. Values observed for the ε' of La-Bi2MoO₆/GO, which were 43.9, 48.89, and 51.28 for 2, 3, and 4% weight of La-Bi2MoO₆, dispersed in a fixed amount of GO. The low ε' was attributed to the increased conductivity of the oxide ions in La-doped Bi2MoO₆ [41].



Figure 8. (a): Comparative graphs between the dielectric constant (ε') and log f for composites X% BM/GO (X = 2, 3, and 4) (b) X% LBM/GO (X = 2, 3, and 4).

The loss tangents (tan δ) for Bi₂MoO₆/GO and La-Bi₂MoO₆/GO plotted against frequency, as shown in Figure 9a,b, show a similar behavior as that of ε' . Values of tan δ were 0.75, 1.82, and 1.79 for 2, 3, and 4% weight of Bi₂MoO₆, respectively, and the values of tan δ of La-Bi₂MoO₆/GO were 0.65, 0.71, and 0.88, respectively. The increase in tan δ with the increase in Bi₂MoO₆ content in GO is attributed to the conductive nature of Bi₂MoO₆ [42], while the increase in tan δ with increase in Bi₂MoO₆/GO is attributed to the conductive network formation, dipole polarization, and interfacial polarization [43], as there exists a relation between electrical conduction ε' and ε'' [44,45].



Figure 9. (a): Comparative graphs between tan δ and log f for composites X% BM/GO (X = 2, 3, and 4) (b) X% LBM/GO (X = 2, 3, and 4).

4. Conclusions

Composites of GO/Bi₂MoO₆ and La-doped GO/B_{i₂MoO₆ were synthesized by sonication. An increase in the dielectric constant with an increase in Bi₂MoO₆ content was observed with an ϵ' of 142.33 at 4 wt.% of Bi₂MoO₆. A similar increasing trend was shown for La-doped Bi₂MoO₆, with an overall value of ϵ' 51.28. Tan δ was 1.79 and 0.88 for 4% GO/Bi₂MoO₆ and La-doped GO/Bi₂MoO₆, respectively. Overall, the present work opens an avenue for the controlled synthesis of GO/Bi₂MoO₆ and La-doped GO/Bi₂MoO₆ and directs our attention to new roles of GO in the controllable synthesis of new materials for possible applications in capacitive and charge storage devices.}

Supplementary Materials: The following are available online at www.mdpi.com/2075-4701/11/4/559/s1, Figure S1: Comparative thermal degradation patterns of (a) BM, LM, GO, 2% BM/GO, 3% BM/GO, 2% LBM/GO, and 3% BM/GO.

Author Contributions: Conceptualization, M.I. and S.F.A.; methodology, S.L., M.W., and S.F.A.; software, M.W.; validation, M.W. and S.F.A.; formal analysis, M.W., M.I., S.N., M.K., and M.R.S.; investigation, S.L., M.I., S.N., M.K., and M.R.S.; resources, M.I. and S.F.A.; data curation, S.L., M.I., S.N., M.K., and M.R.S.; visualization, M.W. and S.F.A.; writing—review and editing, M.W., S.F.A., M.K., and M.R.S.; visualization, M.R.H.; supervision, M.I., S.F.A., and M.R.H.; project administration, M.R.H.; funding acquisition, M.R.H. All authors have read and agreed to the published version of the manuscript.

Funding: The authors extend their appreciation to the Deputyship for Research & Innovation, "Ministry of Education" in Saudi Arabia for funding this research work through the project number IFKSURG-2020-142.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article or Supplementary Material.

Acknowledgments: The authors extend their appreciation to the Deputyship for Research & Innovation, "Ministry of Education" in Saudi Arabia for funding this research work through the project number IFKSURG-2020-142.

Conflicts of Interest: The authors declare no conflict of interest.

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