

On the synthesis and optical absorption studies of nano-size magnesium oxide powder

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ABSTRACT

Magnesium oxide (MgO) nano-size powder is synthesized using magnesium nitrate hexahydrate and oxalic acid as precursors with ethanol as a solvent. The process involves gel formation, drying at 100 °C for 24 h to form magnesium oxalate dihydrate [α -MgC₂O₄·2H₂O] and its decomposition at 500, 600, 800, and 1000 °C for 2 h to yield MgO powder (average crystallite size ~6.5–73.5 nm). The sol–gel products at various stages of synthesis are characterized for their thermal behaviour, phase, microstructure, optical absorption, and presence of hydroxyl and other groups like O=C=O, C=O, C–C, etc. MgO powder is shown to possess an f.c.c. (NaCl-type) structure with lattice parameter increasing with decrease in crystallite size (t_{av}); typical value being ~4.222(2) Å for t_{av} ~6.5 nm as against the bulk value of 4.211 Å. Infrared absorption has shown MgO to be highly reactive with water. Also, a variety of F- and M-defect centres found in MgO produce energy levels within the band gap (7.8 eV), which make it attractive for application in plasma displays for increasing secondary electron emission and reducing flickering effects. The possible application of the intermediate sol–gel products, viz., α -MgC₂O₄·2H₂O and anhydrous magnesium oxalate (MgC₂O₄) in understanding the plants and ESR dosimetry, respectively, has also been suggested.

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1. Introduction

The IIA–VIB compounds, viz., oxides, sulphides, selenides, and tellurides of alkaline earth elements usually exhibit an f.c.c. (NaCl-type) crystal structure. Among them magnesium oxide (MgO) occupies a special position due to its interesting properties and potential industrial applications in pharmaceuticals, semiconductors, liquid crystal/electroluminescence/plasma/fluorescent displays, ferroelectric and superconductor thin films as substrate, reflecting and antireflecting coatings, additives to heavy fuel oils, toxic waste remediation, catalysis, lithium ion batteries, etc. [1–16]. The novel and useful properties of MgO are further enhanced when used as nano-size powder. Many synthesis routes like sol–gel, hydrothermal, flame spray pyrolysis, laser vaporization, chemical gas phase deposition, combustion aerosol synthesis, aqueous wet chemical, and surfactant methods provide nano-size MgO [17–31]. However, the morphology and properties of the resulting MgO differ and depend largely on the synthesis route and processing conditions. The sol–gel process has assumed a special significance for synthesis nowadays because it is simple, cost effective, and capable of yielding unique properties (e.g., large surface area-to-volume ratio, narrow particle size distribution, etc.)

at relatively low temperatures [17–22]. Factors such as temperature, time, pH, catalytic agent for gel formation, and the environmental conditions drastically affect the characteristics of the final product [32–34]. MgO powders have been prepared taking magnesium ethoxide as precursor with different hydrolysis catalysts, namely, HCl, C₂H₄O₂, C₂H₂O₄, or NH₄OH for evolution in the temperature range of 150–900 °C and control of average particle size (16–88 nm) [34]. Thermal decomposition of magnesium alcoholates (via alcoxy/hydroxy intermediates) in air at 450–560 °C can also produce MgO of distinct particle size depending on the alcohol chain length [35]. The addition of 20 mol% diethanolamine (DEA) stabilizes the magnesium methoxide and facilitates the formation of MgO at 400 °C in oxygen [36]. Kim et al. [23] studied the effect of acetic acid addition to magnesium methoxide on the stability of the precursor and the crystallization behaviour of sol–gel-derived MgO nano-size powder. Accordingly, the heat treatment of gel product with addition of acetic acid is found to lower the crystallization temperature significantly. Recently, Chowdhury and Kumar [37] have synthesized MgO with high degree of crystallinity and tubular morphology using magnesium acetate as a precursor. The particular interest lies in producing high-quality MgO for application in plasma display panels so as to provide high secondary electron emission, reduced flickering, and extended service life. To achieve this, introduction of various F- and M-defect centres between valence band of oxygen (2p) and

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conduction band of magnesium (3s and 3p) in MgO is essential. F- and M-defect centres can be created by several methods, such as electron-, neutron-, or γ -irradiation. An attempt has therefore been made to synthesize nano-crystalline MgO with F- and M-centres using an inorganic precursor, magnesium nitrate hexahydrate $[\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, and to study its formation, morphology, infrared (IR) and ultraviolet–visible–near infrared (UV–VIS–NIR) absorption characteristics.

2. Experimental

For synthesis of nano-size MgO, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and oxalic acid $[(\text{COOH})_2 \cdot 2\text{H}_2\text{O}]$ precursors in 1:1 molar ratio are first dissolved separately in ethanol and stirred to obtain two clear solutions. These are then mixed together to yield a thick white gel. The gel product is digested for 12 h and dried subsequently at 100 °C for 24 h, ground, sieved through 240 mesh, calcined at 500, 600, 800, and 1000 °C for 2 h, and cooled at a rate of 10 °C/min. Thermal analysis of the dried product is carried out with a computer-controlled thermogravimetric analysis (TGA) set-up developed in the laboratory to study its stability and formation of MgO. While an X-ray powder diffractometer (Rich Seifert model ISO Debye flux 2002) with the $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) has been used for the identification of the phase(s) and determining the average crystallite size, electron microscopes (FEI Quanta 200HV SEM and FEI Tecnai G^2 TEM) have been employed for observing the microstructure and morphology. In addition, a Fourier transform infrared (FTIR) spectrometer (BRUKER Vertex-70) is used for the detection of hydroxyl (–OH) and other groups, like $\text{O}=\text{C}=\text{O}$, $\text{C}=\text{O}$, $\text{C}-\text{C}$, etc., whereas a UV–vis–NIR spectrophotometer (Varian model Carry 5000) is employed for optical absorption measurements.

3. Results and discussion

3.1. Thermal analysis of sol–gel product

The thermal stability of the oven-dried precursor is monitored through its weight by raising its temperature at the rate of 4 °C/min in air up to 800 °C. Two main stages of weight loss are observed (Fig. 1). In the first stage, a weight loss of ~24% occurs in the temperature range of 201–282 °C corresponding to an endothermic reaction as indicated by differential thermal analysis (DTA) plot given in inset of Fig. 1. This weight loss can be attributed to removal of crystallizing water of $\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, which is ~24.26%; close to the value mentioned above. The $(-dW/dT)$ versus T plot shows a peak around 234 °C where the weight loss is maximum. In the second stage, a weight loss of ~47.5% takes place in the temperature range of 416–564 °C. This reaction is also endothermic in nature (inset of Fig. 1) and yields mainly MgO. Needless to say, anhydrous magnesium oxalate (MgC_2O_4) in giving off MgO should undergo a weight loss of ~48.5% as against ~47.5% observed in the present case. Above 564 °C, the residues and other volatile species come out with a weight loss of ~1%. Considering the above results, the decomposition temperature for the dried gel powder is set in the range of 500–1000 °C for obtaining MgO in the present study. The systematic steps involved in the synthesis of pure MgO powder are shown in Scheme 1.

3.2. Phase evaluation

The X-ray diffraction (XRD) pattern of a sol–gel precursor after drying at 100 °C for 24 h is shown in Fig. 2. Its indexing suggests the formation of magnesium oxalate dihydrate $[\alpha\text{-MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}]$

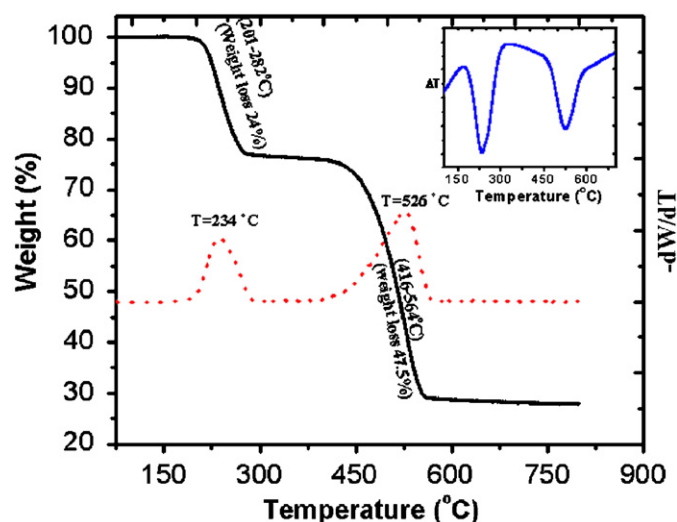
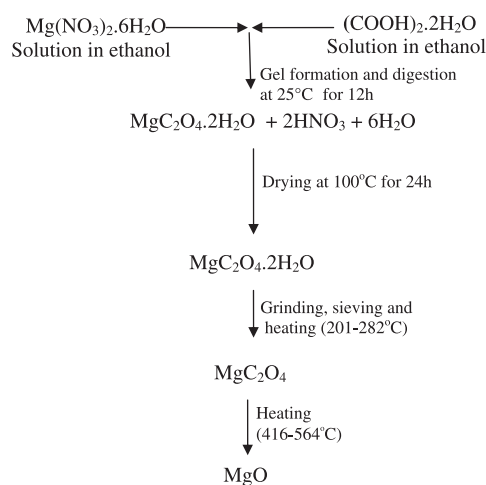


Fig. 1. Weight (W) vs. temperature (T) and $(-dW/dT)$ vs. T plots of sol–gel product dried at 100 °C for 24 h; the temperature is raised at the rate of 4 °C/min in air. The inset shows the differential thermal analysis (DTA) plot.



Scheme 1. The steps involved in sol–gel synthesis as per thermogravimetric analysis.

having monoclinic structure with known lattice parameters $a = 12.680 \text{ \AA}$, $b = 5.391 \text{ \AA}$, $c = 9.977 \text{ \AA}$, $\beta = 129.82^\circ$, and $Z = 4$ [JCPDS # 26-1223]. The decomposition of dried precursor powder at 400 °C for 2 h causes complete removal of crystallizing water and yields MgC_2O_4 (Fig. 3). Its XRD pattern corresponds to a monoclinic phase and matches well with the lattice parameters $a = 9.413 \text{ \AA}$, $b = 6.229 \text{ \AA}$, $c = 5.724 \text{ \AA}$, $\beta = 96.47^\circ$, $Z = 4$, and space group C2/c [JCPDS # 26-1222]. On raising the decomposition temperature further to 500 °C, a single f.c.c. phase of periclase MgO emerges (Fig. 4a). This temperature lies in the range 416–564 °C, where decomposition of MgC_2O_4 takes place; the maximum weight change occurring at 526 °C (Fig. 1). XRD patterns recorded after decomposition of dried sol–gel precursor at 500, 600, 800, and 1000 °C for 2 h each are shown in Fig. 4. All these patterns correspond to periclase phase (NaCl-type) of MgO with the values of lattice parameter as listed in Table 1; standard value for bulk MgO being $4.211 \text{ \AA}$ [JCPDS # 45-0946]. The diffraction peaks are somewhat broader in Fig. 4a but become sharper with increase in the decomposition temperature (Figs. 4b–d) due to resulting increase in the average crystallite size (t_{av}). Table 1 gives the values of average crystallite size as

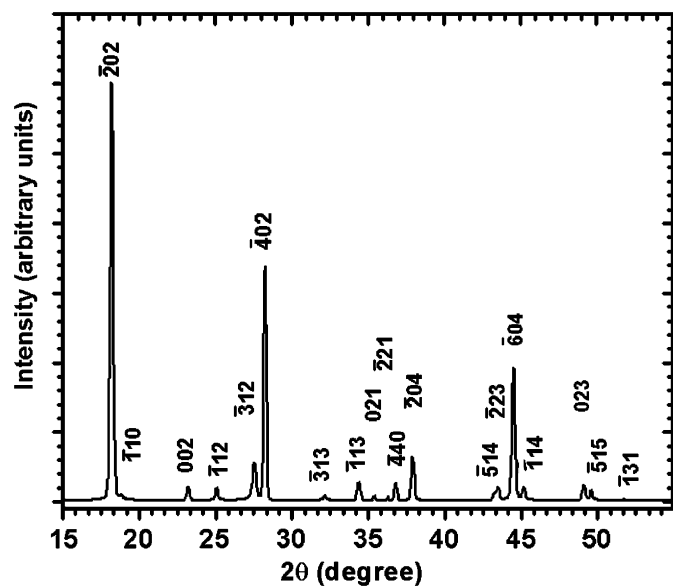


Fig. 2. X-ray diffraction pattern of sol-gel product dried at 100 °C for 24 h; showing emergence of monoclinic phase of α - $\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

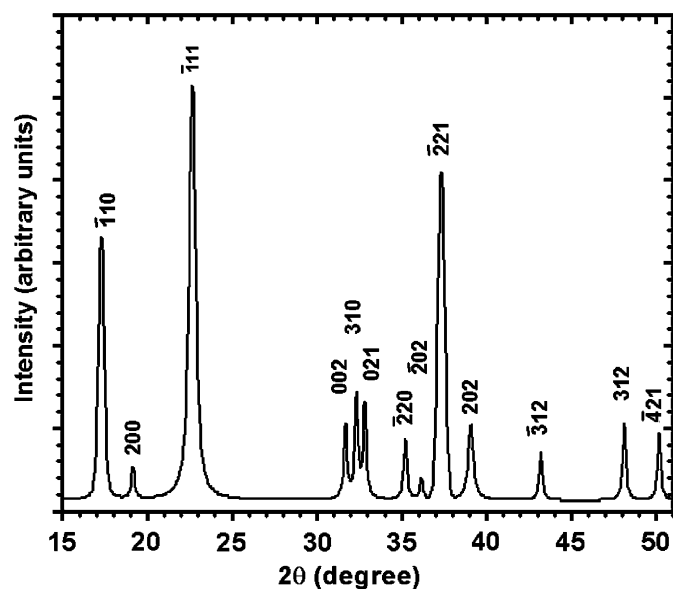


Fig. 3. X-ray diffraction pattern of dried sol-gel product after decomposition at 400 °C for 2 h. It corresponds to monoclinic phase of anhydrous magnesium oxalate (MgC_2O_4).

determined from Scherrer formula with full-width at half-maximum (FWHM) of 200 and 220 diffraction peaks, taking silicon as standard for accounting for the instrumental broadening.

The lattice parameter of the MgO produced is found to decrease with increase in t_{av} (Fig. 5), as reported in other oxides, namely, Fe_2O_3 and yttrium aluminum garnet (YAG) [38,39]. The surface area-to-volume ratio (η ; calculated by considering the crystallites as spherical and using the relation $\eta = 6/t_{av}$; t_{av} being the diameter) also varies in the same manner with t_{av} (Fig. 5). Thus, the increase in lattice parameter with decrease in t_{av} is essentially caused by the corresponding increase in the surface area or underlying effects (e.g., surface stresses). In oxides, the bonds are directional and there exist dangling bonds with unpaired electrons because of reduced coordination on the outer

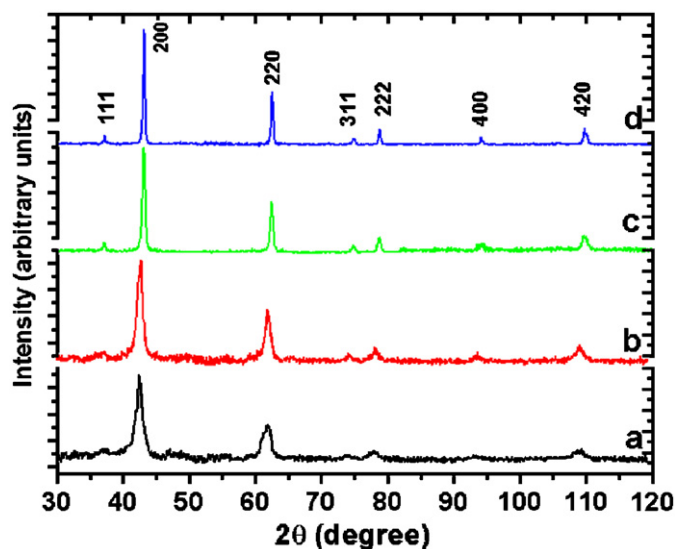


Fig. 4. X-ray diffraction patterns of dried sol-gel product after decomposition at (a) 500, (b) 600, (c) 800, and (d) 1000 °C for 2 h each. These indicate formation of f.c.c. (NaCl-type) phase of magnesium oxide.

Table 1

The lattice parameter and average crystallite size (t_{av}) of MgO powder after decomposition of dried sol-gel product at 500, 600, 800, and 1000 °C for 2 h each

Decomposition temperature (°C)	Lattice parameter (nm)	Crystallite size t_{av} (nm)
500	0.4222(2)	6.5
600	0.4221(2)	9.5
800	0.4213(2)	28.5
1000	0.4212(2)	73.5

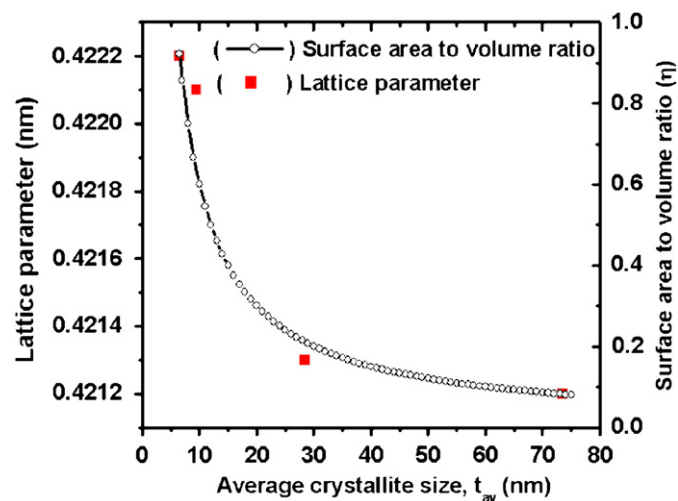


Fig. 5. Lattice parameter and surface area-to-volume ratio as a function of average crystallite size in MgO powder.

surface of crystallites. Also, H_2O being polar forms dipoles on adsorption at the surface. Such features are enhanced with increase in the surface area. The repulsion of dipoles (of polar H_2O and unpaired electrons) then produces tensile stresses on the underlying layer, and, in turn, increases the inter-ionic separation.

The nitrogen adsorption method has been used to determine the BET surface area and pore size distribution of a typical MgO powder obtained by decomposition of oxalate at 600 °C for 2 h.

Fig. 6 shows the pore size distribution curve derived from the nitrogen adsorption isotherm (included in inset). The sample has a BET-specific surface area of about $229.3 \text{ m}^2/\text{g}$, pore volume of $0.84 \text{ cm}^3/\text{g}$, and average pore diameter of 17 nm . The average particle size as deduced from the BET-specific surface area is 7.3 nm , which matches well with the crystallite size ($\sim 9.5 \text{ nm}$) obtained by XRD. The high values of BET surface area and pore

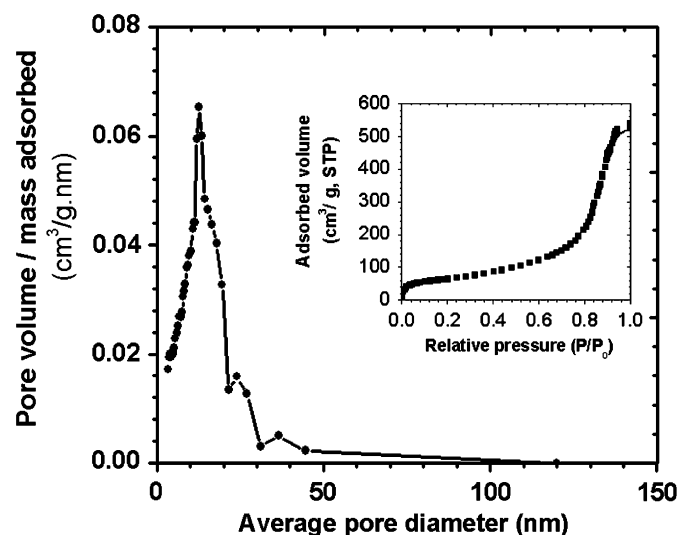


Fig. 6. The pore size distribution curve and the corresponding nitrogen isotherm (inset) of MgO powder, obtained by decomposition of magnesium oxalate dihydrate at 600°C for 2 h in air.

volume can improve characteristics of MgO powder appreciably to make it suitable for catalytic activity (i.e., adsorption and dissociation of molecules like, CH_3OH , CH_4 , NO_2 , H_2O , CO , and CO_2), toxic waste remediation, etc. [12–15].

3.3. Microstructure

Fig. 7 shows a few typical scanning electron micrographs (in SE-mode) at various stages of the synthesis process. The gel after drying at 80°C for 24 h contains numerous rods of nearly the same diameter ($\sim 175 \text{ nm}$) but of various lengths (Fig. 7a). On examining the micrograph closely, rods appear to be made of particles (Fig. 7a). Some spherical particles lying independently can also be noticed. Drying the gel at 100°C for 24 h exhibits $\alpha\text{-MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ crystals of parallelepiped morphology with varying size (Fig. 7b). The length of parallelepipeds lies between 680 and 3940 nm while base dimensions are in the range 200 – 1500 nm . The parallelepipeds with square base and smaller area have higher population density (Fig. 8a). The base grows asymmetrically (i.e., more in any one direction) and thus takes a rectangular shape. However, population density of parallelepipeds decreases progressively with increase in the base area (Fig. 8a). $\alpha\text{-MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ is an important biomineral found in thallus of *Lecanora altra*, rock-lichen interface, and cactaceae plant species or is naturally formed by interaction of living organism with mineral surroundings [40]. By adjusting the digestion and drying conditions of sol–gel product, its morphologies may be varied (parallelepiped, sphere, rod, etc.) and corresponding changes in characteristics can be utilized for a better understanding of the plants. $\alpha\text{-MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ after decomposition at 400°C for 2 h yields MgC_2O_4 crystals,

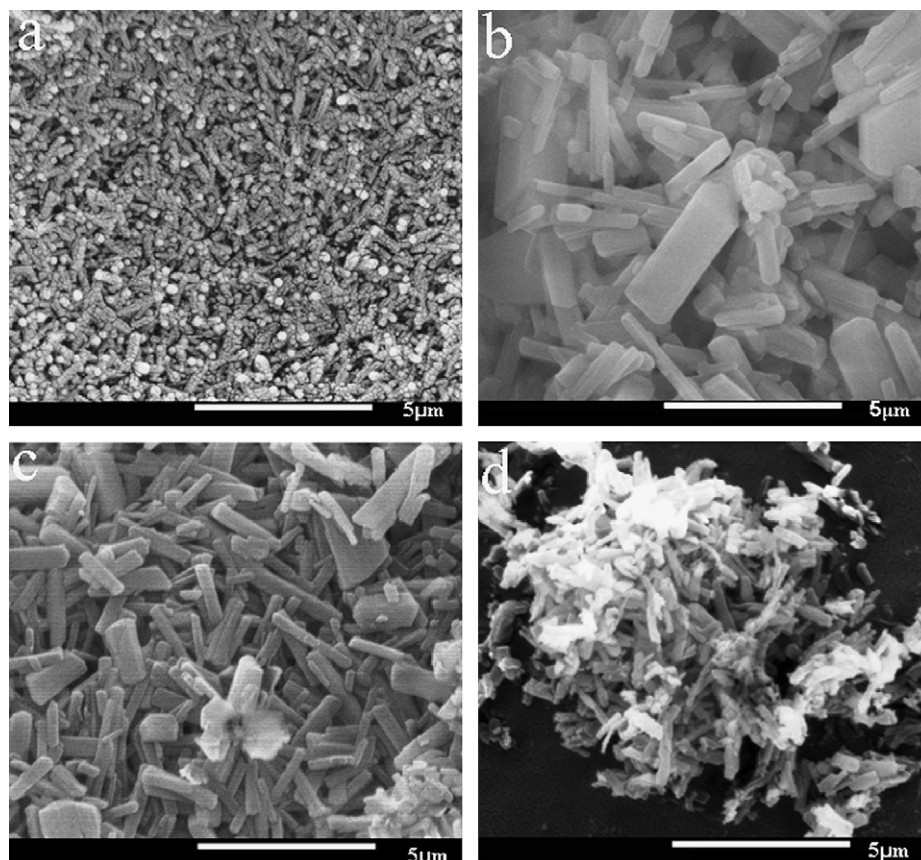


Fig. 7. Scanning electron micrographs of (a and b) sol–gel product after drying at 80 and 100°C for 24 h each, respectively, showing morphology of $\alpha\text{-MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, and (c and d) MgC_2O_4 and MgO formed after sol–gel product dried at 100°C for 24 h is further calcined at 400 and 600°C for 2 h each, respectively, in air.

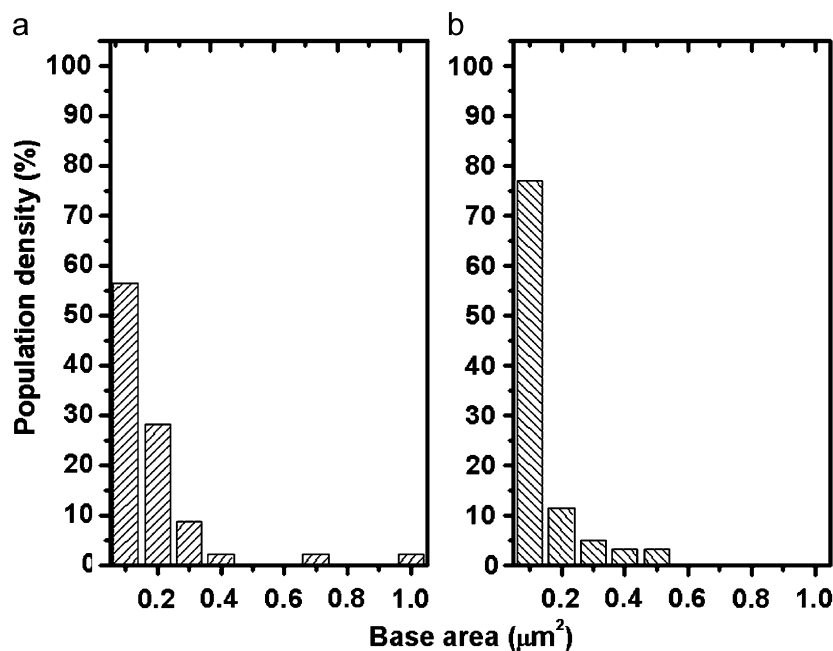


Fig. 8. Population density of parallelopipeds as a function of base area for (a) $\alpha\text{-MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and (b) MgC_2O_4 .

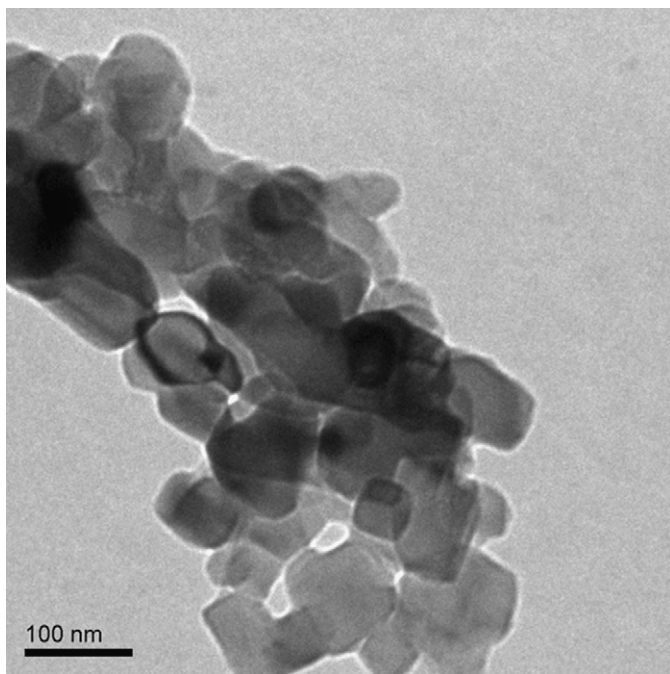


Fig. 9. Transmission electron micrograph of MgO powder obtained by decomposition of dried sol–gel product at 1000 °C for 2 h.

which also have parallelopiped morphology, but of relatively reduced size (Figs. 7c and 8b). Their length varies from 550 to 3110 nm with base dimensions being in the range of 95–710 nm. It can act as a standard reference material for determining concentration of γ -radiation-induced free radicals in electron spin resonance (ESR) dosimetry because of its high sensitivity, stability, and longer life time than alanine in use currently [41]. The addition of aliovalent ions in MgC_2O_4 may further improve its sensitivity and application in a wide dynamic dose range. A further increase in temperature (say, to 600 °C) leads to decomposition of the precursor powder to MgO, exhibiting

emergence of small distorted rods (Fig. 7d) with diameter in the range of 110–330 nm and an average diameter of ~ 195 nm. Fig. 9 shows a typical transmission electron micrograph of MgO powder obtained by decomposition of dried sol–gel product at 1000 °C for 2 h. Here, nano-size crystallites are closely seen as grouping together and forming a rod-like morphology.

3.4. Optical absorption

3.4.1. IR absorption of sol–gel product

The FTIR spectrum of precursor gel after drying at 100 °C for 24 h is shown in Fig. 10. The broad absorption band around 3387 cm^{-1} is composed of several peaks in the range $3100\text{--}3700\text{ cm}^{-1}$. It corresponds to the --OH -group-stretching vibrations. This observation provides evidence for the presence of chemically bound H_2O in the magnesium oxalate. The two absorption bands around 2978 and 2851 cm^{-1} are due to surface --OH stretch arising from hydroxyl groups in dissociated state or C–H stretch of organic residue [42]. An important absorption peak at 1649 cm^{-1} appears due to chelating with carbonyl group ($\nu_a(\text{C=O})$) and formation of an inorganic ester (i.e., magnesium oxalate, in this case). On careful examination, it is found that the peak comprises of a doublet with wave numbers 1653 and 1630 cm^{-1} , which represent symmetrical and asymmetrical vibrations of the carbonyl group, respectively. The deformational mode of water usually seen around 1600 cm^{-1} is, however, masked by the above doublet. The unionized and uncoordinated COO, characterized by a single stretching absorption band at $1750\text{--}1700\text{ cm}^{-1}$, shifts towards the lower frequency and splits into two bands (as observed above) when it combines with metal ions as $(\text{C}_2\text{O}_4)^{2-}$ ion [43]. Thus, IR absorption confirms the formation of $\alpha\text{-MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (revealed by XRD in Section 3.2). The other sharp absorption peaks at 1371 and 1325 cm^{-1} are assigned to $\nu_s(\text{C--O})+\delta(\text{OC=O})$ modes. While the weak band at 1118 cm^{-1} corresponds to C–O stretching, a peak at 688 cm^{-1} is attributed to bending mode of O=C=O and/or libration of water. All the observed absorption bands with respective intensity and possible origin/vibration modes are listed in Table 2.

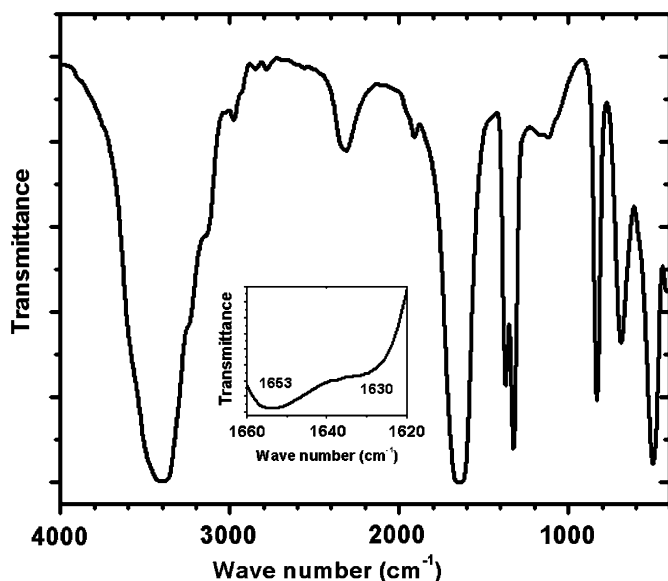


Fig. 10. Fourier transform infrared (FTIR) spectrum of sol-gel product dried at 100 °C for 24 h in air.

Table 2

FTIR spectroscopic data of magnesium oxalate dihydrate obtained by sol-gel process after drying the sol-gel product at 100 °C for 24 h [37,42,43]

Peak position (cm ⁻¹)	Intensity	Vibrational mode(s)
3386.6	Strong	–OH stretching
2977.8	Weak	–OH stretching (in phase)/C–H stretching
2850.5	Very weak	–OH stretching (out phase)
2314.0	Medium	C=O asymmetric stretch
1909.3	Weak	Bending and asymmetric stretching ν_2 modes polarized in the H–H direction of the H ₂ O molecule
1649.4	Strong	ν_a (C=O)/H–O–H stretch and bending association
1371.0	Strong	ν_s (C–O)+ δ (OC=O)
1325.0	Strong	ν_s (C–O)+ δ (OC=O)
1170.0	Very weak	ν_s (C–O)+ δ (OC=O)
1118.0	Very weak	C–O/C–C stretching
831.2	Strong	δ (O–C=O)+ ν (Mg–O)
688.5	Strong	Water libration, O=C=O bending
499.5	Strong	ν (Mg–O)+ ν (C–C)

3.4.2. IR absorption of MgO powder

Fig. 11 shows the FTIR transmittance spectra in the wave number range of 4000–3000 cm⁻¹ for MgO powders produced by decomposition of α -MgC₂O₄ · 2H₂O (derived from sol-gel process) at 500, 600, 800, and 1000 °C each for 2 h. These contain signatures of adsorption and chemisorption of water. The sharp peak centred around 3700 cm⁻¹ (Figs. 11a–c) indicates the presence of hydroxyl group at the low-coordination sites or defects [44]. Since the population of low-coordination sites decreases with increase in crystallite size, the effect is expected to be less pronounced at relatively larger t_{av} . In the present case, t_{av} increases with increase in the decomposition temperature. So, the absorption peak centred around 3700 cm⁻¹ is weakened gradually with increase in the decomposition temperature and disappears completely in MgO powders formed by decomposition at higher temperature ~1000 °C. Further, the FWHM of this absorption peak decreases and the values are 26, 22, and 12 cm⁻¹ for MgO powders obtained by decomposition of sol-gel product at 500, 600, and 800 °C, respectively. This means that the energy

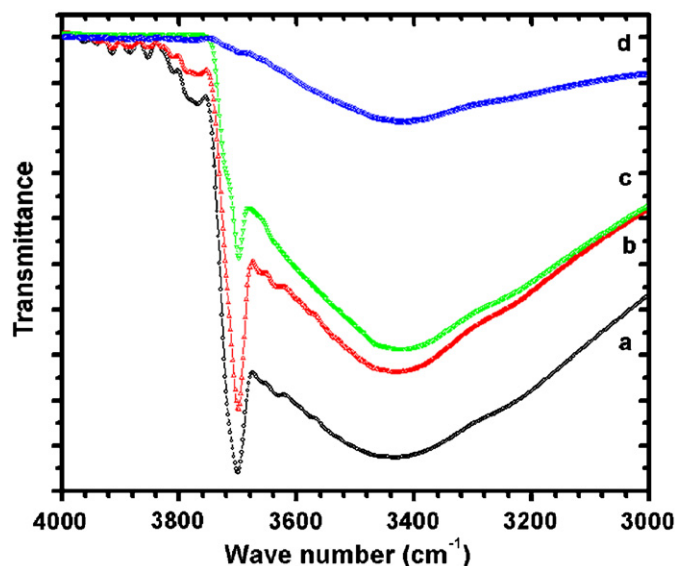


Fig. 11. Fourier transform infrared (FTIR) spectra of MgO powder obtained by decomposition of magnesium oxalate dihydrate at (a) 500, (b) 600, (c) 800, and (d) 1000 °C for 2 h each in air.

Table 3

FTIR spectroscopic data of MgO obtained by decomposition of magnesium oxalate dihydrate at 500, 600, 800, and 1000 °C for 2 h each

Temperature (°C)	–OH stretching (cm ⁻¹)	FWHM (cm ⁻¹)	Relative amount of water
500	3432.2	840	100
600	3432.1	800	71
800	3429.0	732	69
1000	3419.4	500	12

distribution of hydroxyl groups is narrowing with increase of the crystallite size. But, the peak itself undergoes a minor red shift of ~1 cm⁻¹, suggesting weak binding of the hydroxyl groups at Mg²⁺ sites in bigger crystallites. The absorption band in the wave number range 3660–3000 cm⁻¹ is quite broad (FWHM being 500–840 cm⁻¹, Table 3). This is assigned to –OH-stretching mode of adsorbed H₂O on the surface of MgO crystallites. The broadness in the spectra confirms a high degree of hydrogen bonding of water molecules among themselves and with the crystallite surface. Also, the absorption peak undergoes a red shift from 3432 to 3419 cm⁻¹ and becomes weaker with increase in t_{av} , indicating progressive reduction in the degree of binding of H₂O molecules at the crystallite surface. Table 3 summarizes the frequency, FWHM, and intensity values of –OH-stretching vibration modes.

3.4.3. UV–VIS–NIR absorption of MgO powder

Fig. 12 shows absorption spectra of MgO powder obtained by decomposition of the dried sol-gel product in air at 500, 600, 800, and 1000 °C for 2 h each in the wavelength range of 190–1450 nm. While the nature of the spectrum remains essentially the same, the degree of absorption varies somewhat with the crystallite size. A prominent absorption peak observed at ~6.2 eV in all MgO samples except that obtained by decomposition of sol-gel product at 1000 °C for 2 h (Fig. 12) is due to interband transition associated with surface ions of five-fold coordination; notice that the energy value is smaller than the band gap (7.8 eV) of bulk MgO. Other absorption bands can be understood in terms of oxygen vacancy/defect centres created both in the bulk and on the surface of MgO

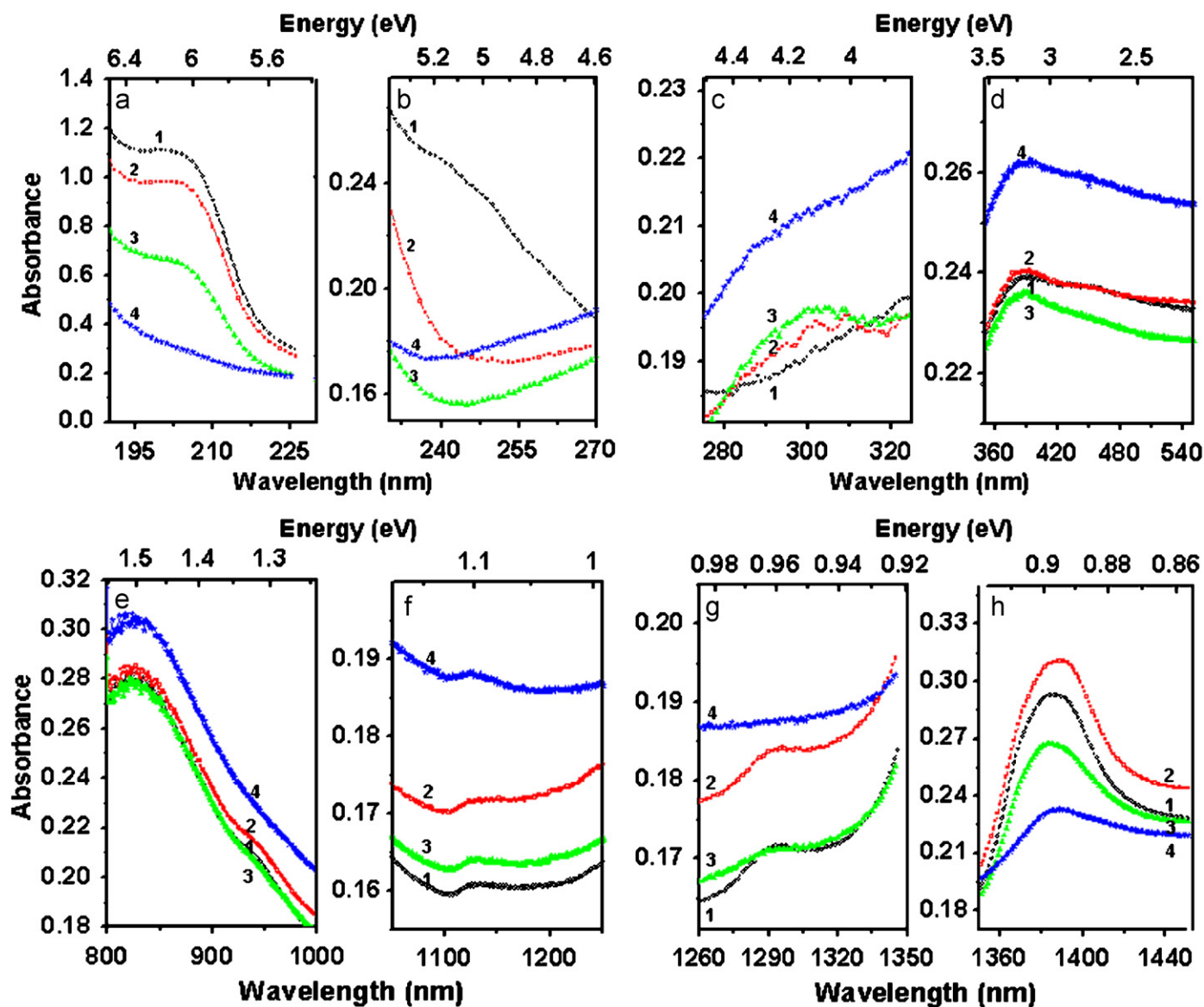
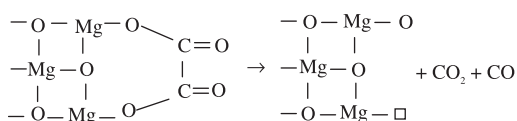


Fig. 12. UV-VIS-NIR spectra of MgO powder obtained by decomposition of magnesium oxalate dihydrate at (1) 500, (2) 600, (3) 800, and (4) 1000 °C for 2 h each in the wavelength range of (a) 190–230, (b) 230–270, (c) 275–325, (d) 350–550, (e) 800–1000, (f) 1050–1250, (g) 1260–1350, and (h) 1350–1450 nm.



Scheme 2. Decomposition of magnesium oxalate; open square stands for oxygen vacancy.

during decomposition of magnesium oxalate itself. The process can be described by Scheme 2.

If the oxygen vacancy retains its two electrons, the defect is called an F-centre (i.e., F for bulk and F_s for surface). This produces an energy level in middle of the valence band (2p oxygen) and conduction band (3s and 3p magnesium) edges, which is symmetric (a_{1g}) in both O_h and C_4 configurations, and can be classified as a 1s-type orbital. The ground state is therefore $^1A_{1g}(1s)^2$ for both bulk and surface defects. When one of the two electrons of F-centre is promoted to the conduction band, the defect F^+ (or F_s^+) is created and its energy level moves downwards,

near the valence band. In F^+ and F_s^+ centres the singly occupied ground state is $^2A_{1g}(1s)^1$. Further, if both the electrons are removed or promoted to the conduction band, a doubly charged vacancy, F^{2+} (or F_s^{2+}) is formed and the associated energy level moves still closer to the valence band. A group of two same defect centres (F, F^+ , or F^{2+}) in close proximity gives rise to M-centres (M, M^+ , or M^{2+}).

A weak and broad absorption band around 5.02 eV in powder produced at the decomposition temperature of 500 °C corresponds to $^1A_{1g} \rightarrow ^1T_{1u}$ transition of F-centres, as observed in a MgO single crystal after reduction at ~1600–1800 °C under magnesium vapour (pressure ~4000 Torr) and predicted by the second-order perturbation theory [45,46]. The characteristic peaks at 2.85, 1.31, and 0.96 eV disappear completely in samples formed at the decomposition temperature of 800 °C and above (i.e., having larger t_{av} and hence reduced surface area). Therefore, the above peaks possibly originate from species located at/or near the surface in smaller crystallites only. Also, the theoretical calculations show splitting of M_s centres into bonding and anti-bonding singlet states, lying 2.18 and 0.82 eV (instead of 1.22 eV in the case

of F_s centre) below the conduction band [47]. As a consequence, the observed peaks at 1.31 and 0.96 eV are assigned to $^1A_1 \rightarrow ^1A_1$ and $^1A_1 \rightarrow ^1B_1$ transitions, respectively, of M_s centres. Time-dependent density functional theory predicts the peaks for the above transitions at somewhat higher energies, viz., 1.48 and 1.19 eV, respectively [45]. A shoulder at 2.85 eV occurs due to $^1A'(gs) \rightarrow ^1A'(1s \rightarrow 2p_{x,y})$ transition from a four-coordinated F-centre, as observed in epitaxially grown thin film of MgO on Ag(100) substrates [46,47]. The splitting of 2p-like levels at the surface gives rise to two singlet-to-singlet, $^1A_{1g} \rightarrow ^1A_{1g}(1s \rightarrow 2p_z)$ and $^1A_{1g} \rightarrow ^1E(1s \rightarrow 2p_x \text{ or } 2p_y)$ transitions and are associated with absorption peaks at 3.2 and 4.2 eV, respectively. The absorption peak at 1.5 eV is related to $^1A'(gs) \rightarrow ^1E(1s \rightarrow 2p_{x,y})$ transition of three-coordinated F-centres. The absorption band found at 1.1 eV is attributed to spin forbidden $^1A_{1g} \rightarrow ^3A_{1g}(1s \rightarrow 2p_z)$ transitions of F_s centres. Further, a broad intense peak at 0.9 eV perhaps arises due to bulk M-centres. The observed peaks at 4.2, 3.2, 1.5, 1.1, and 0.9 eV have also been predicted by multi-reference (MR) and difference dedicated (DD) configuration interactions but with energies higher by ~ 1 eV. Also, MgO thin films exhibit peaks at 3.4 and 1.0 eV in their low energy loss spectra [48,49]. Many absorption peaks, instead of a few observed earlier [50], appear possibly due to different work functions of crystallites because of (i) prevailing size distribution and (ii) variation in the density of H_2O dipoles.

4. Conclusions

MgO powder (average crystallite size ~ 6.5 – 73.5 nm, NaCl-type structure with lattice parameter $a = 4.222$ – 4.212 Å) can be prepared by a simple and cost-effective sol–gel process using $Mg(NO_3)_2 \cdot 6H_2O$ and $(COOH)_2 \cdot 2H_2O$ as precursors with ethanol as a solvent. The sol–gel product is α - $MgC_2O_4 \cdot 2H_2O$ (formed naturally in rocks, plants, etc.) of parallelopiped morphology, which on decomposition at 500°C or above yields pure MgO. Observations indicate that the synthesized MgO is quite suitable for adsorption and dissociation of polar molecules, toxic waste remediation, etc. Further, it contains F- and M-defect centres, which are responsible for creating energy levels within the band gap (7.8 eV) of MgO. Such a characteristic is vital for enhancement of secondary electron emission efficiency, reduction of flickering, etc., and therefore, for its application in plasma display panels.

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