Structure, optical properties and antimicrobial activities of MgO–Bi$_{2-x}$Cr$_x$O$_3$ nanocomposites prepared via solvent-deficient method

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MgO–Bi$_{2-x}$Cr$_x$O$_3$ nanocomposites for $x = 0$ and 0.07 were fabricated using the solvent-deficient route. X-ray diffraction method, scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDXA) and UV–Vis spectroscopy were employed to study the properties. The samples were also evaluated for the antibacterial activity. The $x = 0$ sample showed a dominant monoclinic crystalline structure of $\alpha$-Bi$_2$O$_3$ phase. No peaks attributed to MgO were observed. Cr-doped MgO–Bi$_2$O$_3$ in which Bi was substituted showed that the tetragonal BiCrO$_3$ phase was also present in the MgO–Bi$_2$O$_3$ composite. The Scherrer formula was employed to determine the crystallite size of the samples. The Cr-doped sample showed a decrease in the crystallite size. The microstructures of the non-doped MgO–Bi$_2$O$_3$ and MgO–Bi$_{1.93}$Cr$_{0.07}$O$_3$ composites consisted of micrometer sized grains and were uniformly distributed. Direct transition energy gap, $E_g$ decreased from 3.14 to 2.77 eV with Cr-doping as determined from UV–Vis spectroscopy. The Cr-doped MgO–Bi$_2$O$_3$ nanocomposites exhibited two energy gaps at 2.36 and 2.76 eV. The antibacterial activity was determined against gram-negative bacteria (Salmonella typhimurium and Pseudomonas aeruginosa) and gram-positive bacteria (Staphylococcus aureus) by disc diffusion method. Cr-doping led to a decrease in inhibitory activity of MgO–Bi$_{2-x}$Cr$_x$O$_3$ nanocomposite against the various types of bacteria.

The unique physical and chemical characteristic of nanoparticles have led to intense research in this field in the last few years$^1$. Nanoparticles also have some antibacterial properties due to the inherent dimension, structural and surface characteristics$^2$. Nanotechnology can be capitalized to improve the activity of inorganic antibacterial materials. Bismuth (III) oxide or bismuth trioxide with the chemical formula Bi$_2$O$_3$ is a yellow chemical compound$^3$. It is a highly insoluble and thermally stable compound$^3$. Bi$_2$O$_3$ exists in six distinct polymorphs namely $\alpha$, $\beta$, $\gamma$, $\delta$, $\epsilon$ and $\omega$ for monoclinic, tetragonal, body-centered cubic, cubic face centered, orthorhombic, and triclinic forms, respectively. The $\alpha$-phase is generally formed at a lower temperature (around 873 K) compared to other phases.

Several techniques have been employed to improve the formation of $\alpha$ and $\beta$-Bi$_2$O$_3$ and the thermal stability$^5$. Bi$_2$O$_3$ is a p-type semiconductor with a narrow direct band gap (2.85 eV)$^{6,7}$. The ionic radius of Bi$^{3+}$ is 0.103 nm. Nano-Bi$_2$O$_3$ has good photoluminescence properties, large ionic conductivity and dielectric permittivity, remarkable photoconductivity, non-toxic and excellent catalytic activity$^{8-14}$. It is useful in fuel cells, optical coating, optoelectronics, high temperature superconductors and piezoelectric material$^{15-22}$. Several Bi$_2$O$_3$-containing semiconductor compounds have been used in photocatalysis. However, it has a poor photo-quantum efficiency, limited light response range and inferior catalytic ability in the visible spectrum. These problems limited the application of Bi$_2$O$_3$$^{2,8,21}$.

Bi$_2$O$_3$–MgO have been fabricated by solvent-thermal method and the photocatalytic activity has been reported. Bi$_2$O$_3$–MgO with Bi to Mg molar ratio of 2:1 has the narrowest band gap and it was found more active for photocatalytic decolorization of RhB than Bi$_2$O$_3$ and MgO$^{23}$. CeO$_2$–Bi$_2$O$_3$ nanocomposite was prepared via a two-stage process and the photocatalytic activity has been reported. The results showed that the microstructure and morphology of CeO$_2$–Bi$_2$O$_3$ composite were similar in spite of different inverse proportion. Improved

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photocatalytic activity was observed in the case of CeO$_2$–Bi$_2$O$_3$ composite catalyst compared to the catalytic activity of pure Bi$_2$O$_3$ or CeO$_2$ powder. The suppression of charge recombination in the composite CeO$_2$–Bi$_2$O$_3$ catalyst led to higher catalytic activity for the degradation of RhB$^{24}$. The ZnO–Bi$_2$O$_3$ with tunable optical properties and the antibacterial activity have been studied. The formation of the BZO nanocomposites was confirmed by the coexistence of both ZnO and Bi$_2$O$_3$ phases in diffraction patterns. The decoration of Bi$_2$O$_3$ nanoparticles on the surface of ZnO nano-cones significantly improved the optical quality. The Bi$_2$O$_3$ nanoparticles decoration on ZnO nano-cones reduce surface defects and increased electron–hole recombination rate which strongly influence the antibacterial activity of BZO nanocomposites$^{25}$. Wu et al. synthesized ZnO–Bi$_2$O$_3$ nanocomposite by sonochemical route at low-temperature$^{26}$. It is useful to prepare new effective photocatalysts in the visible region. Bi$_2$O$_3$ has very attractive antimicrobial activity. Generally, Bi$_2$O$_3$ has low cytotoxicity and present notable antibacterial activity$^{27–29}$.

Magnesium oxide is a white solid mineral. Mg has oxidation state +2 and its ionic radius is 0.72 Å$^3$. Magnesium oxide is a semiconductor/insulator which usually display a cubic structure$^9$. The band gap of MgO is around 7.8 eV and this quite large which limited its application. The nano sized magnesium oxide has a lower band gap of 5 eV$^{31}$. Magnesium oxide nanoparticles have high surface reactivity and good chemical and thermal stability$^{32}$. Nano sized MgO has a wide-range of bactericidal property towards gram-positive and gram-negative bacteria$^{33}$. It demonstrates higher mammalian bioactivity and lower toxicity than most metal oxides. Hence, it can be a potential ingredient in drug formulation$^{34}$. Many reports have been published on the synthesis of MgO nanoparticles and nanocomposite due to the wide range of applications$^{35}$. The antibacterial activity lies in the creation of superoxide radicals through the reaction of oxygen with the bacterial surface. The extra electrons are very reactive and can cause damage to the proteins and phospholipids of the bacterial membrane$^{36}$.

Chromium in the trivalent state has an ionic radius of 0.62 Å$^3$. Among the various transition metals, chromium is known to improve the structure and optical characteristics of nanocomposites. The antimicrobial activities of chromium (III) exhibits high biological factor because it contains amino acids as ligand.

In this work, MgO–Bi$_2$O$_3$–Cr$_2$O$_3$ (x = 0 and 0.07) nanocomposite powders were prepared using a low cost solvent-deficient technique. The X-ray diffraction (XRD) method, scanning electron microscope (SEM) and UV–Vis spectrophotometer were used to study the structure, microstructure and optical properties, respectively. The average crystallite size, $D$ was calculated using the Scherrer formula. The antibacterial activity was studied against gram-negative bacteria (Salmonella typhimurium and Pseudomonas aeruginosa) and gram-positive bacteria (Staphylococcus aureus) by means of the disc diffusion method at various concentrations of the prepared nanocomposite.

### Experimental procedure

The MgO, Bi$_2$O$_3$, and MgO–Bi$_2$O$_3$–Cr$_2$O$_3$ for $x =$ 0 and 0.07 nanocomposites were prepared using facile solvent-deficient technique using: Bi(NO$_3$)$_3$·5H$_2$O (≥ 98.5%; Fluka), Mg(NO$_3$)$_2$·6H$_2$O, Cr(NO$_3$)$_3$·9H$_2$O (> 99%; Fluka-Garande) and NaHCO$_3$ (> 99%; Fluka). All chemicals were used as received without further purification. The reaction is as follows:

\[
\begin{align*}
\text{Mg(NO}_3\text{)}_2 & \cdot \text{6H}_2\text{O} + 2\text{NaHCO}_3 & \rightarrow & \text{MgO} + 2\text{NO}_2 + 7\text{H}_2\text{O} + \text{Na}_2\text{O} + 2\text{CO}_2 + 1/2\text{O}_2, \\
2\text{Bi(NO}_3\text{)}_3 & \cdot 5\text{H}_2\text{O} + 6\text{NaHCO}_3 & \rightarrow & \text{Bi}_2\text{O}_3 + 6\text{NO}_2 + 13\text{H}_2\text{O} + 3\text{Na}_2\text{O} + 6\text{CO}_2 + 3/2\text{O}_2, \\
(2-x)\cdot \text{Bi(NO}_3\text{)}_3 & \cdot 5\text{H}_2\text{O} + \text{Mg(NO}_3\text{)}_2 & \cdot \text{6H}_2\text{O} + x\text{Cr(NO}_3\text{)}_3 & \cdot 9\text{H}_2\text{O} + 8\text{NaHCO}_3 & \\
& \rightarrow & \text{MgO} - \text{Bi}_2-x\text{Cr}_x\text{O}_3 + 8\text{NO}_2 + (20 + 4x)\text{H}_2\text{O} + 4\text{Na}_2\text{O} + 8\text{CO}_2 + 2\text{O}_2.
\end{align*}
\]

Stoichiometrically calculated amounts of metal nitrates were mixed with NaHCO$_3$ and grounded together for 20 min in mortar at room temperature. A noticeable degassing reaction due to CO$_2$ release was initially observed. The slurry became more viscous with continuous mixing. After drying overnight at room temperature in the mortar, a dark powder was obtained. The powder rinsed using distilled H$_2$O and filter flask to wash the powders 3 times. The powders were heated in a box oven for 2 h at 773 K and the temperature was increased or decreased at 10 K/min.

An XD-2 X-ray diffractometer (China) located at the Yemeni Geological Survey and Minerals Resources Board was used to identify the phase. The CuK$_\alpha$ radiation was used and the angle $2\theta$ was varied from 20° to 70°. Scanning electron micrographs (SEM) and energy dispersive X-ray analyzer from JEOL-JSM 6360 LV (Japan) were used to determine the microstructure and elemental composition. The optical transmission and absorption were investigated using a UV–Vis spectrophotometer (SPECTORD 200) at room temperature in the wavelength range of 200–900 nm in the Department of chemistry, college of sciences, Sana’a University.

The antibacterial activity of MgO–Bi$_2$O$_3$–Cr$_2$O$_3$ nanocomposites was assessed against gram-negative bacteria (Salmonella typhimurium and Pseudomonas aeruginosa) and gram-positive bacteria (Staphylococcus aureus) by the disc diffusion method. Biochemical test was used to identify the isolates. The samples were suspended in sterile distilled water and diluted in one-fold serial dilution from the stock solution of 50 mg/ml. Four working dilutions were used for disks impregnation. A sterile filter paper disk with 6 mm diameter was impregnated with 20 μl (10 μl to each side) producing 500, 250, 125, 62.5 μg/disk (S1, S2, S3, S4, respectively). Inoculation by swabs resulted in a homogeneous bacterial lawn on the agar surface. The disks were placed on the surface of the inoculated agar with sterile forceps and incubated at 310 K for 18–20 h. After incubation, the zones of inhibition (ZOI) were determined to the closest mm. For the negative control, distilled water was employed.
Cr ions may have resided in the MgO, α-Bi2O3 and MgO–α-Bi2O3 nanocomposites. This suggests a new phase with the Bi and O ions. However, there was no peaks attributed to MgO probably due to the small amount. However, its presence has been confirmed by EDX spectrum. Bi3+ (coordination number = 6) has ionic radius 1.03 Å while Mg2+ ( coordination number = 6) is only 0.72 Å. The presence of MgO may have suppressed the growth of α-Bi2O3, and resulted in a reduction of the lattice parameters of the monoclinic phase. α-Bi2O3 also suppressed the crystallization of MgO. Diffraction peaks other than Bi2O3 were not observed. This indicated that there was no impurity in the MgO–Bi2O3 nanocomposites.

The XRD patterns of MgO–Bi2O3 and Cr-doped MgO–Bi2O3 nanocomposite for 2θ = 15°–65° are presented in Fig. 2. Doping with Cr (x = 0.07) exhibited new peaks at 27.9°, 32.6°, 41.6°, 52.9°, 55.3° and 57.5° (marked as * in Fig. 2) which correspond to (211), (220), (302), (420), (332) and (422) planes, respectively of the tetragonal BiCrO3 phase (JCPDS card number 00-004-0570). Other Cr related peaks were observed which indicated that the Cr may also reside as interstitial ions or resided at the vacancies. This suggests a new single phase monoclinic crystalline structure (space group, P21/c), which can be indexed to JCPDS card number 00-041-1449.

Figure 1. XRD diffraction patterns of MgO, α-Bi2O3 and MgO–α–Bi2O3 nanocomposites.

Results and discussion

XRD analysis. The crystal structure of MgO–Bi2O3 and chromium doped MgO–Bi2O3 were confirmed by X-ray diffraction (XRD) analysis. The XRD patterns of the as-prepared MgO, α-Bi2O3 and MgO–Bi2O3 nanocomposites are very similar to those of pure α-Bi2O3, but they markedly widen against those of pure α-Bi2O3. This implies that the final product possibly has smaller particle size. The XRD pattern of MgO–Bi2O3 nanocomposites verified the existence of α-Bi2O3 monoclinic phase in the single matrix. The peaks can be well matched with JCPDS card number 00-001-1235. An unknown peak was observed near 2θ = 30°. The diffractions pattern of α-Bi2O3 demonstrated a single phase monoclinic crystalline structure (space group, P21/c), which can be indexed to JCPDS card number 00-041-1449.

The Cr-doped MgO–Bi2O3 showed a wider line broadening compared to the pure MgO–Bi2O3 indicating that Cr ions may have resided in the MgO–Bi2O3 lattice. The shifting of MgO–Bi2O3 peaks with Cr-doping can be observed in Fig. 3. The higher angle shift suggested the shrinkage of the c-axis. The intensity was reduced for MgO–Bi2O3 added Cr3+ which has a smaller ionic radius than Bi3+. The intensity for the x = 0.07 sample was higher which showed that the crystal grew in one crystallographic direction with the lowest surface energy. Hence, by doping the crystallinity and crystal orientation along the c-axis can be controlled.

The unit cell parameters a, b, c and β for monoclinic α-Bi2O3 structure were calculated using the following relation:

$$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left( \frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right).$$

The cubic MgO lattice parameters were calculated using:

$$\frac{1}{d^2} = \left( \frac{h^2 + k^2 + l^2}{a^2} \right),$$

where a is the lattice parameter.
Figure 2. XRD diffraction patterns of MgO–Bi$_{2-x}$Cr$_x$O$_3$ nanocomposites for $x = 0$ and 0.07.

Figure 3. XRD patterns showing a slight peak shift toward higher angles 2$\theta$ of MgO–Bi$_{2-x}$Cr$_x$O$_3$ nanocomposites for $x = 0$ and 0.07.
was employed to determine the average crystallite size from the XRD data of MgO–Bi$_{2-x}$Cr$_x$O$_3$ nanocomposite for $x = 0$ and 0.07.

Table 1. Structural parameters of MgO–Bi$_{2-x}$Cr$_x$O$_3$ nanocomposite for $x = 0$ and 0.07.

| Oxides       | $D$ (nm) | $\varepsilon \times 10^{-3}$ | $\delta \times 10^{-4}$ (n m$^{-2}$) |
|--------------|----------|-----------------------------|--------------------------------------|
| MgO (Pure)   | 17       | 5.56                        | 34.36                                |
| Bi$_2$O$_3$ (Pure) | 43     | 3.41                        | 5.46                                 |
| $x = 0$      | Bi$_2$O$_3$ (120) | 36  | 4.07 | 7.69 |
| $x = 0.07$   | Bi$_2$O$_3$ (120) | -   | -    | -    |
|              | BiCrO$_3$ (211) | 23  | 6.20 | 18.35 |

Table 2. Average crystallite size, lattice strain and dislocation density determined using Debye Scherrer formula of MgO–Bi$_{2-x}$Cr$_x$O$_3$ nanocomposite for $x = 0$ and 0.07.

$$D = \frac{0.94}{\delta \cos \theta},$$

where $d$ is the spacing between planes and $h, k, l$ are the Miller indices. The volume ($V$) for the monoclinic phase was calculated using $V = abc \sin \beta$ and for the cubic structure $V = a^3$ (Table 1). The lattice constants and volume of tetragonal BiCrO$_3$ were calculated using (6):

$$\frac{1}{d^2} = \left(\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}\right).$$

$$V = a^2 c.$$  

The mass density, $\rho$ for the cubic, monoclinic and tetragonal phase were calculated using ($Z 

\times 1$)/$(N \times a^3) g cm^{-3}$ where $Z$ is the atom number per unit cell, $M$ is the molecular mass (g/mol) and $N$ is Avogadro's number$^{41}$. The $d$-spacing was calculated using $2\sin \theta = n \lambda$, where $\theta$ is the angle of reflection, $n$ is order of reflection and $\lambda$ is the incident radiation wavelength. The substitution of Cr$^{3+}$ in MgO–Bi$_2$O$_3$ resulted in an increase in the unit cell volume and inter-planar distance (Table 1). The Debye Scherrer formula:

$$D = \frac{0.94}{\delta \cos \theta},$$

was employed to determine the average crystallite size from the XRD data of MgO, α-Bi$_2$O$_3$ and MgO–Bi$_{2-x}$Cr$_x$O$_3$. The micro-strain, $\varepsilon$ was calculated using (9):

$$\varepsilon = \frac{\varphi}{(4\tan \theta)},$$

where $\varphi$ is the full-width at half-maximum (FWHM), $\theta$ is where the peak is and $\lambda = 1.5406 \text{ Å}$. The dislocation density, $\delta = 1/D^2$ due to crystal imperfections was also determined. The crystallite size of undoped MgO–Bi$_2$O$_3$ nanocomposites was 36 nm and decreased to 23 nm for Cr-doped MgO–Bi$_2$O$_3$ (Table 2). The decrease was possibly due to segregation of Cr on MgO–Bi$_2$O$_3$ surface as a result of the difference in the radius of Cr$^{3+}$ and Bi$^{3+}$, in addition to the substitution which restricted the growth of MgO–Bi$_2$O$_3$ crystal$^{43}$.

The increase of FWHM in Cr-doped samples indicated the reduction of the crystallite size. The same result possibly due to segregation of Cr on MgO–Bi$_2$O$_3$ surface as a result of the difference in the radius of Cr$^{3+}$ and Bi$^{3+}$, in addition to the substitution which restricted the growth of MgO–Bi$_2$O$_3$ crystal$^{43}$.

The increase of FWHM in Cr-doped samples indicated the reduction of the crystallite size. The same result was obtained due to micro strain variations was also observed. A smaller crystallite size gave higher strain which increased with decreased in crystallite size. The decrease in strain for larger crystallite size is a result of the decrease in the surface area of the nanocomposites. In addition, $\delta$ increased with a decrease in the grain size and vice-versa$^{44}$.

**Microstructure.** Figure 4 shows the micrographs of MgO–Bi$_{2-x}$Cr$_x$O$_3$ for $x = 0$ and 0.07. MgO–Bi$_{1.91}$Cr$_{0.07}$O$_3$ showed a homogeneous particle distribution with rough surface. The pure and Cr-doped MgO–Bi$_2$O$_3$ showed spherical particle distributed uniformly. The Cr-doped sample grain size decreased because Cr$^{3+}$ diffused evenly at the different sites. Hence, pure MgO–Bi$_2$O$_3$ showed larger grain size, while the Cr-doped showed smaller size which agreed with the XRD calculations.

The crystallite size of MgO–Bi$_{1.91}$Cr$_{0.07}$O$_3$ calculated from the XRD data varies from 320 to 700 nm. Particles aggregation is important in determining the morphology and crystalline structure of the samples. The crystallite size determined using the XRD patterns was not the same as the SEM. In SEM the grain size were estimated...
from the clear grain boundaries. However, the crystalline surface area which diffracts the X-rays effectively were used to determine the crystallite size.

From the energy dispersive X-ray analyzer (EDXA), the peaks belonging to Bi, Mg, O and Cr with the expected composition were observed in the spectra (Fig. 5). The EDXA confirmed the elements present in the $\text{MgO-\text{Bi}_{1.93}\text{Cr}_{0.07}\text{O}_3}$ nanocomposite. No other addition impurity peaks was observed which indicated the formation of $\text{MgO-\text{Bi}_{1.93}\text{Cr}_{0.07}\text{O}_3}$ nanocomposite. In the Cr-doped sample, the Cr content was 0.4%. In the $\text{MgO-\text{Bi}_2\text{O}_3}$ sample, the elemental compositions of Bi, Mg and O were 88.7%, 0.4% and 10.9%, respectively. In the Cr-doped sample, the Cr content was 0.8%. In the $\text{MgO-\text{Bi}_2\text{Cr}_{0.07}\text{O}_3}$, the compositions of Bi, Mg and O were 82.2%, 3.2% and 13.8%, respectively. The annul tendency in the chemical composition of Cr-doped samples may be due to smaller ionic radius of Cr$^{3+}$. The slight variation in Cr was also likely a result of dilution of the ions in $\text{MgO-\text{Bi}_2\text{O}_3}$.

**Optical properties.** *Optical absorption and transmission spectra.* The UV–Visible spectra of $\text{MgO-\text{Bi}_2\text{O}_3}$ and $\text{MgO-\text{Bi}_{2-x}\text{Cr}_x\text{O}_3}$ ($x = 0.07$) showed a strong absorption in the ultraviolet region (Fig. 6). With chromium doping the band edge showed a slight red shift. This shift was due to sp–d exchange interaction between the band electron and localized $d$ electrons of Cr$^{3+}$. The $\text{MgO-\text{Bi}_{2-x}\text{Cr}_x\text{O}_3}$ ($x = 0.07$) showed the main maximum peak at 360 nm, and another peak at 462 nm which was due to the new phase $\text{BiCrO}_3$. The absorption bands decreased with Cr-doping. The red shift was a result of the smaller particle size.

The transmission spectrum of Cr-doped $\text{MgO-\text{Bi}_2\text{O}_3}$ with $x = 0.07$ from 350–650 nm is shown in Fig. 7. The optical transparency of $\text{MgO-\text{Bi}_2\text{O}_3}$ was about 99% in the visible region. The transparency of the nanocomposite decreased due to scattering and absorption from the defects on the surface. The transmission decreased in the visible range with Cr-doping. This was due to the electrons in the outer orbits which absorbed the energy of the incident light where the electrons was excited to higher levels. No emission of radiation was involved because the excited electron occupied vacant states in the allowed bands. Thus, part of the incident light was absorbed and did not penetrate the material.

The decrease in optical transmittance was due to the grain boundaries because the Cr-doped $\text{MgO-\text{Bi}_2\text{O}_3}$ exhibited a smaller grain size and higher density of grain boundary. This led to an increase in scattering. These transitions took place in direct and indirect transitions. The moderate transmittance in the long wavelength UV–Vis range is suitable for optoelectronic application including window layers. A low transmittance in the low wavelength region near UV (360 nm) was observed with further increase towards the higher wavelength region.

The sudden transmittance drop near the UV region was due to absorption of light through electronic excitation.
Absorption coefficient. The absorption coefficient for MgO–Bi₂O₃ and Cr-doped MgO–Bi₂O₃ versus photon energy (E) and shown in Fig. 7. The absorption coefficient, α can be calculated from the transmittance, T and photon absorbance, A. The α values below and near the edge of each curve was calculated using Beer Lambert’s equation:

$$ I = I_0 e^{-\alpha t}, $$  

(10)
where \( I \) is instantaneous photon intensity, \( I_0 \) is initial intensity and \( t \) is the thickness of the cuvette. \( \alpha \) can be calculated using:

\[
\alpha(\lambda) = \left( \frac{1}{t} \right) \left( \ln \frac{I_0}{T} \right) = \left( \frac{1}{t} \right) \left( \ln \frac{1}{T} \right) = \frac{2.303 A}{t}.
\]

(11)

The absorption coefficient decreased exponentially as the wavelength was increased (Fig. 7b). This could be due to the presence of electric fields within the crystal, strain induced imperfection and lattice deformation, and phonons inelastic scattering of carriers.\(^3\) The absorption coefficient of MgO–Bi\(_{2-x}\)Cr\(_x\)O\(_3\) was increased with the Cr-doping. This was due to the increase in the charge carriers resulting in the increase of absorbance and absorption coefficient. The highest \( \alpha \) was observed in the UV region. \( \alpha \) decreased in the low energy regions because the probability of excitation from the valence to conduction band was very small. The probability increased at the edge of the absorbance toward the higher energy.\(^4\)

**Refractive index and extinction coefficient.** The refractive index, \( n \) can be written as.\(^5\)
where, \( R \) is the reflection. The extinction coefficient, \( k \) is the amount of light lost due to absorption and scattering in the material. \( \alpha \) and the incident photon wavelength can be used to determine \( k \):

\[
k = \frac{\alpha \lambda}{4\pi}.
\]  

(13)

The \( n \) and \( k \) versus photon energy plots of MgO–Bi\(_2\)–xCr\(_{x}\)O\(_3\) for \( x = 0 \) and 0.07 are shown in Fig. 8a,b, respectively. \( n \) and \( k \) tend to increase with Cr-doping due to the random grain’s orientation and voids in the sample. Surface roughness can increase the optical scattering which can give rise to an increase in the refractive index.55

\( n \) for Cr-doped sample decreased with a decrease in photon energy from 3.2 to 2.8 eV due to the low absorption coefficient and high transmission from 388 to 443 nm. This is in good agreement with transmittance and absorption coefficient spectra (Fig. 7a,b). The value of \( n \) in the visible region was also determined at a specific photon energy such (2.8 eV) for all samples where \( n \) showed the lowest value. The refractive index showed two distinct regions: an anomalous dispersion at lower energy and normal dispersion at higher energy (Fig. 8a).

The extinction coefficient, \( k \) of MgO–Bi\(_2\)–xCr\(_{x}\)O\(_3\) nanocomposites was enhanced with increase in photon energy. \( k \) was very low in the absorption region which indicated the homogeneity of the particles. \( k \) can be determined from \( \alpha \) as a function of the energy gap. The \( k \) value was close to zero which indicated that the nanocomposites were transparent in the visible region. Figure 8b shows that \( k = 0.07 \) for the Cr-doped MgO–Bi\(_2\)O\(_3\) sample and this was higher when compared with the non-doped sample.

**Optical conductivity.** The optical conductivity, \( \sigma_{\text{opt}} \) can be written as:

\[
\sigma_{\text{opt}} = \frac{\alpha nc}{4\pi},
\]

(14)

where, \( c \) is light speed. The optical conductivity versus photon energy for MgO–Bi\(_{2}\)–xCr\(_{x}\)O\(_3\) (\( x = 0 \) and 0.07) nanocomposites which indicates the free charges are shown in Fig. 9a,b. Cr-doping enhanced the optical conductivity substantially. It also increased pronouncedly above \( h\nu = 2.9 \) eV for the MgO–Bi\(_{2}\)–xCr\(_{x}\)O\(_3\) nanocomposites. This was due to the variations of \( \alpha \) in the MgO–Bi\(_{2}\)–xCr\(_{x}\)O\(_3\) nanocomposites. The larger optical conductivity appeared in the visible region was due to the energy gap of the MgO–Bi\(_{2}\)–xCr\(_{x}\)O\(_3\) which decreased with Cr-doping. The optical conductivity increased with photon energy near the absorption band edge. This was due to the optimal absorption via electron excitation of the photon energy which reduced the free carriers. The optical conductivity was reduced in the lower energy region (visible absorption), which showed the localization of the initially free carriers. The optical conductivity increased with Cr-doping in MgO–Bi\(_2\)O\(_3\) lattice.

**Real and imaginary parts of dielectric constant.** The real part of the dielectric constant, \( \varepsilon_r = n^2 - k^2 \) indicates the ability of a material to reduce the speed of light. The imaginary part, \( \varepsilon_i = 2nk \) gives the absorption of energy due to dipole motion from an electric field [54]. The ratio \( \frac{\varepsilon_i}{\varepsilon_r} = \tan \delta \) gives information about loss factor. Fig-
Figure 9. (a) Optical conductivity, (b) real dielectric constant, (c) imaginary dielectric constant and (d) loss factor versus photon energy of MgO–Bi$_{2-x}$Cr$_x$O$_3$ nanocomposite for $x = 0.00$ and 0.07.

ure 9b–d show the real and imaginary parts of the dielectric constant and loss factor on photon energy. The real part are higher than the imaginary part of the dielectric constant. $\varepsilon_r$ of the dielectric constant indicates the real electrical energy saving and $\varepsilon_i$ shows the absorption loss related to free carriers. The curves of the two parts are naturally oscillatory and relies on the crystal structure. The real part rises and falls and this is similar to refractive index where the effect of $k$ can be omitted. The profile of the imaginary part was similar to the extinction coefficient. The loss factor was nearly constant in the energy range 2.2 to 2.9 eV but increase pronouncedly near 2.9 eV.

Optical band gap ($E_g$). The absorption spectrum can determine the optical band gap, $E_g$ by using the Tauc plot method:

$$\alpha h \nu = A (h \nu - E_g)^n,$$

(15)

where, $\nu$ is incident frequency, $A$ is a constant that depends on electron and hole effective masses. The exponent $n = 1/2, 2, 3/2$ or 3 for direct, indirect, forbidden direct, and forbidden indirect transitions, respectively.

The plot of $(\alpha h \nu)^n$ versus $h \nu$ can be used to obtain $E_g$ of the samples (Fig. 10). The plot exhibits two different slopes. $E_g$ values for MgO–Bi$_{2-x}$Cr$_x$O$_3$ nanocomposite are listed in Table 3. The Cr-doped MgO–Bi$_2$O$_3$ nanocomposites exhibited two energy gaps at 2.36 and 2.76 eV. The second energy gap may be due to BiCrO$_3$. The optical band gap decreased when Cr was doped (red shift), suggesting that Cr$^{3+}$ in the valence band acted as defects which reduced the band gap. The smaller gap with Cr-doping was due to the impurities and increase in free electrons. The excitations occurred from the filled valence band to impurity energy levels.

Cr$^{3+}$ replacing Bi$^{3+}$ sites will create more defects or impurities in the electronic energy gap of MgO–Bi$_2$O$_3$ structures. It may be reason for the decrease in the energy gap and the appearance of the second energy gap. This energy gap was smaller than the undoped MgO–Bi$_2$O$_3$ (3.14 eV) (Fig. 10). The decrease in energy gap value indicated an increase in photocatalytic efficiency. Previous studies have also reported two energy band gap.
Antibacterial activity. In the present investigation, MgO–Bi$_{2-x}$Cr$_x$O$_3$ nanocomposites for $x=0$ and 0.07 with 50, 25, 12.5, 6.25 mg/ml dilutions were prepared and the antibacterial activity was determined against gram-negative bacteria (Salmonella typhimurium, Pseudomonas aeruginosa) and gram-positive bacteria (Staphylococcus aureus) (Table 4). The images of antibacterial studies of MgO–Bi$_{2-x}$Cr$_x$O$_3$ nanocomposites against S. typhimurium, P. aeruginosa and S. aureus bacterial pathogens are shown in Fig. 11.

The antibacterial efficiency was determined by measuring the diameter of the inhibition zone around the disc using antibiotic zone scale in millimeter. Cr-doped MgO–Bi$_{2-x}$Cr$_x$O$_3$ showed lower antimicrobial activity than non-doped MgO–Bi$_2$O$_3$. The inhibition zone has more bacteria S. typhimurium, P. aeruginosa than S. aureus.

### Table 3. Direct transition band gap $E_g$ values of MgO–Bi$_{2-x}$Cr$_x$O$_3$ nanocomposite for $x=0$ and 0.07.

| $x = 0$ | Band gap, $E_g$ (eV) | $x = 0.07$ | Band gap, $E_g$ (eV) |
|---------|----------------------|------------|----------------------|
|         | 3.14                 |            | 2.77                 |
|         | 2.94                 |            | 2.37                 |

### Table 4. Antibacterial activity of MgO–Bi$_{2-x}$Cr$_x$O$_3$ nanocomposite for $x=0$ and 0.07 against gram positive and gram negative bacteria.

| Microorganisms                        | Zone of inhibition (mm) at concentration in (µg/ml) | Con | $x=0$ | $x=0.07$ |
|---------------------------------------|-----------------------------------------------------|-----|-------|----------|
| S. typhimurium (Gram negative)        |                                                     |     |       |          |
| S1                                    |                                                    | 15  | 10    |          |
| S2                                    |                                                    | 15  | 11    |          |
| S3                                    |                                                    | 15  | 11    |          |
| S4                                    |                                                    | 15  | 11    |          |
| S. aeruginosa (Gram negative)         |                                                     |     |       |          |
| S1                                    |                                                    | 14  | 14    |          |
| S2                                    |                                                    | 13  | 15    |          |
| S3                                    |                                                    | 14  | 12    |          |
| S4                                    |                                                    | 15  | 12    |          |
| S. aureus (Gram positive)             |                                                     |     |       |          |
| S1                                    |                                                    | 9   | 7     |          |
| S2                                    |                                                    | 8   | 9     |          |
| S3                                    |                                                    | 8   | 8     |          |
| S4                                    |                                                    | 11  | 7     |          |
The active species from Cr-doping and reduced crystallite size has direct effect on the cellular inhibition. Surface morphology also gave a higher antibacterial activity. The enhanced antibacterial performance of the nano size particle was attributed to the high surface charge and reactive oxygen species (ROS) formation. A strong antibacterial activity against gram-negative was also due to the increase in H$_2$O$_2$ produced from MgO−Bi$_2$O$_3$ surface which is lethal to the bacteria. On the other hand, this might also be due to the difference in the cell structure of the bacteria. As the gram-positive bacteria have a thick lipopolysaccharide cell membrane as related to gram-negative bacteria. The production of heavy metallic ions (Bi$^{3+}$, Mg$^{2+}$ and Cr$^{3+}$) is the second reason for the antibacterial activity. Because of the presence of thiol group (−SH) in the proteins on outer surface of the cell membrane, the metallic ions Bi$^{3+}$, Mg$^{2+}$ and Cr$^{3+}$ are attracted to the cell membrane. The metallic ions then penetrate the cell membrane and denature proteins, hence, causing damage to the membrane of the bacterial cell. In addition, the texture of the nanocomposite surface causes mechanical damage to the membrane.

In this regard, surface defects such as oxygen vacancies and Bi, Mg and Cr interstitial defects have been reported to be the most crucial and matter of intensive research. As in our case, the shape remains unchanged with addition of Cr content and the only variation is in the defects densities as suggested by SEM results.

Conclusions

Samples with nominal starting compositions MgO−Bi$_{2-x}$Cr$_x$O$_3$ (x = 0 and 0.07) nanocomposites were prepared by using a low-cost solvent-deficient method. The phase of MgO−Bi$_{2-x}$Cr$_x$O$_3$ was estimated using XRD method which showed that the samples were dominantly monoclinic crystalline structure of α-Bi$_2$O$_3$ phase at x = 0 and there was no peaks attributed to MgO in the composite. Partial substitutions of Cr in place of Bi in MgO−Bi$_2$O$_3$ showed the tetragonal BiCrO$_3$ phase. Partial substitution of Cr in place of Bi in MgO−Bi$_2$O$_3$ showed a decrease in the crystallite size of MgO−Bi$_2$O$_3$. SEM micrographs showed that the grains were aggregated and uniformly distributed with micrometer size. EDXA revealed the elemental composition of MgO−Bi$_{2-x}$Cr$_x$O$_3$. Uv−Vis spectra showed that MgO−Bi$_{2-x}$Cr$_x$O$_3$ can be applied in optoelectronics, photonic and optical communication. Direct transition $E_g$ decreased with Cr-doping in place of Bi in MgO−Bi$_2$O$_3$ from 3.14 to 2.77 eV. The Cr-doped MgO−Bi$_2$O$_3$ exhibited two energy gaps at 2.36 and 2.76 eV. Cr-doping decreased the inhibitory activity of MgO−Bi$_{2-x}$Cr$_x$O$_3$ nanocomposite against the different types of bacteria.

Data availability

The datasets generated and/or analysed during the current study are available from the corresponding author on reasonable request.

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Author contributions

A.A.-S. designed, performed the experiments, analysed the results and wrote the draft of the manuscript. A.A.-S., K.S.S.S. and A.A.-O. designed, performed the experiments and analysed the results. R.A.-S. designed the research and wrote the final draft. All authors reviewed the final version of the manuscript.
Competing interests
The authors declare no competing interests.

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