Local Electronic Structure Perspectives of Nanoparticle Growth: The Case of MgO

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ABSTRACT: Herein, we reported nanoparticle growth from the point of view of the local electronic structure by taking MgO as a prototype material. These nanoparticles were obtained from the sol–gel autocombustion process. The precursor formed in this process was annealed for various temperatures ranging from 300 to 1200 °C for 0.5 and 1 h. It was observed that the amorphous phase occurred in the material synthesized at an annealing temperature of 300 °C for 1 h. This phase transformed to crystalline when the annealing temperature was increased to 350 °C. Crystallite size increased with annealing temperature; however, annealing time did not influence the crystallite size. To get deeper insights of modifications occurring at the atomic scale during crystallization growth, the local electronic structure of synthesized materials was investigated by measuring near-edge X-ray absorption fine structure at Mg, O, N, and C K-edges. These results envisaged that Mg2+ ion coordination improved with the increase of annealing temperature. It was also observed that both annealing time and annealing temperature are sensitive to the local electronic structural changes.

1. INTRODUCTION

Understanding of grain growth phenomenon is important in the sense as it provides an opportunity to control/improve the characteristics of materials/devices. Yongan et al. reported that the grain growth, induced by nanoparticles, increases efficiency of solar cells based on selenide thin films.1 Crisp et al. observed that solar cell performance of CdTe ink-based photovoltaics depends on the initial crystallite size and shape as well as to the crystalline structure.2 Grain growth not only affects the photovoltaic response of devices but also influences the other properties as well. Amara et al. investigated that the nature of grain growth affects the dielectric behavior of Ti-rich SrTiO3.3 Thus, there have been attempt by researchers to understand this phenomenon in nanoparticles with a suitable technique. Ingham et al. reported aggregation and grain growth phenomena in Au nanoparticle using synchrotron X-ray diffraction (XRD) and the small-angle X-ray scattering.4 This group has also investigated the grain growth of Al-doped zinc oxide nanocrystals and observed higher value of activation energy for Al doping.5 Similar investigations were carried out for nanocrystalline Cr6 and Fe7. Grain growth of anatase TiO2 is described by an Arrhenius equation.6 Enhanced resistivity of electrically conductive nonoxide ceramics is associated with insulating conductive pathways through conductive grains in sintered body by the addition of an insulating grain boundary phase.7 In concurrent with the existing knowledge of grain growth, we focus our attention to investigate the changes occurring at atomic scale. This kind of investigation not only helps to understand the phenomena occurring at microscale but also persists a way to tailor the properties of synthesized nanomaterials in a controlled manner. In the realm of synthesizing nanomaterials, top-down and bottom-up approaches are commonly utilized.8,9 Whereas the top-down approach is the formation of nanoparticles from bulk precursor either by milling10,11 or mechanical attrition,12,13 the bottom-up approach utilizes atom by atom interaction based on chemical reactions.14,15 The bottom-up approaches are preferred because of low-power consumption and their cost effectiveness. Moreover, atom by atom reaction induces grain growth. Thus, stress, strain, and defects induced by milling/attrition are negligible. The most common methods utilizing bottom-up approaches are sol–gel,16 hydrothermal,19,20 and autocombustion synthesis.21,22 The formation of template during synthesis along with nanoparticle is possible. However, most of studies ignore this aspect. Thus, the present work is motivated to investigate the nanoparticle growth using a suitable technique by taking a simple system as a prototype material. In this context, a simple inorganic material, MgO, having a rocksalt structure is selected.

Supporting Information

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this material exhibit \(d^\circ\) ferromagnetism,\(^{24}\) improved optical,\(^{25}\) and dielectric behavior.\(^{26}\) Because of highly insulating nature, it finds applications in magnetic tunnel junctions\(^{27}\) and works as a template for several chemical reactions.\(^{28–30}\) Thus, important findings and applications motivate us to understand the growth of MgO using the sol–gel auto-combustion synthesis. To investigate atom by atom interaction during growth, a technique which provides element-specific information is highly desirable. We utilized near-edge X-ray absorption fine structure measurements (NEXAFS) which not only give information specific to valence state but also intriguing to crystallographic environment.\(^{31}\) Moreover, Mg K-edge spectra of MgO is very sensitive to the local coordination of constituted ions as observed in previous studies from our group\(^{32,33}\) as well as other group.\(^{34–36}\) Thus, investigation specific to local electronic structure during growth will be important to get information at atomic scale. Hence, present work investigates these aspects for MgO nanoparticles using XRD and NEXAFS.

2. RESULTS

2.1. Lower and Upper Threshold of Thermal Treatment for the Observation of Crystallization Growth.

XRD patterns of the precursor annealed at 300 °C for 1 h and 1200 °C for 12 h reflect the change associated with thermal annealing (Figure S1). The XRD pattern at 300 °C for 1 h exhibits two major humps centered at 18° and 35°. There is no other peak in this pattern, revealing the amorphous nature of nanoparticles (Figure S1). When the precursor is annealed at 1200 °C for 12 h, peaks at 36.44°, 44.38°, 62.42°, 74.88°, and 77.62° appear in the XRD pattern (Figure S1). The presence of these peaks in the XRD pattern is associated with the rocksalt phase of MgO (Figure S1). Refined structural parameters for this material are collated in Table 1. The values of lattice parameter and crystallite size are 4.2142 ± 0.0007 Å and ~50 ± 2 nm, respectively (Table 1). Lattice constant is almost equal to that of bulk MgO.\(^{23,24}\) Thus, these observations reveal that crystallization occurs above annealing of 300 °C. Hence, to understand the nature of grain growth, the precursor was annealed at several temperatures ranging from 350 to 1200 °C for 0.5 and 1 h. In order to see the effect of annealing on grain growth, the annealing time was also varied from 0.5 to 12 h at annealing temperatures of 350 and 400 °C. Thus, next two sections elaborate the grain growth under the influence of annealing temperature and time.

Thus, thermal annealing of the precursor at 300 °C for 1 h and 1200 °C for 12 h leads to significant changes in crystalline nature; hence, significant modifications in the chemical nature of these materials are expected. To answer this, NEXAFS measurements for synthesized MgO materials, precursor, magnesium nitrate, and citric acid were carried out. Figure 1 shows the Mg K-edge and O K-edge NEXAFS spectra of these materials. Mg K-edge spectra of precursor and material having annealing temperature at 300 °C for 1 h contain a spectral feature centered on 1307.2 ± 0.1 eV. When the precursor is annealed to 1200 °C for 12 h, spectral features \(A_1, A_2, A_3, A_4,\) and \(A_5\) centered at 1304.6 ± 0.1, 1311.0 ± 0.1, 1322.2 ± 0.1, 1344.1 ± 0.1, and 1357.9 ± 0.1 eV appear in the Mg K-edge spectrum, respectively. The presence of these spectral features is associated with the formation of MgO as observed from the Mg K-edge spectrum of the MgO crystal (Figure S2). The origin of these spectral features is described elsewhere.\(^{30–36}\) Moreover, spectral feature differences, \(\delta A_1A_2, \delta A_1A_4\) and \(\delta A_1A_5\) are estimated from Mg K-edge in order to get information of crystallographic environment of Mg\(^{2+}\) ions in synthesized materials. These values are 6.2 ± 0.2, 17.9 ± 0.2, and 46.2 ± 0.2 eV for materials synthesized at 1200 °C for 12 h. Corresponding values for MgO crystal are 6.3 ± 0.2, 18.0 ± 0.2, and 47.6 ± 0.2 eV (Figure S2). Thus, values of \(\delta A_1A_2, \delta A_1A_4\) and \(\delta A_1A_5\) for this material are almost similar to that of the MgO crystal. This envisages that Mg\(^ {2+}\) ion coordination in materials synthesized at 1200 °C for 12 h is analogous to that of the MgO crystal. These observations are concurrent with the conclusions made from the XRD analysis.

O K-edge spectra of precursor, citric acid along with materials synthesized at 300 °C for 1 h and 1200 °C for 12 h, are shown in Figure 1b. The O K-edge spectrum of each material is different from each other, revealing the significant change of local electronic owing to thermal treatment. The O K-edge spectrum of the material synthesized at 1200 °C for 12 h contains spectral features \(B_1, B_2, B_3, B_4,\) and \(B_5\) centered at 538.2 ± 0.1, 540.8 ± 0.1, 547.2 ± 0.1, 552.6 ± 0.1, and 558.0 ± 0.1 eV in the post-edge region, respectively, which are associated with the local electronic structure similar to bulk (Figure S3). The presence of these spectral features is due to O–Mg and Mg–Mg interactions in the MgO. The origin of these spectral features is discussed in details by Mizoguchi et al. (2001).\(^{36}\)

The pre-edge region of the spectrum of this material contains one spectral feature, \(B_2\) centered at 534.8 ± 0.1 eV (inset: Figure 1b). The pre-edge region of this spectrum for citric acid exhibits spectral features, \(B\) and \(B'\), centered at 532.6 ± 0.1 and 534.9 ± 0.1 eV (inset: Figure 1b), respectively. Spectral features \(B_2\) and \(B_5\) (minor) centered at 533.5 ± 0.1 and 535.0 ± 0.1 eV, respectively, occur in the pre-edge region of spectra for precursor and material synthesized at 300 °C. Thus, pre-edge regions of these spectra exhibit systematical changes from starting materials to its formation in the bulk state, that is, after synthesizing at 1200 °C for 12 h (inset: Figure 1b). This envisages that bonds present in the citric acid modify after annealing treatment. The O K-edge spectrum of the MgO crystal does not exhibit any pre-edge structure (Figure S3). Hence, the presence of the pre-edge region in the spectra of these materials may be ascribed to organic templates.\(^{25,38}\)

To get information of organic impurities attached with crystallites, NEXAFS spectra at C K- and N K-edges of these materials along with citric acid and magnesium nitrate are being investigated (Figure 2). Citric acid which is the matrix for synthesis exhibits spectral features around 284.2 ± 0.1, 287.2 ± 0.1, and 291.6 ± 0.1 eV in the C K-edge spectrum (Figure 2a). These spectral features originate from carbon, C–O (surface)/C–H bonds, and C–O (OH).\(^{39,40}\) These spectral

### Table 1. Simulated and Reliability Parameters Obtained from Rietveld Refinement of XRD Patterns

| parameters | 300 °C | 1200 °C–12 h |
|------------|-------|--------------|
| a (Å)      | amorphous | 4.2142 ± 0.0007 |
| Bragg R-factor | 2.18 | |
| R-factors  | 1.66 | |
| \(\chi^2\) | 8.31 | |
| goodness of fit-factor | 2.9 | |
| D (nm)     | 50 ± 2 | |

\*\*a\* and “D” are the lattice parameter and crystallite size of materials.
features are termed as $C_1$, $S$, and $C_2$. The precursor obtained in the synthesis process exhibits similar spectral features; however, the shape of spectral features is slightly modified. Spectral feature $C_2$ is broadened in the spectrum of the precursor. Spectral feature, $S$, appears like a shoulder. When the precursor is annealed to 300 °C, an additional spectral feature centered at 290.8 ± 0.1 eV evolves in the spectrum. This spectral feature is denoted as $C_3$ and associated with the presence of C–C ($\sigma^*$)-like bonds in these materials. This feature is also believed to have contribution from C–N–C ($\pi^*$) bonds. For materials synthesized at 1200 °C for 12 h, spectral feature $C_3$ dominates. This envisages that carbon in the form of C–C bonds/or C–N–C bonds still exist at such long annealing durations.

Further, to elucidate the presence of nitrogen ions, N K-edge spectra for synthesized materials measured along with Figure 1. NEXAFS measurements at (a) Mg K-edge and (b) O K-edge for materials synthesized at different annealing treatments along with precursor and citric acid. Mg K-edge spectra of precursor and annealing temperature of 300 °C is shown as inset a. Inset (b) shows the pre-edge region of O K-edge spectra for these materials.

Figure 2. (a) C K-edge and (b) N K-edges for materials synthesized at 300 and 1200 °C for 12 h along with precursor, citric acid, and magnesium nitrate.
magnesium nitrate and precursor are shown in Figure 2b. Magnesium nitrate, which is the starting material for synthesizing materials, contains two dominant spectral features $D$ and $D'$ centered at 401.6 ± 0.1 and 405.1 ± 0.1 eV, respectively. Spectral feature, $D'$, is due to $1s \rightarrow \pi^{*}$ transition of nitrate anion; $^{43}$ however, minor spectral feature, $D$, envisages the presence of nitride anions.$^{44}$ In addition to these spectral features, a shoulder-like feature around 400.2 ± 0.1 eV also exists in the spectrum of magnesium nitrate. This shoulder is denoted as $D_1$ and is associated with amino-type species in the starting materials.$^{35,46}$ The N K-edge spectrum of the precursor formed during synthesis process exhibits spectral features $D_1$ and $D_2$. Spectral feature, $D_2$, envisages the existence of N=O and nitrided carbon in the precursor.$^{25-27}$ Spectral features, $D_1$ and $D_2$, exist in the N K-edge spectrum even if the precursor is annealed at 300 °C. Spectral feature, $D_2$, almost disappears for bulk treatment; however, the intensity of spectral feature, $D_1$, improves significantly. Thus, nitrogen in the form of amino-type species exists in the material synthesized at 1200 °C for 12 h. Hence, these investigations envisages the existence of organic impurities in the form of nitric carbon and amino-type nitrogen along with crystallite/grain in synthesized materials.

### 2.2. Variation of Annealing Temperature.

In order to investigate grain growth with annealing temperature, the precursor was annealed at several temperature ranging from 350 to 1200 °C for 0.5 and 1 h. Refined XRD patterns at 350, 400, 600, 800, 1000, and 1200 °C for 0.5 and 1 h are shown in Figure S4. Both the experimental and refined XRD patterns are in close agreement with each other for all nanoparticles. This indicates that annealing at these temperatures for durations of 0.5 and 1 h forms the pure rocksalt phase of MgO. The values of lattice parameter decrease with annealing temperature at both annealing durations (Table S1). At annealing temperature of 1200 °C for both annealing durations, values of lattice parameter are close to that of bulk MgO (4.214 Å). This reveals that crystallinity improves with the increase of annealing temperatures. XRD peaks get narrowed with the increase of annealing temperature, indicating enhancement of crystallite size with annealing (Figure S4). Values of crystallite size are 8.2 ± 0.2, 10.7 ± 0.3, 12.6 ± 0.4, 20.4 ± 0.9, 26.2 ± 1.5, and 31.8 ± 2.3 nm for annealing temperatures of 350, 400, 600, 800, 1000, and 1200 °C for 0.5 h (Figure S5), respectively. These values are 6.9 ± 0.2, 11.8 ± 0.4, 15.8 ± 0.5, 21.6 ± 1.1, 26.6 ± 1.6, and 32.9 ± 1.5 nm for corresponding temperatures at 1 h (Figure S5). Considering, annealing temperature to be denoted by “$T$” variation of crystallite size, $D$, with temperature can be given by following empirical equations

$$D_{0.5} = (0.027 ± 0.002) \times T + (-1.69 ± 1.40) (1)$$

$$D_{1.0} = (0.030 ± 0.003) \times T + (-2.12 ± 1.70) (2)$$

Thus, variation of crystallite size with annealing temperature is described by empirical linear equations at both annealing durations. Hence, these empirical equations reveal the nature of crystallization growth with annealing temperature. It is clear from these equations that annealing temperature promotes grain growth in the nanomaterials. This behavior is reflected by the number of nanoparticle systems including ferrites,$^{48,49}$ oxides,$^{50,51}$ and titanates$^{52}$ synthesized using same method.

To get understanding of local electronic/atomic order modifications with annealing temperature, measured Mg K-edge spectra at various annealing temperatures for 0.5 and 1 h are shown in Figure S6. The presence of spectral features $A_1$, $A_2$, $A_3$, $A_4$, and $A_5$ clearly reveals local electronic structure analogues to MgO for both annealing durations (Figure S6).

To get deeper insights of Mg$^{2+}$ ion coordination, the behavior of $\delta A_1 A_2$, $\delta A_1 A_3$, and $\delta A_1 A_5$ is depicted in Figure 3. Values of $\delta A_1 A_2$ increase exponentially with annealing temperature from 5.6 ± 0.2 to 6.3 ± 0.2 eV for annealing time of 0.5 h (Figure 3a). Similar variation is observed for $\delta A_1 A_3$ as this value increases from 16.7 ± 0.2 to 17.8 ± 0.2 eV as the annealing temperature increases from 350 to 1200 °C at this annealing time (Figure 3a). $\delta A_1 A_5$ increases linearly with annealing temperature from 46.4 ± 0.2 to 47.0 ± 0.2 eV at this annealing time (Figure 3a). At 1200 °C and 0.5 h, values of $\delta A_1 A_2$, $\delta A_1 A_3$, and $\delta A_1 A_5$ are 6.3 ± 0.2, 17.8 ± 0.2, and 47.0 ± 0.2 eV which are close to the value of bulk MgO (Figure S2), respectively. This reveals the existence of Mg$^{2+}$ ions in...
crystallographic environment similar to bulk MgO under this annealing condition.

The values of $\delta A_1A_2$, $\delta A_1A_3$, and $\delta A_1A_5$ are $4.7 \pm 0.2$, $14.2 \pm 0.2$, and $45.6 \pm 0.2$ eV at 350 °C for 1 h (Figure 3b) which are significantly less than the values of bulk MgO (Figure S2), respectively. This envisages the presence of distorted coordination of Mg$^{2+}$ ions in these nanoparticles. On further increasing the annealing temperature, these values remain almost constant within experimental error at values of $5.9 \pm 0.2$, $17.2 \pm 0.2$, and $46.4 \pm 0.2$ eV (Figure 3b). For nanoparticles synthesized at 350 °C, Values of $\delta A_1A_2$, $\delta A_1A_3$, and $\delta A_1A_5$ at 1 h (Figure 3b) are slightly less than that observed for 0.5 h (Figure 3a). This reveals that Mg$^{2+}$ ion coordination is slightly distorted. During synthesis, the precursor was annealed first for 1 h. It took around 6–7 days to synthesize these nanoparticles. Then, after 6–7 days, the precursor was annealed for 0.5 h at different temperatures. It is possible that during this period, self-induced growth takes place and after annealing, the crystallites become more ordered.

Figure 4 shows the O K-edge NEXAFS spectra of nanoparticles synthesized at 350, 400, 600, 800, 1000, and 1200 °C for annealing time of 0.5 and 1 h. The pre-edge region is also shown as the inset in these figures for better
visualization. Spectral features $B_1$, $B_2$, $B_3$, and $B_3$ appear at $537.4 \pm 0.1$, $540.8 \pm 0.1$, $547.8 \pm 0.1$, $553.2 \pm 0.1$, and $558.2 \pm 0.1$ eV, respectively, for nanoparticles annealed at $600$, $800$, $1000$, and $1200$ °C for $0.5$ h (Figure 4a).

These post-edge spectral features are distinguishable in all nanoparticles. At $350$ and $400$ °C, spectral feature, $B_3$, almost disappears. Moreover, the intensity of spectral feature, $B_3$, for these nanoparticles is low. Behavior of post-edge region is more interesting. The spectral features $B_1$, $B_2$, $B_3$, and $B_3$ appear at $537.4 \pm 0.1$, $540.8 \pm 0.1$, $547.8 \pm 0.1$, $553.2 \pm 0.1$, and $558.2 \pm 0.1$ eV, respectively, for nanoparticles synthesized at $600$, $800$, $1000$, and $1200$ °C for $1$ h (Figure 4b). Figure 5 shows the C K-edge spectra of these nanoparticles grown at several temperatures for $0.5$ and $1$ h. Spectral features $C_1$, $C_2$, and $C_3$ appear at $284.2 \pm 0.1$, $288.4 \pm 0.1$, and $290.3 \pm 0.1$, respectively, in the C K-edge spectra of materials synthesized at different annealing temperatures for $0.5$ h (Figure 5a), respectively. A shoulder, $S$, around $287.4 \pm 0.1$ eV also appears in the spectra of these materials. Appearance of these spectral features at various annealing temperatures is associated with quinine-type carbon, C–O (surface)/C–H bonds, C–O ($\sigma^*$), and C–C ($\sigma^*)$/C–N–C ($\pi^*$) bonds. For annealing time of $1$ h, the presence of the features $C_1$, $S$, $C_2$, and $C_3$ in the spectra of materials synthesized at different annealing temperatures reveal existence of these bonds in these materials (Figure 5b). Spectral features, $D_1$ and $D_2$, present in all of the nanoparticles irrespective of annealing temperature (Figure S7) which envisions the presence of amino, N–O, and nitride carbon-type species in these materials. We further investigated the effect of annealing time on the growth of MgO nanoparticles and discussed in next section.

### 2.3. Variation of Annealing Time

A further attempt was made to investigate the grain growth with annealing time; the precursor was annealed at $350$ and $400$ °C for $0.5$, $1$, $3$, $6$, $9$, and $12$ h. Refined XRD patterns for various annealing times reveal the formation of rocksalt phase in these nanoparticles (Figure S8). Refined parameters are collated in Table S2. The values of lattice parameter decrease slightly within experimental error at annealing times at $350$ and $400$ °C (Table S2). At both temperatures and various annealing durations, the value of lattice parameter is around $4.225$ Å (Table S2). This reveals that longer annealing does not play significant role to improve crystallinity of materials. Variations of crystallite size with annealing time at annealing temperatures of $350$ and $400$ °C are shown in Figure S9. Values of crystallite size are $8.2 \pm 0.2$, $6.9 \pm 0.2$, $9.0 \pm 0.4$, $11.1 \pm 0.4$, $9.3 \pm 0.4$, and $9.7 \pm 0.4$ nm for $0.5$, $1$, $3$, $6$, $9$, and $12$ h for an annealing temperature of $350$ °C, respectively. These values are $10.7 \pm 0.2$, $10.9 \pm 0.3$, $11.3 \pm 0.3$, $10.9 \pm 0.3$, $11.0 \pm 0.3$, and $11.0 \pm 0.3$ nm at corresponding temperatures for $1$ h. At $400$ °C, values of crystallite size are $10.7 \pm 0.3$, $10.9 \pm 0.3$, $11.2 \pm 0.3$, $10.9 \pm 0.3$, $10.9 \pm 0.3$, and $11.0 \pm 0.3$ nm for annealing durations of $0.5$, $1$, $3$, $6$, $9$, and $12$ h. Variation of crystallite size with annealing temperature is better represented by a linear fitting for both annealing durations (Figure S9). Considering annealing time by ‘$t$’, fitting can be represented as

$$
(D)_{350} = (0.36 \pm 0.02) \times t + (6.93 \pm 0.08)
$$

$$
(D)_{400} = (0.01 \pm 0.02) \times t + (10.91 \pm 0.11)
$$

when annealing temperature is $350$ °C, the value of slope is $0.36 \pm 0.02$ s$^{-1}$; however, this value is $0.01 \pm 0.02$ s$^{-1}$ for annealing temperature of $400$ °C. This reveals that annealing time promotes crystallization at $350$ °C; however, the role of annealing duration is almost nonsignificant on crystallite growth at $400$ °C. Because with the increase of annealing duration, heat confinement will increase inside the crystallites; hence, investigation for determining local electronic structure at these durations is also performed.

Mg K-edge spectra for various annealing times at $350$ and $400$ °C are shown in Figure S10. The presence of spectral features, $A_1$, $A_2$, $A_3$, $A_4$, and $A_5$ for all annealing durations clearly reveals the presence of local electronic structure similar to bulk MgO at $350$ and $400$ °C; however, variations of $\delta A_1 A_2$, $\delta A_1 A_3$, and $\delta A_1 A_4$ with annealing times reflect modification of Mg$^2+$ ion coordination (Figure 6). Values of $\delta A_1 A_2$ are $5.6 \pm 0.2$, $4.7 \pm 0.2$, $5.8 \pm 0.2$, $5.9 \pm 0.2$, $5.7 \pm 0.2$, and $5.7 \pm 0.2$ eV for annealing durations of $0.5$, $1$, $3$, $6$, $9$, and $12$ h at $350$ °C (Figure 6a). $\delta A_1 A_3$ values are $16.7 \pm 0.2$, $14.1 \pm 0.2$, $16.9 \pm 0.2$, $17.2 \pm 0.2$, $17.1 \pm 0.2$, and $17.0 \pm 0.2$ eV for

Figure 6. Variations of Mg K-edge spectral feature energy difference ($\Delta E$) with annealing duration for annealing temperature of (a) 350 and (b) 400 °C.
corresponding annealing time. Variation of $\delta A_1A_3$ is analogues to $\delta A_1A_2$ and $\delta A_1A_4$ as can be seen from Figure 6a. $\delta A_1A_5$ values are $46.4 \pm 0.2$, $33.9 \pm 3.1$, $46.3 \pm 0.2$, $46.5 \pm 0.5$, $46.3 \pm 0.2$, and $46.2 \pm 0.2$ eV for annealing durations of 0.5, 1, 3, 6, 9, and 12 h, respectively (Figure 6a). Thus, these values are maximum at annealing duration of 6 h and always less than the values of these parameters for bulk MgO (Figure S1). This reveals that annealing duration at such low annealing temperature does not improve the Mg$^{2+}$ ion coordination even if it is increased to 12 h.

We further focus our attention to understand the behavior of Mg$^{2+}$ ion coordination under annealing temperature of 400 °C. The parameters $\delta A_1A_2$, $\delta A_1A_3$, and $\delta A_1A_5$ at various annealing times are shown in Figure 6b.

Figure 6b reflects that variation of these three parameters with annealing time is different from each other. The $\delta A_1A_2$ values are $5.9 \pm 0.2$, $5.9 \pm 0.2$, $6.1 \pm 0.2$, $5.9 \pm 0.2$, $5.6 \pm 0.2$, and $5.7 \pm 0.2$ eV for annealing durations of 0.5, 1, 3, 6, 9, and 12 h, respectively. These values are almost similar for annealing duration up to 6 h. However, values reduce significantly for annealing durations of 9 and 12 h. This reveals pertinent of bulk-like coordination up to 6 h; however, it deteriorates slightly at higher annealing duration. Values of $\delta A_1A_3$ increase slightly from $17.3 \pm 0.2$ to $17.7 \pm 0.2$ eV as annealing duration...
increases from 0.5 to 12 h. These parameters also lower than that of bulk MgO. Figure 6b also envisages that $\delta A_2 A_3$ too lower than that of the corresponding value for bulk MgO (Figure S2). The value of this parameter decreases slightly from $46.4 \pm 0.2$ to $46.1 \pm 0.2$ eV for the increase of annealing duration from 0.5 to 12 h. Thus, behavior of these parameters reveals slight modification of Mg$^{2+}$ ion coordination with annealing time. It is clear from the behavior of these parameters that mere increase of annealing duration does not form the perfect coordination but annealing temperature plays important role. Increase of annealing temperature induces crystallization growth as discussed in the previous section.

Figure 7 shows the O K-edge NEXAFS spectra of nanoparticles synthesized at 0.5, 1, 3, 6, 9, and 12 h for annealing temperature of 350 and 400 °C. The pre-edge region is also shown as the inset in this figure for better visualization. The spectral features $B_1, B_2, B_3,$ and $B_4$ appear at $537.4 \pm 0.1, 540.8 \pm 0.1, 547.8 \pm 0.1, 553.2 \pm 0.1,$ and $558.2 \pm 0.1$ eV, respectively, for nanoparticles synthesized at annealing times of 0.5, 1, 3, 6, 9, and 12 h (Figure 7a). These post-edge spectral features are distinguishable in all nanoparticles. At lower annealing times for both annealing temperature, that is, 350 and 400 °C, spectral feature, $B_4$ almost disappears. Moreover, the intensity of spectral feature, $B_5,$ for these nanoparticles is low. Behavior of post-edge region is more interesting. The spectral features $B_6$, $B_7$, $B_8$, and $B_9$ appear at $537.4 \pm 0.1, 540.8 \pm 0.1, 547.8 \pm 0.1, 553.2 \pm 0.1,$ and $558.2 \pm 0.1$ eV for nanoparticles synthesized at annealing times of 0.5, 1, 3, 6, 9, and 12 h (Figure 7b). Spectral features, $B_6$ and $B_7,$ in the pre-edge region exhibit systematic variation of intensity with annealing durations at both annealing temperatures. In both cases, spectral feature, $B_7,$ disappears at higher annealing temperatures. Again, it is clear from Figure S4 that these pre-edge structures are not characteristics of MgO and are associated with organic templates attached with crystallites. Nature of these templates is investigated from the C K and N K-edge NEXAFS measurements.

Figure 8 shows the C K-edge spectra of these nanoparticles grown at several annealing durations for annealing temperature of 0.5 and 1 h. Spectral features $C_1, C_2,$ and $C_3$ appears at $284.2 \pm 0.1, 288.4 \pm 0.1,$ and $290.3 \pm 0.1$ eV in the C K-edge spectra of materials synthesized at different annealing times for annealing temperature of 350 °C (Figure 8a). A shoulder, $S_1$ around $287.4 \pm 0.1$ eV also appears in the spectra of these nanoparticles. Appearance of these spectral features at various annealing temperatures is associated with quinine-type carbon, C−O (surface)/C−H bonds, C−O ($\sigma^*$), and C−C ($\sigma^*$) bonds. C−N (C) (C) bonds. For annealing temperature of 400 °C, the presence of the features $C_1, S_1, C_2,$ and $C_3$ in the spectra of nanoparticles synthesized at different annealing times reveals existence of these bonds (Figure 8b).

Spectral features $D_1$ and $D_2$ appear in the N K-edge spectra of all of the nanoparticles irrespective of annealing time (Figure S11) which envisages the presence of amino, N−O, and N−O. Similar investigations were also observed from the Fourier transform infrared (FTIR) spectroscopic investigation of zinc ferrite nanoparticles synthesized using similar methods.55 These impurities are always attached with nanoparticles and cannot be removed even if these nanoparticles are kept under intense beam of heavy ions.55,54 High-temperature annealing to chemically synthesize nanoparticles also shows onsets of carboneous-like impurities.55 Even washing of nanoparticles synthesized using chemical methods is not able to give these nanoparticles free from organic impurities.56 Thus, the presence of these impurities may lead to high dielectric and magnetic loss in the materials synthesized using these methods even having modified dielectric,59 optical, and magnetic behavior.55,58 Thus, attachment of these carbon-like impurities with crystallites is intrinsic properties of chemically synthesized materials. This aspect is also investigated by FTIR spectroscopy for magnesium oxides and calcium oxide nanoparticles.38

3. DISCUSSION

Further, the role of thermal annealing on the crystallization growth can be understood by following equation which relates Gibbs energy to the thermal energy:

$$\Delta G = \frac{3(N\Delta H - T^2NkT \ln 2)}{4\pi R^2} \quad (5)$$

The grain growth can be described for specific annealing duration can be given as

$$D^2 \left(1 - \frac{D}{D_0}\right)^2 = k_0 a \exp\left(-\frac{Q}{NkT}\right) \quad (6)$$

where $D$ is the final grain size and $D_0$ is the initial grain size, $k_0$ is a constant, $T^\circ$ is the absolute temperature, and $Q$ is the activation energy for grain boundary mobility. $t$ is the time required to reach the given grain size.53 Activation energy for grain boundary mobility was calculated from the linear fitting $\ln(D^2 - D_0^2)$ versus $1/T^\circ$ curves which are shown in Figure 9.

![Figure 9](image_url)

Figure 9. Linear fittings of $\ln(D^2 - D_0^2)$ versus $1/kT$ for estimation of activation energy of grain boundary mobility.

The detailed description is described in S1 (Supporting Information). The activation energies for grain boundary mobility are $0.24 \pm 0.02$ and $0.025 \pm 0.03$ eV nm$^2$/mol for annealing times of 0.5 and 1 h, respectively. Thus, the value of activation energy is equivalent for both annealing durations. Thus, the nanoparticle system grown using chemical methods can be better described by a mixture of organic template and inorganic crystallites. Similar findings are also being observed from combined investigation of EDX, NEXAFS, and X-ray photoelectron spectroscopy for selected MgO nanoparticles and published elsewhere.59 XRD measure-
ments which depend on the crystallinity detect only the crystal. However, when these nanoparticles are detected using NEXAFS which depends on the atomic nature, a significant change is observed in NEXAFS measurements especially at C and N K-edge. Thus, it is stated that organic templates are pertinent with crystallite and seems to be independent from thermal treatment.

To establish the fact again, NEXAFS measurements in bulk sensitive, total fluorescence yield (TFY) mode were performed for selected nanoparticles at Mg and O K-edges. TEY mode spectra were also measured along with TFY measurements. TEY & TFY measurements reflect same nature for corresponding nanoparticles (Figure 10). To get deeper insights of this effect, difference and ratio of spectral features $A_1$ and $A_2$ in TEY and TFY mode are estimated. These values are collated in Table S3. It is clear that these values are comparable except the nanoparticle synthesized at 350 °C for 9 h. This effect is associated with the presence of minor phase of magnesium hydroxide phase at such treatment (Figure S13). Moreover, O K-edge spectra also exhibit same kind of behavior at surface and bulk of the nanoparticles (Figure S12). This again supports the association of carboneous impurities attached with crystallites. If compared from previous work of our group, then it is observed that O K-edge spectra, in comparison of Mg K-edge, are more sensitive to organic templates in the case of MgO nanoparticles. These spectra seem to be insensitive to these templates in the case of nanoparticles such as CaO, ZnFe$_2$O$_4$, MgFe$_2$O$_4$, CoFe$_2$O$_4$, and ZnO when synthesized using chemical methods. More- ever, control of these species during synthesis is very tedious; hence, variation of O K-edge spectra either with annealing time or temperature is not as systematic as Mg K-edge.

**4. CONCLUSIONS**

Thus, the present work investigates the effect of annealing treatment on the crystallization growth of MgO nanoparticles by means of XRD and NEXAFS fine structure measurements. The precursor obtained in this method is amorphous in nature and exhibits onset of organic impurities as observed from NEXAFS measurements. When annealing is performed at 300 °C, amorphous phase along with several organic impurities occurred. XRD studies reveal that crystallization occurs above 300 °C. Values of crystallite size increases linearly with annealing temperature. Thus, enhancement of annealing temperature promotes grain growth. The organic impurities are attached to these crystallites at several annealing temperatures. When annealing duration is increased, nonsignificant growth of crystallite occurs with no de-attachment of organic impurities. At lower annealing time, Mg$^{2+}$ ion coordination improves with the increase of annealing temperature; however, there is negligible modification of coordination for annealing time of 1 h. At lower annealing temperature, Mg$^{2+}$ ion coordination first improves, then weaken slightly with annealing duration. At other annealing temperature, Mg$^{2+}$ ion coordination weakens with the increase of annealing time.

**5. EXPERIMENTAL SECTION**

**5.1. Synthesis of Nanoparticles.** Mg(NO$_3$)$_2$·6H$_2$O (AR Grade) was mixed into citric acid solution by keeping cations to citric acid ratio as 1:3. The mixture was placed on a magnetic stirrer at 90 °C for almost 6 h. Thus, the obtained viscous solution was heated at 100 °C for 16 h. The precursor formed after heating was annealed at various temperatures ranging from 300 to 1200 °C for 0.5 and 1 h. The precursor was also annealed at 350 and 400 °C by varying annealing durations ranging from 0.5 to 12 h for investigation of annealing time influence on nanoparticle growth. One material was obtained by annealing precursor at 1200 °C at 12 h which is termed as bulk in this investigation. The detailed procedure of thermal treatment for obtaining MgO nanoparticles is depicted in Figure S14.

**5.2. Characterization of Nanoparticles.** XRD patterns were recorded on a D/MAX2500 (RIGAKU, Japan) X-ray diffractometer by using Cu Ka ($\lambda = 1.5418$ Å) radiation. NEXAFS measurements on these nanoparticles were carried out at 10D XAS-KIST beamlines.

**5.3. Analysis/Simulation Details.** The obtained XRD patterns were refined using Fullprof programme. The crystallite size ($D$) of these nanoparticles was estimated from the most intense peak using Scherrer’s formula. NEXAFS spectra at Mg and O K-edges are normalized by removing pre-
edge and post-edge backgrounds, resulting in intensity = 0 and 1 for pre-edge and post-edge backgrounds, respectively. Such routine could be not followed for spectra measured at C and N K-edges because of weak signal; thereby, the intensity is the relative intensity.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00262.

Text discussing the growth of nanoparticle; tables depicting the parameters estimated from Rietveld refinement; refined XRD patterns of MgO bulk and MgO nanoparticles; NEXAFS spectra of MgO nanoparticles at Mg and N K-edges; and O K-edge NEXAFS spectra in TEF and TTF mode for selected nanoparticles (PDF)

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**Notes**

The authors declare no competing financial interest.

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