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# Structural, optical, magnetic, and enhanced antibacterial properties of hydrothermally synthesized Sm-incorporating $\alpha$ -MoO<sub>3</sub> 2D-layered nanoplates

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In this study, we have synthesized pristine and [0.5, 1.5, and 2.5] M% samarium (Sm)-incorporating  $\alpha$ -MoO<sub>3</sub> 2D-layered nanoplates utilizing a facile hydrothermal process, and investigated the physical properties along with antibacterial effectiveness. X-ray diffraction (XRD) patterns confirmed the single-phase, stable orthorhombic polycrystalline structure of the as-prepared samples. The crystallite size, lattice strain, and dislocation density were measured using both Debye–Scherrer (D–S) and Williamson–Hall (W–H) techniques. Both pristine and Sm-incorporating  $\alpha$ -MoO<sub>3</sub> samples showed two-dimensional (2D) layered nanoplate-type surface morphology, revealed by field emission scanning electron microscopy (FE-SEM) images. Energy dispersive X-ray spectroscopy (EDS) confirmed the presence of Sm contents in the  $\alpha$ -MoO<sub>3</sub> matrix. After Sm incorporation in  $\alpha$ -MoO<sub>3</sub>, the different functional groups as well as vibrational groups were observed by Fourier-transform infrared (FTIR) spectroscopy and Raman spectroscopy analyses, respectively. The optical band gaps were measured from UV-vis diffuse reflectance spectroscopy (DRS) by employing the Kubelka–Munk formula and interestingly it is found that the bandgap energy ( $E_g$ ) gradually decreased from 2.96 to 2.83 eV with the increment of Sm content. When compared to pristine  $\alpha$ -MoO<sub>3</sub>, the Sm-incorporating samples experienced a steady improvement in room temperature ferromagnetic (RTFM) behavior as Sm content increased, as measured by hysteresis loops. The antibacterial activities of both samples were assessed against Gram-positive: *Staphylococcus aureus* (*S. aureus*), and Gram-negative: *Escherichia coli* (*E. coli*) and *Salmonella enteritidis* (*S. enteritidis*) bacteria by the agar well diffusion method and enhanced antibacterial activity was observed as the Sm concentration increased, compared to pristine nanoplates. The obtained results suggest that the synthesized Sm-incorporating  $\alpha$ -MoO<sub>3</sub> 2D-layered nanoplate could be a potential antibacterial agent.

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## 1 Introduction

Because of the large influence on patient wellbeing and environmental safety issues, healthcare-associated (nosocomial) infections (HAIs) have been a serious worry among scientists in recent years due to rapidly rising death rates and increasing annual costs for HAI prevention.<sup>1,2</sup> The ubiquitous nature and

ability of bacteria in the environment to grow, transfer, and develop multidrug resistance are significant challenges in this sector. A variety of detailed studies are required to produce new and effective antibacterial drugs to eliminate the ever-increasing concerns about bacterial infections. Nanotechnology, a new multidisciplinary discipline combining physics, chemistry, biology, and materials science, has enabled the most promising new insights to overcome the drawbacks of current antimicrobial treatments and the ongoing growth of bacterial resistance.

The increased interest in nanomaterials, particularly inorganic nanomaterials, for bioscience applications is due to their distinct features such as the high surface area to volume ratio, uniform size, shape, size distribution, morphology, surface functionalization, improved stability, and safety compared to organic antimicrobial agents.<sup>3–7</sup> Antimicrobial nanostructures offer a wide range of uses, including antibacterial textiles, catheter devices, biofilm suppression, and additions in paints

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for antimicrobial surfaces, among others.<sup>8</sup> In the last few decades, antimicrobial characteristics of nanoparticles such as Ag, Au, Cu, ZnO, CuO, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, CaO, Fe@Co<sub>3</sub>O<sub>4</sub>, MoS<sub>2</sub>, and MgO have become an interesting area of investigation.<sup>9–13</sup> However, these oxide materials' limited active surface area, low durability, significant cytotoxicity in nature, and high costs limit their applicability as antibacterial devices. As a result, the scientific community faces a challenge in producing a new antibacterial agent using a low-cost nano-oxide material. Among several reported semiconductor nanomaterials, detailed studies of ZnO, CuO, Fe<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> have been reviewed and reported by several groups as compared to other materials as antimicrobial agents.<sup>14–18</sup>

Transition metal oxides (TMO) have recently received a lot of study attention due to their wide range of prospective applications in the emerging fields of photodetectors,<sup>19</sup> thin-film transistors,<sup>20</sup> photo-catalytic, optoelectronic, magneto-optic, photonic, gas sensors, transparent conductors, and photovoltaic solar cells, among others.<sup>21–27</sup> These materials can be used by incorporating transition metal (TM) ions into cation sites in host conventional semiconductors like MoO<sub>3</sub>, ZnO, and TiO<sub>2</sub>, and then introducing ferromagnetic properties into nonmagnetic semiconductors, allowing for simultaneous utilization of charge and spin carriers.<sup>28–30</sup> Moreover tuning the properties of various nanostructured materials like CdS, boron nitride (BN), PbS, and PbO have received attention for various applications.<sup>31–33</sup>

Molybdenum trioxide (MoO<sub>3</sub>), in particular, among intrinsic n-type II–VI semiconductors, has a wide direct band gap of 2.8–3.2 eV at room temperature.<sup>34</sup> One of the most important and extensively studied TMO is MoO<sub>3</sub> because of its rich chemistry associated with multiple states, high thermal-chemical stability, suitable electronic, electrical, and optical properties, and numerous potential technological applications in the fields of spintronic devices, optoelectronic devices, magneto-optic devices, photonic devices, organic light-emitting diodes (OLEDs), charge injection or extraction layer in organic photovoltaic (OPVs), gas sensors, transparent conductors, photo-catalytic, and photovoltaic solar cells.<sup>35,36</sup>

There are three basic crystal forms in MoO<sub>3</sub> material. The orthorhombic MoO<sub>3</sub> phase ( $\alpha$ -MoO<sub>3</sub>) is based on an octahedral MoO<sub>6</sub> basis, with all of the MoO<sub>3</sub> components sharing edges and corners, resulting in a zigzag chain and layered structure.<sup>37</sup> Whereas, there are two metastable MoO<sub>3</sub> phases namely monoclinic MoO<sub>3</sub> ( $\beta$ -MoO<sub>3</sub>) and hexagonal MoO<sub>3</sub> (h-MoO<sub>3</sub>) exist. It is necessary to modify the physical properties of MoO<sub>3</sub> nanoparticles to expand their applications in a variety of nanotechnology sectors, and this tuning may be accomplished *via* a variety of methods, including doping, annealing, and modifying production techniques.<sup>38,39</sup>

Doping, or the inclusion of a particular extrinsic element, is another straightforward, practical, and very effective method for altering and/or enhancing many properties of fundamental materials, such as electrical, magnetic, and optical capabilities.<sup>40</sup> Thus, as previously reported, the characteristics of MoO<sub>3</sub> may be altered by alloying it with a variety of elements such as cobalt (Co),<sup>29</sup> europium (Eu),<sup>41</sup> and dysprosium (Dy).<sup>42</sup> It is important to consider the radius of the dopant element since

dopant atoms with comparable radii are recommended for producing compounds with minimum lattice imperfections.<sup>42</sup> Previously many research groups had replaced the small ionic radius Mo<sup>6+</sup> (0.65 Å) with various larger ionic (0.74–0.97 Å) elements like Eu<sup>3+</sup> (0.96 Å),<sup>43</sup> Cd<sup>2+</sup> (0.97 Å),<sup>44</sup> Ce<sup>3+</sup> (0.87 Å),<sup>45</sup> Dy<sup>3+</sup> (0.91 Å),<sup>46</sup> Zn<sup>2+</sup> (0.74 Å),<sup>47</sup> and Tb<sup>3+</sup> (0.92 Å)<sup>48</sup> in order to get the desired properties for various applications. The benefit of doping metal oxides with rare earth metals such as Dy, Sm Ce, *etc.* is that the 4f empty orbitals make them easily mix with functional groups. Additionally, doping rare earth metals leads in an absorbance shift to the visible portion of the electromagnetic spectrum by manipulating structural parameters. As the rare-earth samarium ion (Sm<sup>3+</sup>) has a radius of 1.08 Å, therefore, it would also be a good dopant for replacing the Mo ion (Mo<sup>6+</sup>) in the MoO<sub>3</sub> lattice. Some recent reviews on rare-earth oxides and rare-earth elements as doping agents in various applications are also notable.<sup>49–54</sup> Another significant parameter affecting the quality of nanostructured materials is the annealing temperature. Several studies have been conducted on the influence of annealing temperature on unincorporated MoO<sub>3</sub> nanomaterials.<sup>46,55</sup>

The properties of generated nanostructures vary according to their size, shape, and many aspects such as synthesis processes. Thus far, unincorporated and incorporated nanostructured  $\alpha$ -MoO<sub>3</sub> may be manufactured utilizing a variety of approaches, including hydrothermal synthesis, solution combustion synthesis, and probe ultrasonic synthesis, among others, to enhance the performance of these nanomaterials.<sup>40,56</sup> Each synthesis approach offers several distinct benefits over others. According to a review of the literature, the hydrothermal process is the most practical and effective method for modifying the size, shape, and other features of nanomaterials. Furthermore, the hydrothermal process is an enthralling, simple, affordable, and successful strategy.<sup>43,57</sup> However, the effects of Sm-incorporated in nanostructured  $\alpha$ -MoO<sub>3</sub> synthesized by the hydrothermal method have not been explored so far.

In this work, nanostructured pristine  $\alpha$ -MoO<sub>3</sub> and [0.5, 1.5, and 2.5 M%] Sm-incorporated  $\alpha$ -MoO<sub>3</sub> were synthesized by a facile environment-friendly hydrothermal approach. The effect of Sm incorporation on the microstructural (lattice parameters, average crystallite size, crystalline nature, *etc.*), morphological, functional, Raman, optical and magnetic properties of the  $\alpha$ -MoO<sub>3</sub> nanoplates are then investigated comprehensively using a variety of characterization techniques such as FE-SEM, XRD, EDX, FTIR, Raman spectroscopy, UV-vis spectroscopy, and a vibrating sample magnetometer (VSM) of a Quantum Design Physical Property Measurement System (PPMS). In addition, the antimicrobial activity of both samples was investigated against one Gram-positive (*S. aureus*) and two Gram-negative (*E. coli* and *S. enteritidis*) bacteria by the agar well diffusion method.

## 2 Experimental details

### 2.1 Materials

The ammonium heptamolybdate tetrahydrate (AHM), (NH<sub>4</sub>)<sub>6</sub>-Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, was employed as the precursor material of Mo for the hydrothermal synthesis of pristine and [0.5, 1.5, 2.5] M%



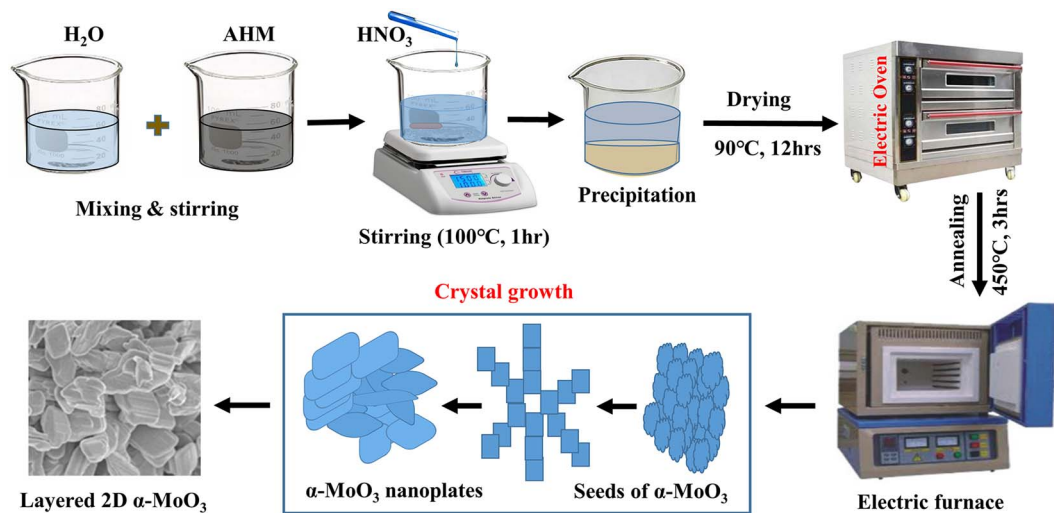
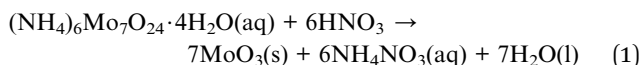


Fig. 1 The schematic diagram for the synthesis of pristine and Sm-incorporated  $\alpha$ -MoO<sub>3</sub> nanoplates.

Sm-incorporated  $\alpha$ -MoO<sub>3</sub> samples. Samarium(III) oxide (Sm<sub>2</sub>O<sub>3</sub>) was used as the source of the samarium. Other chemicals including concentrated nitric acid (37% HNO<sub>3</sub>), de-ionized (DI) water, and ethanol were utilized in this process. All chemicals (Sigma Aldrich Ltd, USA) were analytical grades used without further purification.

## 2.2 Nanoplates preparation

To obtain a pure MoO<sub>3</sub> sample, 6 g of AHM was dissolved in 250 mL de-ionized (DI) water. The aqueous solution was magnetically stirred for 1 h at 75 rpm at room temperature. After that to achieve yellow precipitation, 24.5 mL of 37% HNO<sub>3</sub> was added drop by drop at 100 °C for 1 h using a hotplate with magnetic stirring. The precipitated MoO<sub>3</sub> was cleaned several times with ethanol and DI water. Following that, the washed MoO<sub>3</sub> was desiccated for 12 h at 90 °C in an electric oven to obtain MoO<sub>3</sub> nanopowders. Finally, the resulting MoO<sub>3</sub> nanopowder was annealed at 450 °C for 3 h in an electric furnace to obtain the final product of  $\alpha$ -MoO<sub>3</sub> nanoplates. The above procedures were followed to obtain 0.5, 1.5, or 2.5 M% Sm-incorporated  $\alpha$ -MoO<sub>3</sub> nanoplates. For this, the required amount of samarium(III) oxide (Sm<sub>2</sub>O<sub>3</sub>) was added with AHM. The possible chemical reaction to synthesize  $\alpha$ -MoO<sub>3</sub> is given by eqn (1). In Fig. 1, the creation of  $\alpha$ -MoO<sub>3</sub> nanoplates is depicted as well.



## 2.3 Characterization

An X-ray diffractometer (3040-X'Pert PRO, Philips) was used to collect the X-ray diffraction (XRD) patterns of the pure and Sm-incorporated MoO<sub>3</sub> powder samples to evaluate phase purity and structural features. XRD analysis was performed using CuK $\alpha$  radiation of wavelength 1.54056 Å, where  $2\theta = 10^\circ$  to  $70^\circ$ , operating voltage = 40 kV, current = 30 mA, and scanning speed =  $1^\circ \text{ min}^{-1}$ . An FE-SEM integrated with EDS (JEOL JSM-7600F)

was utilized to investigate the surface morphologies along with elemental composition<sup>58,59</sup> of the synthesized samples, where the accelerating electric field was 5 kV. An FTIR (FTIR-ATR, Model: PerkinElmer Spectrum Two) with a scanning wavenumber range of 4000–400 cm<sup>-1</sup> was used to identify the existing functional groups. A confocal Raman spectrometer (Monovista CRS+500) was used to obtain the Raman spectra with laser excitation at 532 nm. The optical investigation was carried out using a UV-vis DRS (Lambda 1050, PerkinElmer, USA) in the wavelength range of 250 to 800 nm. A vibrating sample magnetometer (VSM) of a Quantum Design PPMS was used to measure magnetic characteristics at room temperature.

## 2.4 Antibacterial testing of pristine and Sm-incorporated $\alpha$ -MoO<sub>3</sub> nanoplates

The antimicrobial effects of pristine and Sm-incorporated  $\alpha$ -MoO<sub>3</sub> nanoplates against a Gram-positive bacterium, *Staphylococcus aureus* (ATCC 6538), and two Gram-negative bacteria, *Escherichia coli* (ATCC 8739) and *Salmonella enterica* (ATCC 14028) were analyzed using the agar well diffusion method with Mueller–Hilton Agar (MHA). Bacterial strains were cultured on Nutrient Agar media overnight at 37 °C. The bacterial colonies were suspended in 10 mL of sterile normal saline. Using UV-vis spectroscopy (Hitachi, Model: U-2910, Japan), the optical density (OD) was recorded at 580 nm and adjusted to achieve a cell density of 10<sup>6</sup>–10<sup>7</sup> CFU mL<sup>-1</sup>. The good diffusion experiment was performed by pouring 25 mL of sterile MHA into Petri plates and allowing them to set. MHA plates were uniformly infected after solidification by swabbing test microorganisms with sterile cotton buds. Wells were bored into MHA plates after swabbing with a sterile borer (6 mm in diameter). Then, 100  $\mu$ l of each concentration of 20 k, 40 k, 50 k, and 80 k ppm pristine and Sm-incorporated  $\alpha$ -MoO<sub>3</sub> were added to each well. The plates were then incubated for 24 hours at 37 °C. To examine the antibacterial properties of both pristine and Sm-incorporated  $\alpha$ -MoO<sub>3</sub>, the zone of inhibition (ZOI) was measured in millimeters after incubation with a slide caliper.



### 3 Results and discussion

#### 3.1 Structural properties

Fig. 2 demonstrates the XRD patterns of as-prepared pristine and [0.5, 1.5, 2.5] M% Sm-incorporated MoO<sub>3</sub> powder samples. The diffracted peaks at (020), (110), (040), (021), (111), (060), (002), and (081) planes are clearly distinguishable which are well-matched with the orthorhombic phase of MoO<sub>3</sub> (JCPDS # 05-0508) with space group *Pbnm* having  $a = 3.962 \text{ \AA}$ ,  $b = 13.858 \text{ \AA}$ ,  $c = 3.697 \text{ \AA}$ .<sup>60</sup> All samples show polycrystalline in nature. The sharp and well-defined peaks indicate a good crystalline structure and the absence of unwanted peaks confirms the phase purity of all samples. The most intense peak (021) at 27.28° of pristine  $\alpha$ -MoO<sub>3</sub> is defined as the preferred orientation and no remarkable shifting was observed after the incorporation of Sm into the MoO<sub>3</sub> lattice. The lattice parameters determined from equation<sup>61</sup> are  $a = 3.962 \text{ \AA}$ ,  $b = 13.858 \text{ \AA}$ , and  $c = 3.697 \text{ \AA}$ , which are in good agreement with the literature values and presented in Table 1. Using Debye Scherrer (D-S) equation (eqn (2)),<sup>42</sup> the crystallite size ( $D_{D-S}$ ) is determined from the full width at half maximum (FWHM) values of the XRD peaks.

$$D_{D-S} = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

Where,  $D_{D-S}$ ,  $\lambda$ ,  $K$ ,  $\beta$ , and  $\theta$  signify the crystallite size, X-ray wavelength ( $\lambda = 1.54056 \text{ \AA}$  for CuK $\alpha$ ), shape factor ( $K = 0.90$ ), FWHM of the corresponding diffraction peak (in radian) positioned at  $2\theta$ , and Bragg angle (in degree), respectively. With the inclusion of Sm<sup>3+</sup> atoms, the lattice strain ( $\epsilon$ ) and dislocation density ( $\delta$ ) develop in the  $\alpha$ -MoO<sub>3</sub> lattice which can be determined from the Stokes–Wilson formula eqn (3) and eqn (4), respectively.<sup>62</sup>

$$\epsilon = \frac{\beta}{4 \tan\theta} \quad (3)$$

$$\delta = \frac{1}{D^2} \quad (4)$$

Table 2 summarizes the estimated crystallite sizes, dislocation density, lattice strain, and other parameters. According to Table 2, the average crystallite sizes ( $D_{D-S}$ ) considering all major peaks estimated from Debye–Scherrer formula is 44.8, 40.6, 35.8, and 39.8 nm for 0, 0.5, 1.5, and 2.5 M% Sm-incorporated  $\alpha$ -MoO<sub>3</sub>, respectively. The  $D_{D-S}$  value declined steadily from 44.8 to 35.8 nm up to 1.5 M% Sm, then increased slightly for 2.5 M% but was still lower than the pristine sample. As a result, the incorporated samples exhibited reduced crystallites. It's important to note that the corresponding dislocation density and strain values follow the reverse way of  $D_{D-S}$  assessed from Debye–Scherrer formula. To get more precise crystallographic properties, the Williamson–Hall (W-H) method is used.<sup>63</sup> The W-H approach is the most often employed method that takes into account size (Scherer) broadening ( $\beta_D$ ), and strain broadening ( $\beta_S$ ). Using this technique, eqn (5) represents the individual contribution to the broadening of reflection.

$$\beta = \beta_D + \beta_S \quad (5)$$

Applying the formula  $\beta_D = \beta_D = \frac{k\lambda}{D \cos\theta}$  and  $\beta_S = 4\epsilon \tan\theta$ , one gets eqn (6).

$$\beta = \frac{k\lambda}{D \cos\theta} + 4\epsilon \tan\theta \quad (6)$$

The crystallite size,  $D_{WH}$  and lattice strain,  $\epsilon_{WH}$ , are calculated using the following format (eqn (7)) of the above equation (eqn (6)):

$$\beta \cos\theta = \frac{k\lambda}{D_{WH}} + 4\epsilon_{WH} \sin\theta \quad (7)$$

The linear equation (eqn (7)) is known as the W-H equation. As illustrated in Fig. 3, the lattice strain ( $\epsilon_{WH}$ ) and crystallite size ( $D_{WH}$ ) of pristine and Sm-incorporated  $\alpha$ -MoO<sub>3</sub> can be estimated from the slope and y-intercept of linear fitted eqn (7), respectively. Using Fig. 3, the measured values of crystallite size ( $D_{WH}$ ) are found to be 45.0, 41.5, 44.6, and 44.9 nm for 0, 0.5, 1.5, and 2.5 M% Sm-incorporated  $\alpha$ -MoO<sub>3</sub>, respectively. It can be noted that the reduction of  $D_{WH}$  as well as the increment of

Table 1 Lattice parameters ( $a$ ,  $b$ ,  $c$ ) of pristine and Sm-incorporated  $\alpha$ -MoO<sub>3</sub>

Sample (M%)	Lattice parameters		
	$a$ (Å)	$b$ (Å)	$c$ (Å)
0%	3.9675	13.9223	3.6981
0.5%	3.9633	13.9351	3.6981
1.5%	3.9638	13.9351	3.6983
2.5%	3.9642	13.9128	3.6975

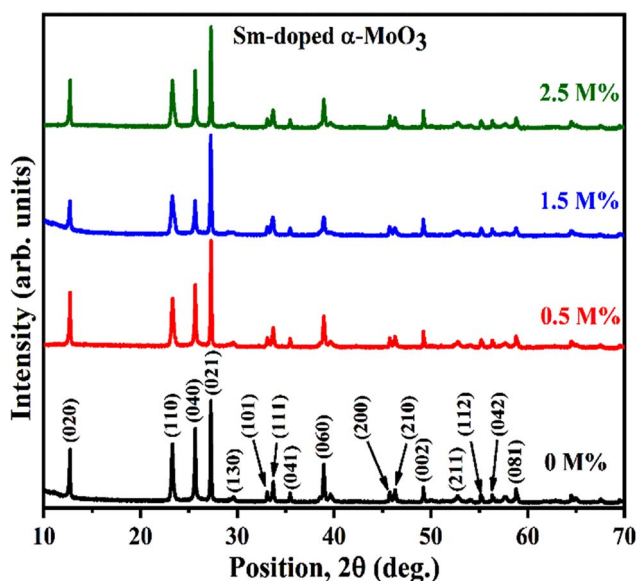
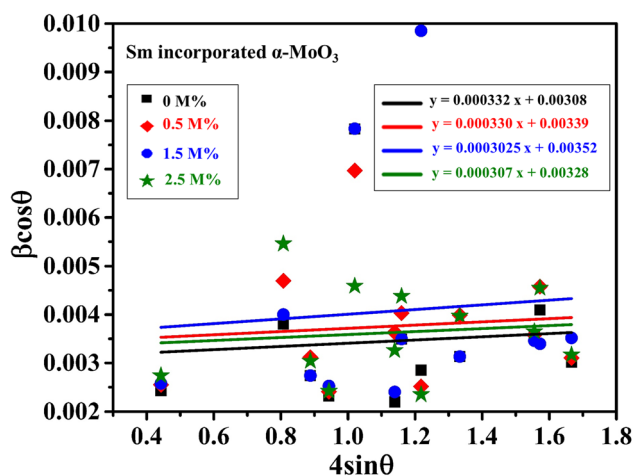


Fig. 2 XRD patterns of pristine and Sm-incorporated  $\alpha$ -MoO<sub>3</sub> nanoparticles.



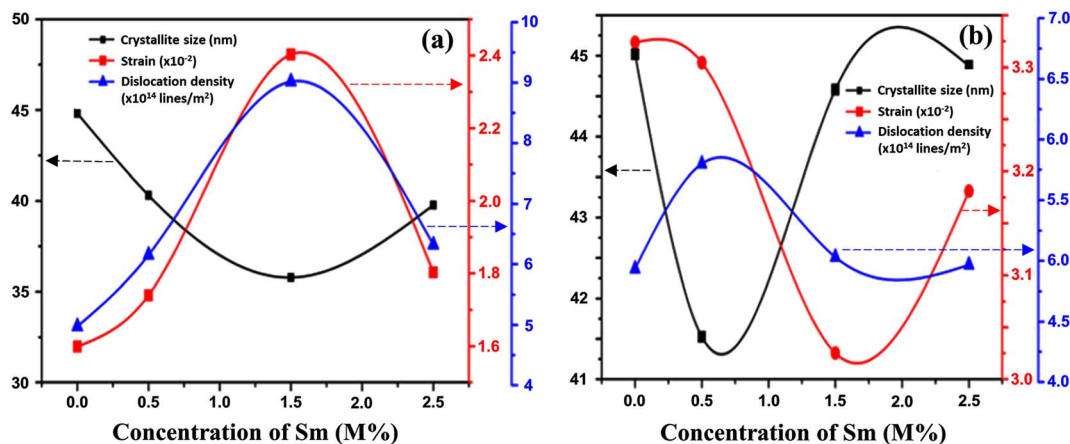
Table 2 Structural parameters for pristine and Sm-incorporated  $\alpha$ -MoO<sub>3</sub>

Sample (M%)	Debye-Scherrer method			W-H method				
	Strain, $\epsilon \times 10^{-2}$	$\delta$ (lines per m <sup>2</sup> ) $\times 10^{14}$	$D$ (nm)	Strain, $\epsilon_{WH} \times 10^{-4}$	$\delta$ (lines per m <sup>2</sup> ) $\times 10^{14}$	$D_{WH}$ (nm)	SF	Crystallinity (%)
0%	1.60	4.98	44.8	3.32	4.93	45.0	0.10	72.1%
0.5%	1.74	6.15	40.6	3.30	5.80	41.5	0.11	56.6%
1.5%	2.40	9.02	35.8	3.02	5.03	44.6	0.15	66.7%
2.5%	1.80	6.32	39.8	3.18	4.97	44.9	0.11	70.7%

Fig. 3 W-H plot assuming UDM of 0.0, 0.5, 1.5, and 2.5 M% Sm-incorporated  $\alpha$ -MoO<sub>3</sub>.

$\epsilon_{WH}$  and  $\delta$  resembles the Debye-Scherrer trend. The varied nature of structural characteristics calculated using both methods are presented in Table 2 and the graphical representation is depicted in Fig. 4(a) and (b). According to calculated crystallite size values in both Debye-Scherrer and Williamson-Hall (W-H) formulae, a deterioration of crystallinity is observed as the crystallite size decreases from pristine to 1.5 M% Sm incorporated samples. The crystallite size is decreasing

which might be the segregation of crystallites into smaller ones. In another way, the crystallite size decreases with increasing Sm amount, which may be attributed to the Sm cation interfering with the  $\alpha$ -MoO<sub>3</sub> crystalline lattice. This interference effect could be attributable to the deformation of the crystal lattice caused by the larger ionic radius of Sm<sup>3+</sup> (1.04 Å) compared to Mo<sup>6+</sup> (0.74–0.97 Å). The lattice expands as the Sm concentration rises, which is also caused by the higher ion radius of Sm than that of Mo resulting in the declination of crystallinity.<sup>64</sup> Lattice strain is a measurement of the distribution of lattice constants brought on by crystal defects, particle size, dislocations, and oxygen vacancies, and more information regarding the number of crystal defects in the materials is revealed by the dislocation density. But for 2.5 M% Sm-incorporated  $\alpha$ -MoO<sub>3</sub>, the strain and dislocation density showed lower values and inversely crystallite size increased slightly. Here, it was expected to the movement of defects and atoms for a larger amount (2.5 M%) of Sm, and thus consequently, a larger cluster was formed due to the agglomeration of minute crystallites by crumbling the grain boundary that enhances the average crystallite size.<sup>63</sup> Some research groups reported a similar trend of change in crystallite size after doping. For example, Boukhachem *et al.*<sup>7</sup> investigated the Sn-doped MoO<sub>3</sub>, and observed a considerable increase in crystallite size for 1 and 2 M% and then decreased for 3 and 4 M% Sn-doped MoO<sub>3</sub>. Similarly, Al-Otaibi *et al.*<sup>8</sup> studied Zn-doped MoO<sub>3</sub> nanobelts and found that the crystallite size increased from 42.63 to 46.56 nm for 2 wt% Zn doping,

Fig. 4 Changes in strain, dislocation density, and crystallite size with Sm concentration variation in  $\alpha$ -MoO<sub>3</sub> using (a) Debye-Scherrer, and (b) Williamson-Hall methods.

decreased to 45.30 nm for 2.5 wt% Zn, increased to 51.98 nm for 3.3 wt% Zn, and finally decreased to 43.07 nm for 5 wt% Zn. The stacking fault indicates the crystal imperfections follow the decrement trend of  $\epsilon_{\text{WH}}$  and  $\delta$ . The crystallinity trended in the same manner as the crystallite size. The intensity and full width at half maximum (FWHM) of the XRD peaks are widely considered indicators of crystallinity and crystallite size.

### 3.2 Surface morphology and elemental analysis

Fig. 5(a)–(d) show the FE-SEM images of surface morphology of pristine and Sm-incorporated  $\alpha$ - $\text{MoO}_3$  nanoplates. The multi-layered heap structure was clearly constructed from a two-dimensional (2D) nanoplate-like structure of  $\alpha$ - $\text{MoO}_3$ . To build these 2D layered  $\alpha$ - $\text{MoO}_3$  structures, these layers are stacked in a staggered pattern and possibly held together by weak van der Waals forces.<sup>65</sup> In the FE-SEM micrographs shown in Fig. 5(a)–(d), the number of convolution layers ranges from three to forty-four. The thickness of a stack constructed with 44 layers is about 1  $\mu\text{m}$ . A similar nanoplate morphology has been reported by various research groups.<sup>66,67</sup> The FE-SEM images of the doped and pristine  $\alpha$ - $\text{MoO}_3$  samples show almost identical structures.

EDS has been used to determine the percentages of basic compositions present in the experimental samples. Fig. 6(a)–(d) show the EDS profile of pristine and doped  $\text{MoO}_3$  nanoplates respectively. The elemental mass and atoms' presence is shown

in Table 3. In Fig. 6(a) the EDS spectra peak at 0.525 keV and 2.36 keV confirm oxygen (O) and molybdenum (Mo), respectively. The atomic percentage shows the molar ratio of Mo : O is around 1 : 3 confirming the stoichiometry of  $\text{MoO}_3$ . The EDS peak at 2.36 keV in Fig. 6(b)–(d) shows the Sm-incorporation in  $\alpha$ - $\text{MoO}_3$  nanoplates. As the atomic percentages of Sm increase with doping percentage variation are clearly in Table 3 confirmed that Sm was successfully incorporated into the  $\alpha$ - $\text{MoO}_3$  matrix.

### 3.3 Functional properties

Functional groups have been identified at room temperature using Fourier transform infrared (FTIR) spectroscopy. Fig. 7 reveals the FTIR spectra of all samples in the wavenumber range of 400 to 4000  $\text{cm}^{-1}$  (desired range 1000 to 450  $\text{cm}^{-1}$ ). All (pristine and Sm-incorporated)  $\alpha$ - $\text{MoO}_3$  samples show three main characteristic vibrational bands of orthorhombic crystal structure ( $\alpha$ - $\text{MoO}_3$ ) and no unwanted vibrational bands, confirming the chemical stability of the orthorhombic phase of as-synthesized materials after Sm incorporation and which results support the XRD examination. The two major vibrational zones (*i.e.*, 1000–600  $\text{cm}^{-1}$  and 600–400  $\text{cm}^{-1}$ ) were observed in the spectra of all the samples. Four significant vibrational peaks are seen in the IR spectra of pristine  $\alpha$ - $\text{MoO}_3$  nanoplates, located at 570.45, 812.88, 861.06, and 982.58  $\text{cm}^{-1}$ , respectively; where a weaker peak is observed at 486.26  $\text{cm}^{-1}$ . For pristine  $\alpha$ - $\text{MoO}_3$ ,

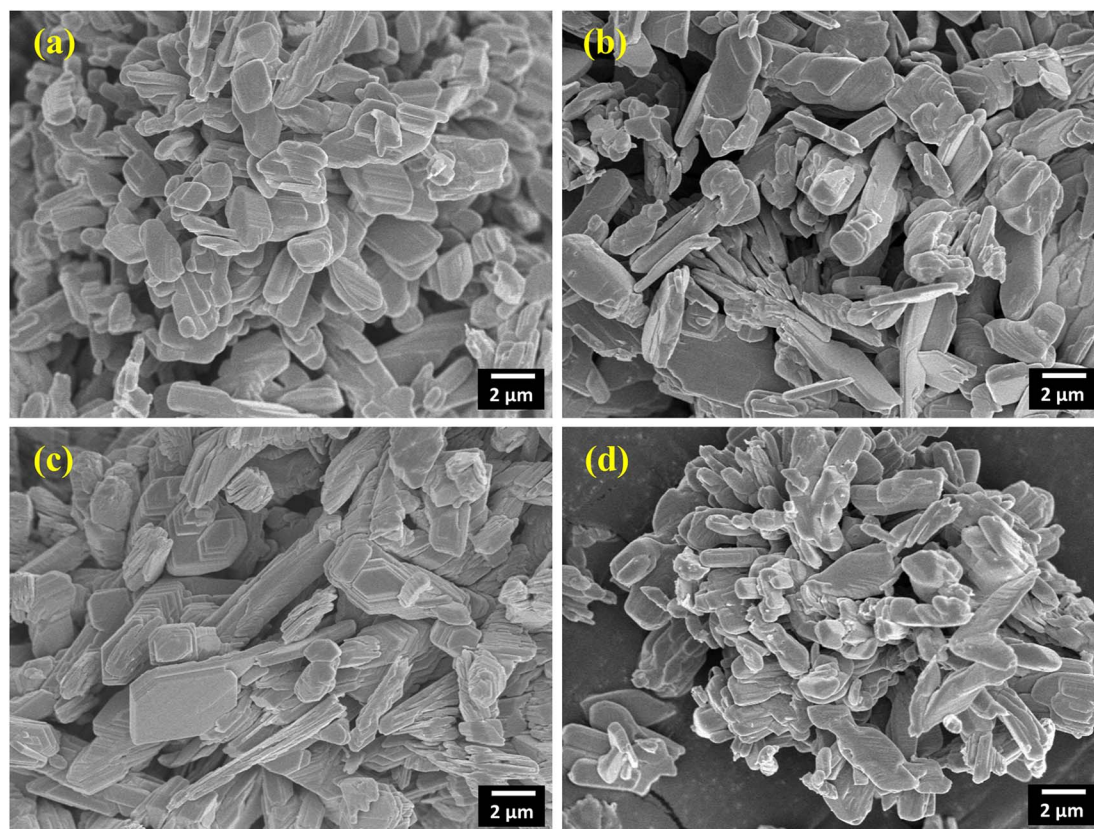


Fig. 5 2D layered nanoplate type micrographs of (a) pristine (b) 0.5 M%; (c) 1.5 M% and (d) 2.5 M% Sm-incorporated  $\alpha$ - $\text{MoO}_3$ .



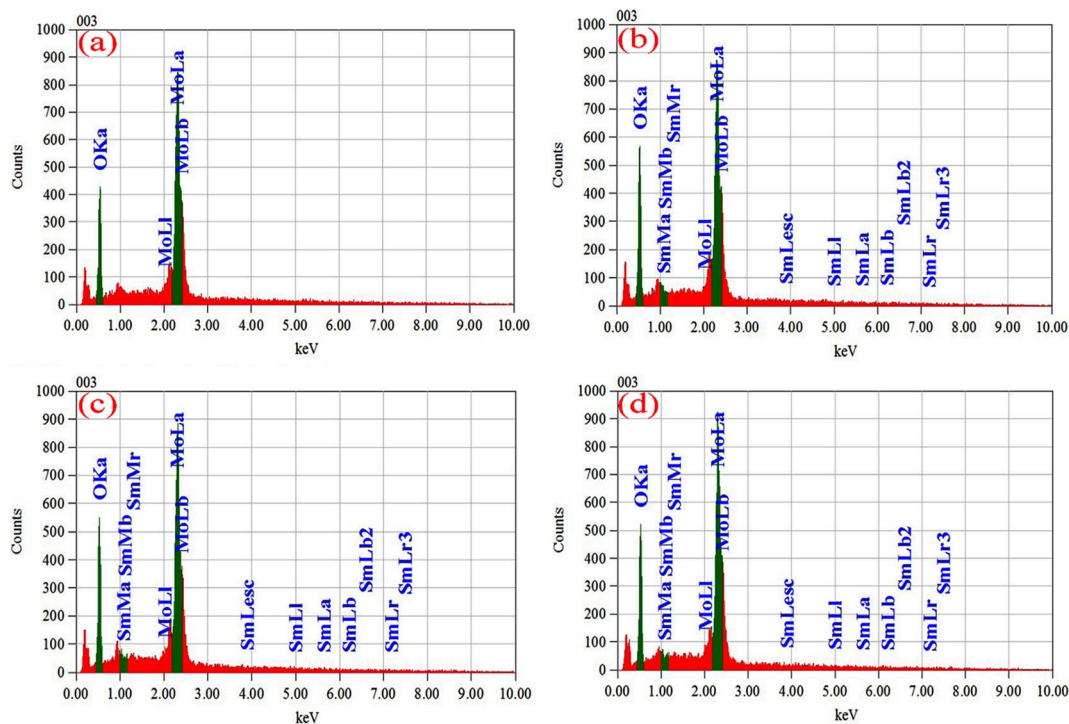


Fig. 6 EDX spectra of (a) pristine, (b) 0.5 M%, (c) 1.5 M%, (d) 2.5 M% Sm-incorporated  $\alpha$ -MoO<sub>3</sub> nanoplate.

Table 3 The mass% and atom% of pristine and Sm-incorporated  $\alpha$ -MoO<sub>3</sub>

Sample	Elements	Mass%	Atom%
Pure $\alpha$ -MoO <sub>3</sub>	O	37.40	78.18
	Mo	62.60	21.82
0.5% Sm-incorporated $\alpha$ -MoO <sub>3</sub>	O	30.48	72.45
	Mo	68.67	27.26
1.5% Sm-incorporated $\alpha$ -MoO <sub>3</sub>	Sm	0.85	0.29
	O	38.73	78.66
	Mo	60.15	20.89
2.5% Sm-incorporated $\alpha$ -MoO <sub>3</sub>	Sm	1.12	0.45
	O	29.03	70.31
	Mo	69.27	28.96
	Sm	1.70	0.73

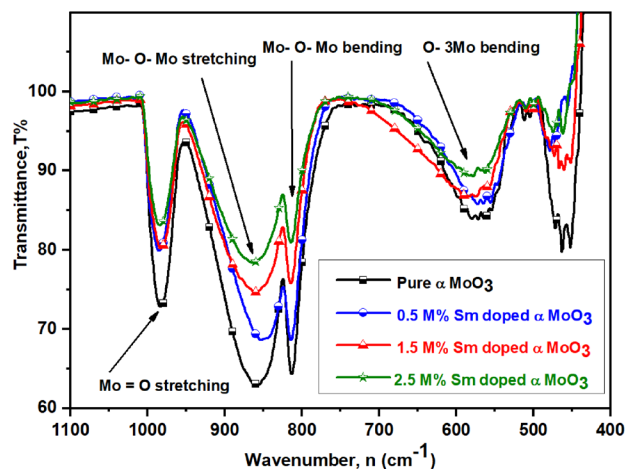


Fig. 7 FTIR spectra of pristine and Sm-incorporated  $\alpha$ -MoO<sub>3</sub> nanoplates.

the sharp and intense peak at 982.58 cm<sup>-1</sup> corresponds to the stretching vibration between oxygen and molybdenum atoms (Mo=O), which confirms the possible layered orthorhombic phase ( $\alpha$  phase) or structure of MoO<sub>3</sub>.<sup>67–69</sup> This band is found at 981.82, 981.82, and 983.48 cm<sup>-1</sup> for 0.5, 1.5, and 2.5 M% Sm-incorporated  $\alpha$ -MoO<sub>3</sub>, respectively.

The pristine sample has a highly-intense signal at 861.06 cm<sup>-1</sup>, which is attributed due to stretching vibrations of the bridge oxygen bond (O–Mo–O)<sup>56</sup> and is seen at 860.15, 861.82, 861.82 cm<sup>-1</sup> for 0.5, 1.5, and 2.5 M% Sm-incorporated  $\alpha$ -MoO<sub>3</sub>, accordingly. Interestingly, it is clearly seen that the peak intensity of stretching vibration of O<sub>(3)</sub> atoms in the Mo–O–Mo units gradually decreased with rising Sm concentration in  $\alpha$ -MoO<sub>3</sub> whereas almost no change in peak location is observed. A strongly sharp band is identified ascribed for Mo–O–Mo

bending vibration located at the same position (812.88 cm<sup>-1</sup>) of pristine and all Sm-incorporated  $\alpha$ -MoO<sub>3</sub> samples although peak intensity sharply decreased with increasing Sm contents. The peak at 570.45 cm<sup>-1</sup> is related to the bending vibrations of an oxygen atom (O<sub>(2)</sub>) coupled to three metal atoms  $\nu$ (O–3Mo) in pristine  $\alpha$ -MoO<sub>3</sub> nanoplates<sup>70,71</sup> and this bending vibration can also be detected at 572.27, 573.18, and 576.67 cm<sup>-1</sup> in 0.5, 1.5, and 2.5 M% Sm-incorporated  $\alpha$ -MoO<sub>3</sub>, respectively. A faint peak at 461.97 cm<sup>-1</sup> is attributed to Mo<sub>(2)</sub>–O<sub>(4)</sub> interaction with the water molecule and its strength declined as the Sm content increased.<sup>72</sup> Table 4 indicates the comparison of functional groups of  $\alpha$ -MoO<sub>3</sub> nanoplates as a function of wavenumber



**Table 4** Functional groups in pristine and (0.5, 1.5, and 2.5 M%) Sm-incorporated  $\alpha$ -MoO<sub>3</sub>

Functional groups	Wavenumber, $n$ (cm <sup>-1</sup> )			
	0 M%	0.5 M%	1.5 M%	2.5 M%
Mo=O stretching vibration	982.58	981.82	981.82	983.48
Mo-O-Mo stretching vibration	861.06	860.15	861.82	861.82
Mo-O-Mo bending vibration	812.88	812.88	812.88	812.88
O-3Mo bending vibration	570.45	572.27	573.18	576.67

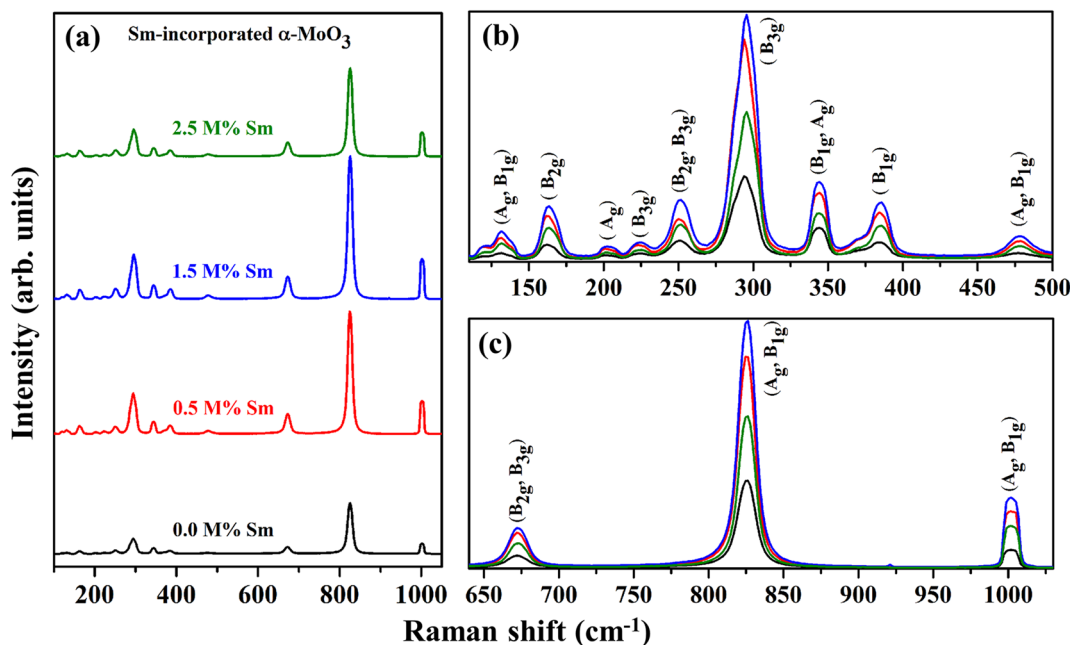
values after Sm incorporation. From the above discussion, it is clearly concluded that Sm contents affect the peak position and intensity of FTIR spectra of  $\alpha$ -MoO<sub>3</sub> nanoplates without destroying the orthorhombic crystal structure.

### 3.4 Raman spectroscopy

In addition to the information provided by XRD patterns, Raman spectroscopy is an effective technique that can be used to investigate further changes in the phase formation, defect generation (oxygen vacancy), and microstructural parameters of the prepared nanocrystalline pristine and Sm-incorporated  $\alpha$ -MoO<sub>3</sub> nanoplates due to Sm incorporation. Py and Maschke reported the Raman active phonon modes/characteristic Raman bands of the orthorhombic structure of molybdenum trioxide (space group: *Pbnm*) at 157 (A<sub>g</sub>, B<sub>1g</sub>), 195 (B<sub>2g</sub>), 217 (A<sub>g</sub>), 244 (B<sub>3g</sub>), 287 (B<sub>2g</sub>, B<sub>3g</sub>), 295 (B<sub>3g</sub>), 337 (B<sub>1g</sub>, A<sub>g</sub>), 375 (B<sub>1g</sub>), 470 (A<sub>g</sub>, B<sub>1g</sub>), 666 (B<sub>2g</sub>, B<sub>3g</sub>), 819 (A<sub>g</sub>, B<sub>1g</sub>) and 995 (A<sub>g</sub>, B<sub>1g</sub>).<sup>73</sup> The room-temperature typical Raman spectra within the wavenumber range of 50–1100 cm<sup>-1</sup> of pristine and Sm-incorporated  $\alpha$ -MoO<sub>3</sub> nanoplates were collected using 632.8 nm excitation

and are shown in Fig. 8. The positions (Raman shift) of the Raman vibrational bands and their corresponding active phonon modes are presented in Table 5. All of the detected Raman bands exhibit inappropriate positions that are very similar to those described in the nature of the orthorhombic layered structure of molybdenum trioxide ( $\alpha$ -MoO<sub>3</sub>) in the literature.<sup>74</sup> The characteristic bands of molybdenum trioxide in the 1050–600 and 500–100 cm<sup>-1</sup> ranges are predominantly due to Mo-O stretching ( $\nu_{as}$ ) and bending ( $\delta$ ) modes, according to the vibrational analysis of Raman spectra as depicted in Fig. 8(b) and (c), respectively. The distinct, sharply intense peaks corresponding to molybdenum trioxide suggest that all  $\alpha$ -MoO<sub>3</sub> have good crystallization.

The pristine samples exhibit Raman peaks at 132, 161, 201, 225, 251, 294, 343, 384, 477, 673, 825, and 1001 cm<sup>-1</sup>, all of which are indicative of the  $\alpha$ -MoO<sub>3</sub> phase.<sup>74</sup> The most intense peak positioned at 1001 cm<sup>-1</sup> (A<sub>g</sub>, B<sub>1g</sub>) is ascribed due to the asymmetric stretch of the terminal oxygen atoms ( $\nu_{as}$  Mo<sup>6+</sup>=O) along the *a*- and *b*-axis of pristine  $\alpha$ -MoO<sub>3</sub>. This is the main characteristic vibrational mode of the  $\alpha$ -phase.<sup>41</sup> The formation of oxygen vacancies should result in anion vacancies along the *c*-axis. As a result of the loss of bridging oxygen, the Mo atom is expected to shift towards the terminal oxygen in the *b*-direction, weakening the terminal bond along the *a*-axis.<sup>41,76</sup> The phonon mode observed at 825 cm<sup>-1</sup> (A<sub>g</sub>, B<sub>1g</sub>) is assigned to the doubly coordinated oxygen (Mo-O-Mo) in the stretching mode of  $\alpha$ -MoO<sub>3</sub>.<sup>77</sup> Mo-O-Mo bridge is stretched asymmetrically along the *c* axis at 673 cm<sup>-1</sup> (B<sub>2g</sub>, B<sub>3g</sub>). 343 and 384 cm<sup>-1</sup> vibrational bands are attributed to  $\delta$  (O-Mo-O) bending (B<sub>1g</sub>, A<sub>g</sub>) mode and  $\delta$  (O-Mo-O) scissoring (B<sub>1g</sub>) mode, respectively for pristine sample.<sup>48</sup> The peak at 294 and 251 cm<sup>-1</sup> are due to the wagging mode of the terminal



**Fig. 8** Raman spectra (in the wavenumber range of (a) 100–1050 cm<sup>-1</sup>, (b) 75–500 cm<sup>-1</sup>, and (c) 640–1030 cm<sup>-1</sup>) of (0.0, 0.5, 1.5, and 2.5 M%) Sm-incorporated  $\alpha$ -MoO<sub>3</sub> nanoplates.





Table 5 Raman shift of active phonon modes in pristine and (0.5, 1.5, and 2.5 M%) Sm-incorporated  $\alpha$ -MoO<sub>3</sub>

Raman active phonon modes	Assignment	Raman shift (cm <sup>-1</sup> )				
		Standard (ref. 73,75)	0%	0.5%	1.5%	2.5%
(A <sub>g</sub> , B <sub>1g</sub> )	Translational rigid MoO <sub>4</sub> -chain mode, (T <sub>b</sub> )	157	132	131	131	132
(B <sub>2g</sub> )	Twisting mode of the terminal oxygen, (τ O=M=O twist)	195	161	162	164	163
(A <sub>g</sub> )	Rotational rigid MoO <sub>4</sub> -chain mode, (R <sub>c</sub> )	217	201	200	201	201
(B <sub>3g</sub> )	Twisting mode of the terminal oxygen, (τ O=M=O twist)	244	225	223	225	224
(B <sub>2g</sub> , B <sub>3g</sub> )	Wagging modes of the terminal oxygen, (δ O=M=O wagging)	287	251	250	251	251
(B <sub>3g</sub> )	δ O=M=O wagging	295	294	293	295	294
(B <sub>1g</sub> , A <sub>g</sub> )	δ O-M-O bend	337	343	343	343	344
(B <sub>1g</sub> )	δ O=M=O scissor	375	384	383	385	385
(A <sub>g</sub> , B <sub>1g</sub> )	ν <sub>as</sub> O-M-O stretch and bend	470	477	477	479	477
(B <sub>2g</sub> , B <sub>3g</sub> )	Asymmetric stretching of Mo-O-Mo bridge along the <i>c</i> axis, (ν <sub>as</sub> O=M=O stretch)	666	673	682	673	677
(A <sub>g</sub> , B <sub>1g</sub> )	Symmetric stretch of the terminal oxygen atoms, (ν <sub>s</sub> O=M=O stretch)	819	825	822	831	826
(A <sub>g</sub> , B <sub>1g</sub> )	Asymmetric stretch of the terminal oxygen atoms, (ν <sub>as</sub> M=O) stretch	995	1001	1002	1002	1001

oxygen atoms, denoted as δ (O=M=O). Some low intense Raman peaks located at the lower Raman shift as a function of wave-number value (Fig. 8(b)) at 132, 161, 201, 225, and 477 cm<sup>-1</sup> originated due to the translational rigid MoO<sub>4</sub>-chain mode (T<sub>b</sub>) of (A<sub>g</sub>, B<sub>1g</sub>) symmetry, twisting mode of the terminal oxygen τ (O=M=O twist) of (B<sub>2g</sub>), rotational rigid MoO<sub>4</sub>-chain mode (R<sub>c</sub>) of (A<sub>g</sub>), twisting mode of the terminal oxygen τ (O=M=O twist) of (B<sub>3g</sub>) and symmetric ν<sub>as</sub> O-M-O stretching and bending vibration of (A<sub>g</sub>, B<sub>1g</sub>) mode, respectively.<sup>78</sup> There is no extra Raman peak due to the incorporation of Sm<sup>3+</sup>, although the intensity of the phonon modes fluctuates with Sm admixing, indicating that Sm might only cause crystallographic defects and oxygen vacancies, not structural transformation.

### 3.5 Optical properties

Fig. 9(a) and (b) show the optical absorbance and reflectance spectra of pristine and Sm-incorporated  $\alpha$ -MoO<sub>3</sub> nanoplates in the wavelength range 200–800 nm at room temperature utilizing UV-vis-NIR diffuse reflectance spectroscopy (DRS). Pristine and Sm-incorporated  $\alpha$ -MoO<sub>3</sub> nanoplates exhibit high bandgap absorption in the UV spectra, as illustrated in Fig. 9(a) and (b). Absorption levels climb to peak values and then progressively decline over time in the visible range of the reflected light spectrum. An absorption band edge ranging from 375 to 425 nm was found in all samples, which may be due to the electronic bandgap transition. An explanation for the electronic bandgap transition is provided by the absorption of visible light by hybridized O-2p orbital with Mo 4d in the valence and conduction bands, respectively (which is mainly composed of Mo 4d orbital hybridized with O 2p).<sup>79,80</sup> Here, for the  $\alpha$ -MoO<sub>3</sub> powder sample, Kubelka–Munk (K–M) function was

utilized to estimate the optical bandgap ( $E_g$ ) as follows (Eq. (8)).<sup>63</sup>

$$F(R) = (1 - R)^n/2R \quad (8)$$

As it is known to us, absorption co-efficient ( $\alpha$ ) is proportional relation to the K–M function, it can be written as eqn (9).

$$F(R) \propto \alpha = (h\nu - E_g)^n/h\nu \quad (9)$$

Where  $F(R)$  is the Kubelka–Munk (K–M) function,  $R$  is the diffuse reflectance,  $\alpha$  is the absorption coefficient,  $h$  is the plank's constant ( $6.626 \times 10^{-34}$  J s),  $\nu$  is light frequency,  $h\nu$  is incident light energy, and  $E_g$  is the optical bandgap of the nanoplates. The presence of a straight line in the spectra indicates the optical bandgap of the as-synthesized nanoplates is of direct type. The characterization of the optical transition process is indicated by the factor  $n$ , and the value of  $n$  depends on the transition modes.  $n = 1/2, 2, 3/2,$  and  $3$  for direct allowed, indirect allowed, direct forbidden, and indirect forbidden modes, respectively.

The optical band gap energy of the corresponding materials is calculated by extrapolating the linear portion of the plot of  $[F(R) \times h\nu]^2$  versus  $h\nu$ , and the tangent line with  $[F(R) \times h\nu]^2 = 0$ .<sup>81</sup> Fig. 10 shows that the direct bandgap energies ( $E_g$ ) of pristine and 0.5, 1.5, and 2.5 M% Sm-incorporated  $\alpha$ -MoO<sub>3</sub> nanoplates are found to be 2.96, 2.92, 2.89, and 2.83, respectively (Table 6). The bandgap energy is gradually reduced from 2.96 to 2.83 eV after incrementing of samarium contents up to 2.5 M%. Sm incorporation changes the optical characteristics vis-a-vis pristine  $\alpha$ -MoO<sub>3</sub> nanoplates, as seen by the considerable shift of optical band gap energy into the visible region. It is generally



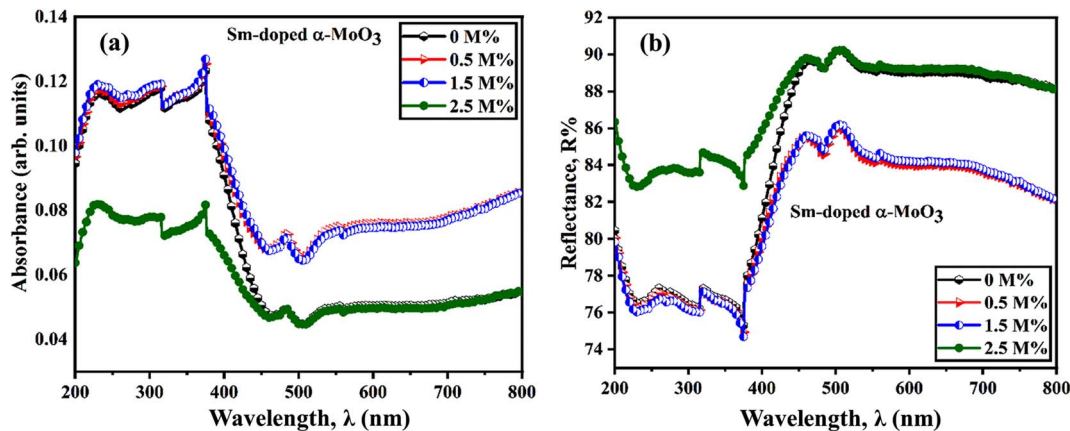


Fig. 9 (a) UV-vis absorbance spectra, and (b) UV-vis reflectance spectra derived from diffused reflectance spectroscopy of pristine and Sm-incorporated  $\alpha$ -MoO<sub>3</sub> nanoplates, respectively.

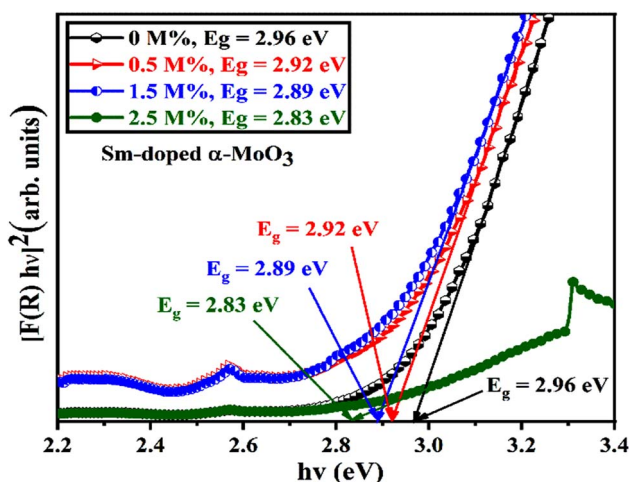


Fig. 10  $[F(R) \times hv]^2$  vs. incident photon energy,  $h\nu$  plots to calculate bandgap energy of pristine and Sm incorporated  $\alpha$ -MoO<sub>3</sub> nanoplates.

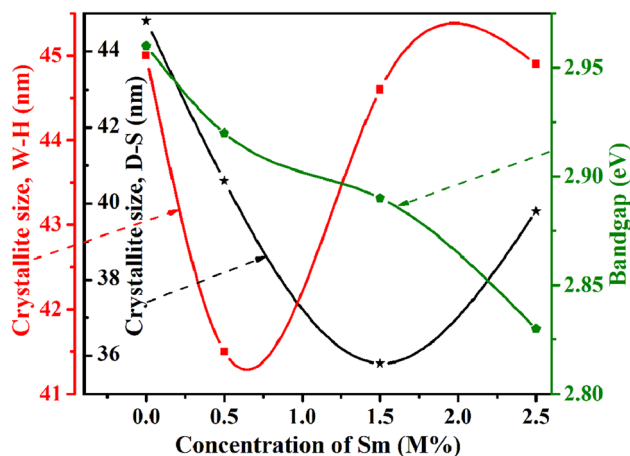


Fig. 11 Relation of crystallite size and bandgap with Sm concentration.

known that the value of  $E_g$  in bulk semiconductors is constant, but in nanostructured materials it can fluctuate according to the size of crystallites or crystal defects. The red shift trend of  $E_g$  values with increased Sm contents could be explained by the overall reduction of crystallite size caused by an increase in defects, disorders, and lattice strain, which is consistent with

Table 6 Summary of the band gap energy, saturation magnetization ( $M_s$ ), and coercivity ( $H_c$ ) of the pristine and Sm-incorporated  $\alpha$ -MoO<sub>3</sub>

Sample (M%)	Band gap energy (eV)	Magnetic properties		
		Saturation magnetization, $M_s$ (emu g <sup>-1</sup> )	Remanence, $M_r$ (emu g <sup>-1</sup> )	Coercivity, $H_c$ (kOe)
0%	2.96	0.0810	0.0100	0.1178
0.5%	2.92	0.3792	0.0292	0.0323
1.5%	2.89	0.3261	0.0121	0.0297
2.5%	2.83	0.3040	0.0190	0.0496

the findings of X-ray diffraction as shown in Fig. 11. When the Mo<sup>6+</sup> ion in the MoO<sub>3</sub> matrix is replaced by Sm<sup>3+</sup> ion, strain, defects, and charge imbalance might occur in the nanoplates. This may cause the valence band of incorporated nanoplates to broaden or the bandgap to narrow. In addition, the formation of sub-stoichiometric product,<sup>82,83</sup> as well as oxygen vacancies capable of capturing one or two electrons may contribute to the lowering of optical bandgap; the oxygen vacancies occupied by electrons act as donor centers. As a consequence, the impurity band is pushed farther into the forbidden gap region. Since the optical bandgap of the  $\alpha$ -MoO<sub>3</sub> nanoplates has been reduced by substituting Sm<sup>3+</sup> ions for Mo<sup>6+</sup>, this may be the reason for this reduction. In the forbidden gap area, Sm<sup>3+</sup> ions may create an impurity band.<sup>84,85</sup> Using Sm incorporation in  $\alpha$ -MoO<sub>3</sub> to induce impurity levels suggests that a novel antibonding orbital has been discovered. There were two types of molecular orbitals: bonding and antibonding. The new antibonding orbital with lower energy provided unoccupied orbitals between the valence and conduction bands. There were changes in the valence and conduction bands due to oxygen vacancies as well as lattice instability, which reduced the bandgap.<sup>78</sup>



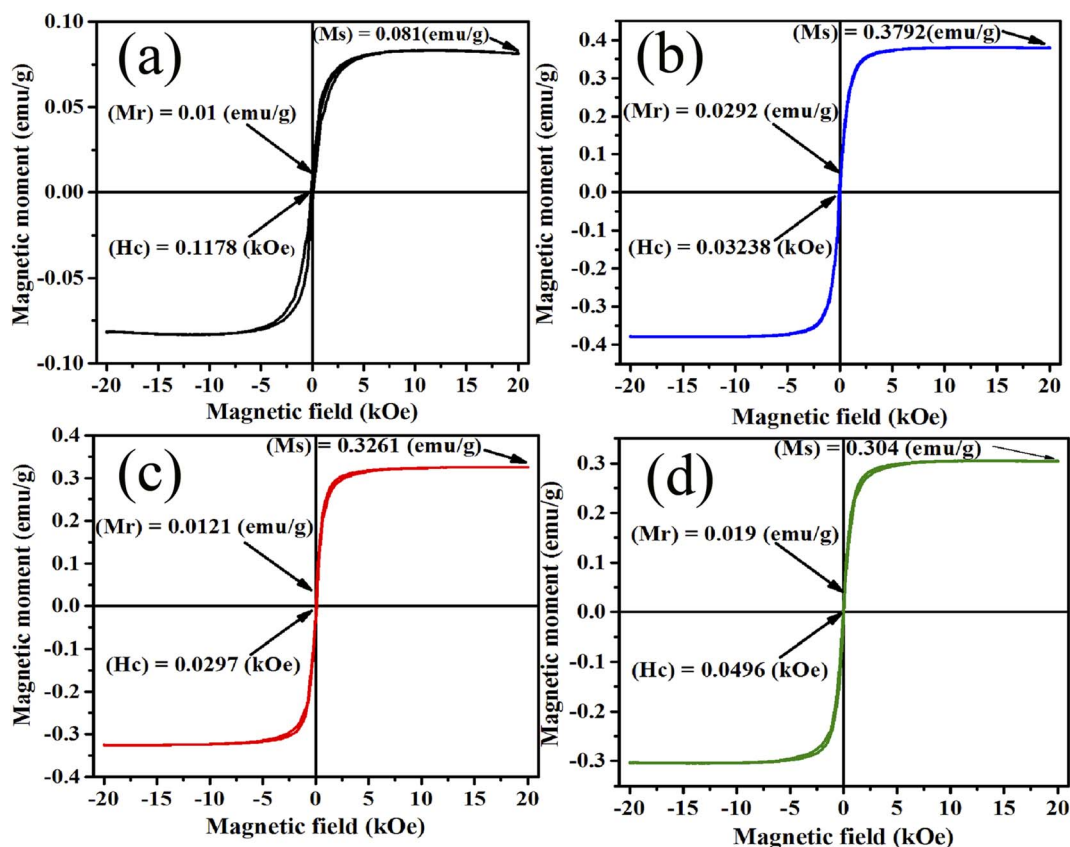


Fig. 12  $M-H$  curve (a) 0% (b) 0.5% (c) 1.5% and (d) 2.5% Sm-incorporated  $\alpha$ - $\text{MoO}_3$ .

### 3.6 Magnetic properties

The PPMS technique was used to study the magnetic properties of pristine and samarium-incorporated 2D layered  $\alpha$ - $\text{MoO}_3$  nanoplates. The behavior of magnetism of all samples was observed from the typical magnetization hysteresis ( $M-H$ ) loops depicted in Fig. 12 by plotting the magnetic moment ( $M$ ) against the applied magnetic field ( $H$ ).<sup>86</sup> Magnetic properties such as saturation magnetization ( $M_s$ ), remanence ( $M_r$ ), and coercivity ( $H_c$ ) of samples are listed in Table 6. All doped samples, including the pristine  $\alpha$ - $\text{MoO}_3$  nanoplates, exhibited ferromagnetic hysteresis behaviors at room temperature. Similarly, the ferromagnetic nature of pristine  $\alpha$ - $\text{MoO}_3$  was observed in several studies.<sup>30,87</sup> However, some previous reports also mentioned that the stoichiometric  $\text{MoO}_3$  (bulk) is a paramagnetic semiconductor with no unpaired electron spins.<sup>88,89</sup>

In this experiment, the saturation magnetization ( $M_s$ ) remarkably increased from 0.081 to 0.3792  $\text{emu g}^{-1}$  after only 0.5% Sm incorporation in  $\alpha$ - $\text{MoO}_3$  and remains high with increasing doping concentration. However, the coercivity ( $H_c$ ) decreased with Sm incorporation. Because of oxygen vacancies, the ferromagnetic behavior observed in the pristine sample could be related to the non-stoichiometry composition found in  $\text{MoO}_3$  nanoplates.<sup>29</sup> Ferromagnetic property enhanced after Sm incorporation may be due to (i) defect formation after doping in  $\text{MoO}_3$  matrix, and (ii) generation of micro-cluster of Sm.<sup>90</sup> The relatively large radius of Sm increased strain in the  $\text{MoO}_3$  matrix

may lead to the segregation of Sm clusters in the doped sample. Raman and XRD studies show that the crystallinity has decreased; and the defects, oxygen vacancies, and faults increased with Sm doping concentration which clearly indicates the ferromagnetism enhancement at room temperature.

### 3.7 Antibacterial activity

Pristine and Sm-incorporated  $\alpha$ - $\text{MoO}_3$  nanoplates were examined to determine their efficacy as a potential material for various biological uses, primarily as an antibacterial agent due to their lower toxicity. Fig. 13 shows the antimicrobial properties as a function of the zone of inhibition of pristine and Sm-incorporated  $\alpha$ - $\text{MoO}_3$  nanoplates with varying concentrations against three bacteria. The images as a function of the inhibition zone seen in this figure are indicative of the results obtained after three repetitions of antimicrobial treatment of both nanoplate samples. According to the results, both nanomaterials are successful in producing a zone of inhibition against Gram-positive and Gram-negative bacterial strains, as depicted in Table 7. Nevertheless, Sm-incorporated  $\alpha$ - $\text{MoO}_3$  nanoplates were found to be more active against the examined bacteria than pristine nanoplates.

In the context of pristine  $\alpha$ - $\text{MoO}_3$  nanoplates, the largest zone of inhibition (16.68 mm in diameter) was recorded against *S. aureus* for the concentration of 80 000 ppm, which is good agreement with our previously reported largest zone of



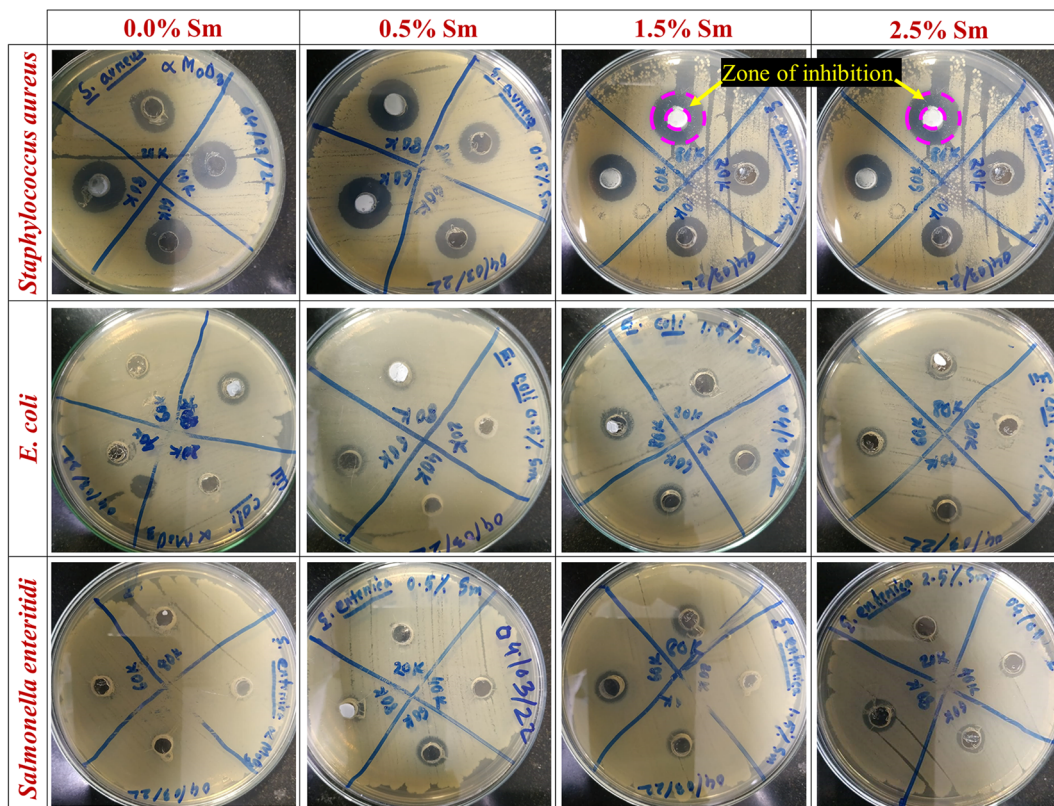


Fig. 13 Antibacterial activity of pristine and Sm-incorporated  $\alpha$ -MoO<sub>3</sub> nanoplates against Gram-positive (*S. aureus*) and Gram-negative (*E. coli* and *S. enteritidis*) bacteria as a function of diameter (mm) of the zone of inhibition.

Table 7 Zone of inhibition (diameter in mm) caused by pristine and Sm-incorporated  $\alpha$ -MoO<sub>3</sub> nanoplates

Organisms	Conc. (ppm)	Zone of inhibition (mm)			
		0.0% Sm	0.5% Sm	1.5% Sm	2.5% Sm
<i>Staphylococcus aureus</i>	20 000	12.56	13.47	11.25	14.74
	40 000	15.09	13.80	15.03	15.90
	60 000	15.61	17.12	16.15	16.21
	80 000	16.68	16.70	16.25	18.27
<i>Escherichia coli</i>	20 000	N/A	N/A	10.01	9.31
	40 000	10.51	N/A	10.96	10.21
	60 000	8.50	10.81	11.50	10.25
	80 000	11.45	10.87	11.52	10.29
<i>Salmonella enteritidis</i>	20 000	N/A	N/A	N/A	8.31
	40 000	8.34	9.01	9.71	8.76
	60 000	8.44	9.20	9.86	9.03
	80 000	9.03	9.33	9.91	10.35

inhibition for orthorhombic molybdenum trioxide nanoplates.<sup>61</sup> At a lower concentration (20 000 ppm), the pristine sample was inactive against both Gram-negative bacterial strains such as *E. coli* and *S. enteritidis*, and no zone was identified in Petri plates. Therefore, the ZOI of bared  $\alpha$ -MoO<sub>3</sub> linearly depends on concentration and after increasing the concentration of molybdenum trioxide, its ZOI increased up to 11.45 and 9.03 mm for *E. coli* and *S. enteritidis*, respectively.

The antibacterial activity of  $\alpha$ -MoO<sub>3</sub> nanoplates showed its increased value of ZOI due to 0.5% Sm admixing against all examined bacteria and the observed highest ZOI is (17.12 mm) against *S. aureus* at the concentration of 80 000 ppm. Although, no ZOI was found at comparatively lower concentrations against *E. coli* (20 000 and 40 000 ppm) and *S. enteritidis* (20 000 ppm) for 0.5% Sm. Similar enhanced inhibiting bacterial growth or killing bacterial cells (highest 17.25 mm, against *S. aureus* at 80 000 ppm) was identified for 1.5% Sm-incorporated  $\alpha$ -MoO<sub>3</sub>



nanoplates. From Fig. 13 and Table 7, it is clearly seen that the highest ZOI (18.27 mm) was determined against *S. aureus* at the concentration of 80 000 ppm for 2.5% Sm compared to other samples. As a result, these findings suggest the enhanced antibacterial effectiveness of  $\alpha$ -MoO<sub>3</sub> nanoplates due to samarium incorporation in the  $\alpha$ -MoO<sub>3</sub> matrix. It has been revealed that Sm-doped  $\alpha$ -MoO<sub>3</sub> nanoplates are highly effective and that the growth of bacteria is inhibited when concentrations of Sm-doped  $\alpha$ -MoO<sub>3</sub> nanoplates rise.

Understanding the interaction between the pure orthorhombic phase of MoO<sub>3</sub> nanomaterials and bacterial cell walls, which results in cell wall degradation, is a crucial one.<sup>91</sup> Several studies have suggested that the antibacterial properties of various nanomaterials are highly influenced by their morphologies (crystallite size and shape), crystallographic structure, surface defects, and composition of nanomaterials.<sup>2,9,92–94</sup>

In the case of metal oxide semiconductor nanomaterials, suitable doping element also plays a vital role in antimicrobial applications.<sup>95,96</sup> Chandar *et al.* reported that the incorporation of the Ni element in the MoO<sub>3</sub> matrix enhanced the antibacterial activity of MoO<sub>3</sub> nanomaterials compared to the undoped sample.<sup>97</sup> Ag also increased the effectiveness of MoO<sub>3</sub> against bacterial strains, explored by Raj *et al.*<sup>95</sup> Among various dopant elements, samarium is considered a less toxic and good one for enhancing the physical properties of transition metal oxides in the case of biological and other relevant applications.<sup>96</sup> As a result, samarium doping may improve the antimicrobial activity of  $\alpha$ -MoO<sub>3</sub> nanoplates. The experimental results of the antibacterial activity of doped MoO<sub>3</sub> nanomaterials compared with previous reports are shown in Table 8.

The antimicrobial activity of the Sm doped  $\alpha$ -MoO<sub>3</sub> nanoplates can be explained by three main mechanisms namely: (a) production of enhanced levels of reactive oxygen species (ROS)<sup>98</sup> on the surface of  $\alpha$ -MoO<sub>3</sub> nanoplates, (b) release of Mo<sup>6+</sup> ions from the  $\alpha$ -MoO<sub>3</sub> nanoplates, and (c) size of the nanomaterials.<sup>96,97,99</sup> Fig. 13 clearly reveals inhibitory zones against bacterial strains, indicating that the Sm-doped  $\alpha$ -MoO<sub>3</sub> nanoplates have damaged the bacteria's membrane wall. Bacteria are destroyed when oxygen species are released from the surface of Sm-incorporated  $\alpha$ -MoO<sub>3</sub> nanoplates. Tables 2 and 7 show that the reduction in crystallite size of the Sm-incorporated  $\alpha$ -MoO<sub>3</sub> nanoplates increased the size of the inhibitory zone resulting in increased surface area to volume ratio and formation of more

H<sub>2</sub>O<sub>2</sub>.<sup>95</sup> The interstitial occupancy of the Sm-incorporated  $\alpha$ -MoO<sub>3</sub> lattice structure increased as the percentage of Sm increased, resulting in free carriers in the  $\alpha$ -MoO<sub>3</sub> lattice. The free carriers play a crucial role in antibacterial effectiveness. The antibacterial efficiency as a function of ZOI of examined Sm-incorporated  $\alpha$ -MoO<sub>3</sub> nanoplate samples is inversely proportional to crystallite size and linearly proportional to the surface area to volume ratio. Thus, the crystallite size of Sm-incorporated  $\alpha$ -MoO<sub>3</sub> 2D layered type nanoplate orthorhombic structure has a significant impact on activity most likely due to a large number of nanomaterials with oxygen species accumulating in the cell membrane.

The substitution of Sm ions (Sm<sup>3+</sup>) into the Mo positions leads to a larger amount of Mo interstitials, causing more molybdenum ions to be released into the system. Interstitial Mo<sup>6+</sup> ions are expected to have a higher chance of breaking out from the  $\alpha$ -MoO<sub>3</sub> lattice. The liberated Mo<sup>6+</sup> ions may have a strong electrostatic interaction with bacterial cell membranes, causing significant bacterial cell destruction. Therefore, the formation of Mo<sup>6+</sup> ions is also one of the causes of the enhancement of antimicrobial activities of Sm-incorporated  $\alpha$ -MoO<sub>3</sub> nanoplates. Furthermore, Sm ions (Sm<sup>3+</sup>) contribute to damage to the bacterial cell membranes.

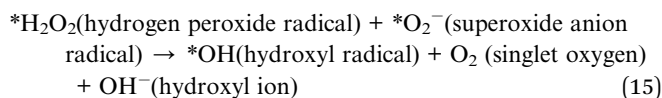
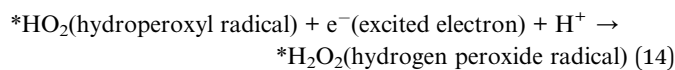
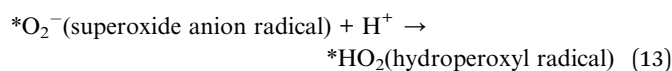
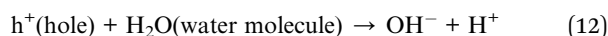
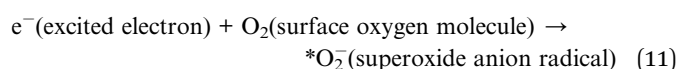
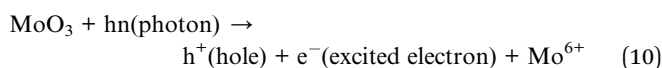
Basically, the antibacterial activity of Sm-incorporated  $\alpha$ -MoO<sub>3</sub> 2D layered nanoplates can be explained by the photocatalysis process under UV-vis irradiation depending on two mechanisms. Firstly, the physical process in which disruption of the bacterial membrane occurs by rupturing the potential and integrity due to surface interactions between the cell wall and nanoplates. Secondly, the chemical process includes the production of enhanced levels of ROS such as superoxide anion radical (\*O<sub>2</sub><sup>-</sup>), hydroxyl radical (\*OH), and hydrogen peroxide radicals (\*H<sub>2</sub>O<sub>2</sub>). The capacity of Sm-incorporated  $\alpha$ -MoO<sub>3</sub> nanoplates to generate ROS is the primary cause for their improved antibacterial activity. Generally, many transition metal oxides are sportive against micro-organisms due to the interaction of hydrophobic and electrostatic forces.<sup>100</sup> The production of enhanced levels of these ROS can be explained as follows:<sup>96,97,99</sup> when 2D layered nanoplates of pristine and Sm-incorporated  $\alpha$ -MoO<sub>3</sub> are exposed to light with the energy of photon equal to or higher than the energy bandgap of the  $\alpha$ -MoO<sub>3</sub> semiconductor, electrons from the valence band (VB) are transferred to the conduction band (CB), leaving holes in the

Table 8 Comparative assessment of antibacterial activity (highest ZOI) of doped MoO<sub>3</sub> with earlier reports

Sl. no.	Materials	Dopant	Bacteria	Zone of inhibition (mm)		Ref.
				Pure	Doped	
1	h-MoO <sub>3</sub> nanorods	Ag	<i>B. cereus</i>	12 ± 0.4	07 ± 0.9	95
			<i>C. koseri</i>	16 ± 0.7	22 ± 0.5	
			<i>P. aeruginosa</i>	17 ± 0.3	23 ± 0.4	
2	$\alpha$ -MoO <sub>3</sub> nanorods	Ni	<i>E. coli</i>	16 ± 0.5	18 ± 0.5	97
			<i>S. aureus</i>	16 ± 1	19 ± 0.5	
3	$\alpha$ -MoO <sub>3</sub> nanoplates	Sm	<i>S. aureus</i>	16.68	18.27	Present
			<i>E. coli</i>	11.45	10.29	
			<i>S. enteritidis</i>	9.03	10.35	



valence band (eqn (10)). These excited electrons ( $e^-$ ) in the CB can be trapped by the oxygen molecules ( $O_2$ ) present on the surface, producing superoxide anion radicals ( $*O_2^-$ ) (eqn (11)). Simultaneously, the holes ( $h^+$ ) in the VB reacts with the water molecules ( $H_2O$ ), emitting hydroxyl ion ( $OH^-$ ) and hydrogen ion ( $H^+$ ) (eqn (12)). The superoxide anion radicals ( $*O_2^-$ ) thereafter interacts with  $H^+$  to produce hydroperoxyl radical ( $*HO_2$ ) (eqn (13)). The hydroperoxyl radical ( $*HO_2$ ) combines with  $e^-$  and  $H^+$  once more, resulting in hydrogen peroxide radical ( $*H_2O_2$ ) (eqn (14)). At the same time, hydrogen peroxide radical ( $*H_2O_2$ ) can react with superoxide anion radicals ( $*O_2^-$ ) to generate hydroxyl radical ( $*OH$ ), hydroxyl ion ( $OH^-$ ) and singlet oxygen ( $^1O_2$ ) (eqn (15)). The reactions that occur in this mechanism are illustrated in the following eqn (10–15):



The electron–hole pairs serve as the primary unit for the generation of ROS. The gradually decreasing optical band gap (from 2.96 to 2.83 eV) accelerates this ROS-producing mechanism by creating more electron–hole pairs as the Sm admixing level increases in the  $\alpha$ - $MoO_3$  semiconductor. The negatively charged radicals (hydroxyl radicals and superoxide anions) cannot penetrate the cell membrane of micro-organisms, but they can induce critical damage to the bacteria's outer surface, whereas positively charged hydrogen peroxide radicals ( $*H_2O_2$ ) can penetrate easily through the negatively charged bacterial cell membranes and kill the bacteria. Therefore, hydrogen peroxide radical ( $*H_2O_2$ ) is highly harmful to damaging bacterial cell membranes. Further, the superoxide dismutase (SOD) mimetic/catalase assay analysis would be helpful to understand the levels of ROS with the incorporation of Sm. The detailed mechanism of SOD and catalase mimic activities of  $MoO_3$ -based materials like  $MoO_{3-x}$  nanodots were explained by Han *et al.*<sup>101</sup> It is worth noting that when the Sm level was increased up to 2.5 M%, in the  $\alpha$ - $MoO_3$  semiconductor, the antibacterial efficiency against all three micro-organisms was found to be higher than that of the pristine. In this experiment, the improved antibacterial activity of  $\alpha$ - $MoO_3$  nanoplates after Sm-incorporation is due to the following factors: decreased crystallite sizes, formation of defects and oxygen vacancies, two-dimensional plate type layered shape, improved

ferromagnetic behavior, sinking optical band gap, increased levels of ROS, and ( $Mo^{6+}$  and  $Sm^{3+}$ ) ions formation from the  $\alpha$ - $MoO_3$  nanoplates.

## 4 Summary

Here, we have reported the impact of Sm contents on the physical properties and antibacterial activity of hydrothermally synthesized  $\alpha$ - $MoO_3$  nanoplates. The single-phase orthorhombic structure with the polycrystalline nature was revealed by XRD patterns, supported by FTIR and Raman results. The overall crystallite size decreased with the increment of Sm contents, resulting in an increment of defects, strain, and dislocation density. The EDX spectra confirmed the Sm incorporation and the plate-type 2D layered shape was identified from the FE-SEM micrograph. The bandgap energy decreased gradually from 2.96 to 2.83 eV as the Sm content increased. The measured magnetic hysteresis loops lead to the ferromagnetic behavior of  $\alpha$ - $MoO_3$  nanoplates. The room temperature ferromagnetism of 2.5 M% Sm  $\alpha$ - $MoO_3$  increased compared to the pristine sample which is attributed to the existence of a large number of oxygen vacancies, supported by Raman studies as well. In comparison to the pristine one, the antibacterial activity enhanced as Sm contents increased in both Gram-positive (*S. aureus*) and Gram-negative (*E. coli* and *S. enteritidis*) bacteria. The reason might cause the decreased crystallite sizes, formation of defects and oxygen vacancies, 2D plate type layered morphology, enhanced ferromagnetic behavior, lowering optical band gap, enhanced levels of ROS, and ( $Mo^{6+}$  and  $Sm^{3+}$ ) ions formation in the  $\alpha$ - $MoO_3$  nanoplates. The investigated opto-structural and magnetic properties suggested that the synthesized Sm-incorporated 2D layered  $\alpha$ - $MoO_3$  nanoplates might be suitable for photocatalysts, magneto-optic, and spintronic nanodevice applications. The enhanced antibacterial activity postulated that Sm-incorporated 2D layered  $\alpha$ - $MoO_3$  nanoplates could be an innovative antibacterial approach for eradicating microorganisms in medicinal as well as public health sectors.

## Data availability

All data used to evaluate the conclusion of this study are presented in the manuscript. Additional data can be available from the corresponding authors upon reasonable request.

## Author's contributions

S. K. Sen: conceptualization, methodology, software, validation, formal analysis, investigation, data curation, writing – original draft, writing – review & editing, supervision, project administration; M. R. Munshi: software, writing – original draft; A. Kumar: investigation, data curation; A. A. Mortuza: writing – review & editing, software; M. S. Manir: resources, investigation, data curation; M. A. Islam: writing – review & editing; M. N. Hussain: data curation; M. K. Hossain: software, visualization; validation, writing – review & editing.



## Conflicts of interest

The authors declare that they have no competing interests.

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