Preparation and Characterization of Magnesia-Based Powder Added with Transition Metal

Bong-Gu Kim¹, Hyun-Hee Choi¹, Jung-Hun Son¹, SeungCheol Yang¹, Min-Seok Kwon², Asimiyu A. Tiamiyu³, Jing Zhang³, Yeon Gill Jung¹,*

¹School of Nano & Advanced Materials Engineering, Changwon National University, 20 Changwondaehak-ro, Changwon, Gyeongnam 51140, Republic of Korea

²Steelmaking Research Group, Technical Research Laboratories, POSCO1, Goedong-dong, Nam-gu, Pohang-shi, Gyeongbuk

³Department of Mechanical Engineering, Indiana University-Purdue University Indianapolis,, 723 West Michigan Street, Indianapolis, IN 46202

*Corresponding author

E-mail address: jungyg@changwon.ac.kr (Y.G.Jung)
ABSTRACT
The solid-phase reaction method for preparing forsterite ($\text{Mg}_2\text{SiO}_4$) using MgO and SiO$_2$ powders has the disadvantages of high reaction temperature, long reaction time, and inhomogeneous reaction depending on the particle size of MgO. Therefore, MgO-based powders with a high reactivity were synthesized using a coprecipitation method with substitutional elements (Mn or Ni), and the effects of processing parameters on synthesizing MgO-based binary composition powders were investigated through the particle characteristics. The crystal structure continuously changed with the contents of the substitutional element, showing the same trend as the atomistic simulation results. The MgO-based powders showed higher reactivity than the conventional MgO powder, which could be confirmed in the particle characteristics, such as particle size and crystallinity, obtained in a short reaction time, and at a relatively low temperature. The optimum composition ratio in the binary composition powder for forming the $\text{Mg}_2\text{SiO}_4$ depended on the type of substitutional element, and the reaction mechanism was identified based on the particle characteristics.

Keywords:
Magnesia
Coprecipitation
Substitutional element
Binary composition powder
Reactivity
1. Introduction

Ceramic powders are synthesized using various methods, such as solid state reaction, sol–gel reaction, hydrothermal synthesis, and coprecipitation [1–4]. The solid state reaction method is the most widely used for producing polycrystalline ceramic powders from mixtures of solid starting materials [5,6]. There is no waste disposal problem in the solid state reaction method because there is no need for solvent in the reaction [5], while there is a disadvantage of expensive construction and its maintenance because it should be conducted at a high temperature of 1000–1500 °C [6]. In addition, this process requires a long reaction time, and the uniformity in the reaction depends on the particle size and distribution [7].

Forsterite (Mg₂SiO₄) is employed as an insulator in tubes, substrate for resistors, substrate for integrated circuits, and an implant material, owing to its excellent properties, such as excellent insulation performance, low dielectric loss, high mechanical strength, excellent thermal stability, and large coefficient of thermal expansion [7–10]. Therefore, the various synthetic methods mentioned above have been studied for the successful synthesis of Mg₂SiO₄ [7–16]. Among these methods, the solid state reaction from mixtures of magnesia (MgO) and silica (SiO₂) powders has been generally utilized for the simple synthesis of Mg₂SiO₄ without post-solvent and environmental problems. However, the solid state reaction between powders requires a high temperature of over 1500 °C and longer reaction time during the reaction compared with other methods [1,5,6]. To improve the issues of high process temperature and long reaction time in the solid state reaction for preparing Mg₂SiO₄, various studies have been undertaken to increase the reactivity of MgO and SiO₂ powders [12–16]. Ta-Wui Cheng et al. reported that the reaction temperature in the solid state method could be reduced to 1500 °C by adding serpentine [12]. Lin Cheng et al. increased the surface activity by employing nanosized MgO and SiO₂ powders prepared using a high-energy milling method, and reduced the heat-treatment temperature to 850 °C [13]. Liugang Chen et
al. synthesized Mg$_2$SiO$_4$ at 850 °C using MgO precursors such as magnesium hydroxide (Mg(OH)$_2$) or magnesium carbonate (MgCO$_3$) [15,16].

MgO, which can be utilized for synthesizing Mg$_2$SiO$_4$ by the solid state reaction, has been prepared by several methods, such as coprecipitation, electrodeposition, sol–gel technique, hydrothermal, solvothermal, preparation using a bubbling setup, and microwave-assisted synthesis [17]. Among the various methods, the coprecipitation technique is a simple and cost-effective method to produce ceramic powder, including MgO, by adding a chemical precipitant to a cation-containing solution or by changing temperature and/or pressure. It is possible to synthesize powder under various conditions by adjusting the concentration, pH, mixing and stirring speed, and solution temperature [18–21]. In addition, coprecipitation can be an efficient manufacturing procedure to produce MgO-based binary powders with uniform properties across their surface, thereby controlling the physical and chemical properties of MgO-based binary powders and assisting the determination of the structure–activity relationships [22].

The three oxides, MgO, nickel oxide (NiO), and manganese oxide (MnO), play similar roles in minerals because the cations have the same charge and similar radii. Each combines to form an olivine structure (structure of Mg$_2$SiO$_4$), and undoubtedly there is complete miscibility between these three olivine members at high temperatures [23,24]. NiO and MnO are of particular interest in the solid solution research on MgO, having the same rock salt crystal structure as MgO, and all three compounds have approximately the same unit cell dimensions [25], confirming that the addition of MnO and NiO to MgO lowers the melting point of the solid solution and tends to decrease in temperature as the addition amount increases. Based on this concept, it is necessary to develop a new composition and/or a new MgO-based powder for preparing Mg$_2$SiO$_4$ at a lower temperature with a short reaction time and a uniform reactivity.
Therefore, in this study, new MgO-based binary composition powders were prepared using the coprecipitation method, in which it is easy to control the various parameters mentioned above. The Ni and Mn as substitutional elements were employed to prepare the binary powders. The reactivity of MgO and binary powders with SiO₂ was compared in preparing Mg₂SiO₄ through particle characteristics. The optimal composition ratio in the binary powders was induced with the type of substitutional element, and its reaction mechanism for forming Mg₂SiO₄ was proposed and discussed based on the particle characteristics, such as particle size and crystallinity.

2. Material and methods

2.1. Preparation of MgO-based binary powder

Magnesium chloride (MgCl₂; Yakuri Pure Chemicals Co., Ltd., Kyoto, Japan), nickel chloride (NiCl₂; Daejung Chemicals & Metals Co., Ltd., Shiheung, Republic of Korea), and manganese chloride (MnCl₂; Sigma-Aldrich Korea, Yong-in, Republic of Korea) were used as starting materials, in which the NiCl₂ and MnCl₂ were employed as precursors of substitutional elements. Sodium hydroxide (NaOH; Daejung Chemicals & Metals Co., Ltd.) was used as a reaction catalyst. Each starting material was dissolved in distilled water to 0.5 M concentration and then mixed with mole ratios as shown in Table 1. In this study, two binary powders of Mg₁₋ₓNiₓO and Mg₁₋ₓMnₓO were prepared with the composition ratios shown in Table 1.

In addition, the single-composition powders of MgO, NiO, and MnO were synthesized as reference powders. Each precursor solution was mixed by stirring at 300 rpm for 30 min at room temperature, and then the pH of each mixed solution was adjusted to 9, 11, and 13 by dropwise addition of NaOH. In addition, the pH was fixed at 11 with controlling the concentration of NaOH as 0.1, 0.5, and 1 M to investigate the effect of catalytic concentration
on the nuclei growth rate. Again, stirring at 300 rpm for 1 h was conducted for uniform dispersion of each metal hydroxide converted from each metal chloride (each precursor). The reacted and precipitated powder was washed five times with distilled water, dried at 100 °C for 24 h, and then ground. Each powder was heat-treated at 600, 800, 1000, and 1200 °C in an inert atmosphere for the Mg–Ni binary powder and in a reducing atmosphere for the Mg–Mn binary powder [26]. To investigate the effects of the pH value and the concentration of catalyst on the particle size and morphology, the heat treatment was conducted using a specified composition of Mg$_{0.7}$M$_{0.3}$O (M = Ni and Mn) at 1200 °C in an inert atmosphere for the Mg–Ni binary powder and in a reducing atmosphere for Mg–Mn binary powder. The detailed process for preparing the MgO-based binary powders is illustrated in Fig. 1.

In addition, to evaluate the reactivity of the synthesized powder with SiO$_2$, the pellet-type sample was prepared by mixing each powder (MgO, Mg–Ni binary powder, Mg–Mn binary powder) and SiO$_2$ with a mole ratio of 2:1, followed by ball milling for 24 h, and then heat treatment was performed at 1200 °C in a reducing atmosphere. The heat-treatment atmosphere for the reactivity test was decided based on a real application condition. The MgO-based powders for the reactivity test were prepared at 800 °C in an inert atmosphere for the Mg–Ni binary powder and in a reducing atmosphere for the Mg–Mn binary powder, while the MgO powder heat-treated in the inert atmosphere was employed in the reactivity test.

2.2. Characterization

The phase analysis for the synthesized MgO-based binary powders and the Mg$_2$SiO$_4$ samples obtained from the reactivity test were characterized using X-ray diffraction (XRD; MiniFlex II; Rigaku, Tokyo, Japan) with Cu Kα radiation ($\lambda = 1.54060$ Å) in the 2θ range from 20° to 80° with a scan speed of 2°/min. The average crystallite size ($D$) was calculated from the full width at half maximum (FWHM) of the XRD peak using the Scherrer equation
where $K$ is a constant (0.94), $\lambda$ is the wavelength of the X-rays (0.15406 nm), $B$ is the FWHM of a diffraction peak, and $\theta$ is the diffraction angle. The morphology and size of the synthesized powders were investigated using a field emission scanning electron microscope (FE-SEM; CZ/MIRAI LMH/H.S. Code: 9012.10.1000; TESCAN, Brno, Czech). The cross-sectional microstructure of Mg$_2$SiO$_4$ samples was observed using an SEM (JSM-5610; JEOL, Japan) and its chemical composition was identified using an energy-dispersive spectrometer (EDS; Oxford Instruments, UK) attached to the SEM.

2.3 Atomistic simulation for crystal structural property in MgO-based powder

Two types of atomistic simulations were conducted. The first is a molecular dynamics (MD) model to simulate Young’s modulus of MgO and doped MgO ($i.e.$, Mg$_{1-x}$Ni$_x$O and Mg$_{1-x}$Mn$_x$O, where $x = 0.03$, 0.06, and 0.12) using a simulated tensile test. The MD model uses the pairwise potential with partial charges proposed by Pedone et al. [28] and is implemented with customized codes in the LAMMPS MD simulation package [29]. This potential includes a Morse potential with an additional repulsive term and long-range Coulomb interaction. Compared with the commonly used BKS potential, a pairwise potential has the advantage of more stable convergence at a wide range of temperature.

The second atomistic model is to simulate the phases in XRD using Materials Studio’s Reflex module. The calculation is based on models of crystalline materials of MgO and doped MgO. A $2 \times 2 \times 2$ supercell structure of MgO was geometrically optimized. The XRD spectrum of pure MgO was calculated. Then, compositions of 1.5, 3, 6, and 12% for each doping element (Mn or Ni) were compared with one another to establish the phase-shift
relationship in crystal structures, and the theoretical and experimental results were compared.

3. Results and discussion

3.1. Powder characteristics with the species and content of the substitutional element

The XRD patterns of the Mg$_{1-x}$Ni$_x$O ($x = 0–1$) powders synthesized at pH 11 are shown in Fig. 2 before and after heat treatment in an inert atmosphere (Ar atmosphere). As the temperature increased, the width of the peak narrowed, indicating that the phase was stable [27,30]. As the amount of Ni in the Mg$_{1-x}$Ni$_x$O composition was increased, the peak was slightly shifted to a higher angle. The peak should be shifted according to Bragg’s law [31,32] because the ion radius of Ni (69 pm) is smaller than that of Mg (72 pm). Through this result, it was confirmed that the Mg–Ni binary powder was completely synthesized as a solid solution until the composition of Mg$_{0.5}$Ni$_{0.5}$O. Therefore, the Mg$_{0.7}$Ni$_{0.3}$O powder with an intermediate composition was used for investigating the particle size and morphology.

Fig. 3 shows the particle size and morphology of the MgO, Mg$_{0.7}$Ni$_{0.3}$O, and NiO powders synthesized at each temperature. The particle size in all powders increased with increasing temperature, showing a bigger particle size in the NiO powder, while the particle size of Mg$_{0.7}$Ni$_{0.3}$O powder did not grown much with the temperature, compared with those of the MgO and NiO powders. In particular, the particle size of MgO powder was too small at 600 °C, which was employed as the reference powder. The particle morphology of the MgO, Mg$_{0.7}$Ni$_{0.3}$O, and NiO particles became polygonal at 1000, 1200, and 800 °C, respectively. Based on the XRD analysis and particle size observation, the most suitable heat-treatment temperature was considered to be 800 °C for preparing the Mg–Ni-based binary powder, showing a similar particle size of 0.09 ± 0.04 μm and crystallinity with the MgO powder of 0.08 ± 0.04 μm.
The XRD patterns of the Mg$_{1-x}$Mn$_x$O ($x = 0$–$1$) powders synthesized at pH 11 are shown in Fig. 4 before and after heat treatment in a reducing atmosphere of 95% Ar–5% H$_2$. Because Mn(OH)$_2$ forms Mn$_3$O$_4$ during the drying process in an ambient atmosphere, the OH$^-$ should be removed during the heat treatment for synthesizing the Mg–Mn binary and MnO powders [32]. In the Mg–Mn binary system, the XRD peak was shifted to a lower angle with increasing Mn content because the ionic radius of the Mn$^{(II)}$ (83 pm) ion is larger than that of the Mg ion, according to Bragg’s law [33,34]. When the amount of Mn in the Mg$_{1-x}$Mn$_x$O composition was increased, an amorphous phase was detected in the as-synthesized powders as shown in Fig. 4(A). This phenomenon was also observed at a relatively low temperature of 600 °C (Fig. 4(B)). The difference in the ionic radius between Mg and Mn is larger than that between Mg and Ni, showing a certain peak shift and a phase transition from Mg(OH)$_2$ to Mn$_3$O$_4$ with increasing Mn content, even though the following Hume-Rothery rules are satisfied—The ionic radii of Mn and Mg ions are within 15%, showing the same structure (rock salt), valence, and electronegativity [33]. On increasing the temperature, the crystallinity was enhanced and the solid solution was formed with a single phase. Finally, the Mg–Mn binary powders were completely synthesized in all compositions of Table 1 at 1000 °C, even in the reducing atmosphere.

The particle size and morphology of the MgO, Mg$_{0.7}$Mn$_{0.3}$O, and MnO powders synthesized with the temperature in the reducing atmosphere were observed as shown in Fig. 5. The MgO powder did not show any grain growth with the temperature, showing the particle size of 0.05 ± 0.01 μm at 1200 °C. The particle size in the Mg$_{0.7}$Mn$_{0.3}$O and MnO powders increased with increasing temperature, showing a bigger particle size in the MnO powder. The particle morphology of the Mg$_{0.7}$Mn$_{0.3}$O and MnO particles became polygonal at 1000 and 800 °C, respectively, but the MgO did not change its morphology until 1200 °C.
The grain-growth behaviors were different from those powders shown in Fig. 3, especially the MnO powder showing a sudden grain growth at 1200 °C because the atmosphere for heat treatment was different. The severe grain growth at 1200 °C in the MnO powder is due to the low activation energy for grain growth. The activation energy of MnO (about 184.7 kJ/mol) is lower than that of NiO (about 266.2 kJ/mol) [34,35]. Based on the XRD analysis and particle size observation, the most suitable heat-treatment temperature was also considered to be 800 °C for preparing the Mg–Mn-based binary powder, even though the particle size of the Mg$_{0.7}$Mn$_{0.3}$O powder (0.08 ± 0.04 µm) was slightly larger than that of the MgO powder (0.06 ± 0.03 µm) at 800 °C in the reducing atmosphere, but the same as the MgO powder of 0.08 ± 0.04 µm prepared in the inert atmosphere. The crystallite size calculated from the XRD patterns using Scherrer’s formula [36] is shown in Table 2 for each powder synthesized at 600, 800, and 1000 °C. When the MgO powder was heat-treated in the inert atmosphere, there was almost no difference in the crystallite size. Similarly, the crystallinity was not significantly different for the binary and NiO powders synthesized in the inert atmosphere. When the heat treatment was performed in the reducing atmosphere, the crystallite sizes for the MgO and binary powders were much smaller than those in the inert atmosphere till 800 °C, and then increased significantly at 1000 °C, except for the binary powder. The smaller crystallite size at the relatively low temperatures in the reducing atmosphere is seen as an effect of hydrogen [37].

3.2 Effects of pH and catalyst concentration

The effects of pH in the mixed solution on the powder characteristics, such as crystallinity, particle size, and particle morphology, were investigated for both binary powders with the Mg$_{0.7}$Mn$_{0.3}$O composition after heat treatment at 1200 °C in an inert atmosphere for the Mg–Ni binary powder and in a reducing atmosphere for Mg–Mn binary powder. In the XRD
analysis, there was no difference in crystallinity with the pH value, as shown in Fig. 6, without any peak shift in both compositions, indicating that both powders were completely synthesized as the solid solution with a binary composition. However, the particle size showed a tendency to decrease with increasing pH values in the microstructure (Fig. 7), showing a polygonal morphology in all cases. In the Mg–Ni binary powder, the particle size was not much changed after showing a small change between pH 9 and pH 11, while the Mg–Mn binary powder showed a transition point between pH 11 and pH 13 in the particle size. The particle size of the Mg–Mn binary powders was larger than that of the Mg–Ni binary powders because the activation energy was low, as mentioned above [34,35]. In addition, the isoelectric points of Mg(OH)$_2$, Ni(OH)$_2$, and Mn$_3$O$_4$ would affect its nucleation behavior [38], which are pH 10–12, pH 7–8, and pH 5–6, respectively, including the atmosphere for the heat treatment. Therefore, the agglomeration phenomenon would be hindered at pH 13 above the isoelectric point, resulting in refining the particle size in both cases.

The crystallinity, particle size, and particle morphology with changing the concentration of the catalyst to 0.1, 0.5, and 1.0 M were investigated for both binary powders of Mg$_{0.7}$M$_{0.3}$O composition. At that time, the pH value was fixed as 11. As shown in Fig. 8, there was no significant difference in the crystallinity with the concentration of catalyst. However, as the concentration of catalyst increased, the particle size of both Mg$_{1-x}$M$_{x}$O powders became fine, showing the effect of the heat-treatment atmosphere (Fig. 9). The Mg$_{0.7}$Mn$_{0.3}$O showed a bigger grain size than Mg$_{0.7}$Ni$_{0.3}$O at all pH values. These phenomena shown in the particle size seem to be due to the faster growth rate than the nucleation rate at a relatively low concentration of catalyst [39]. In addition, it could be seen that the heat-treatment atmosphere had a great influence on the grain growth behavior of the Mg$_{0.7}$M$_{0.3}$O powders synthesized by the coprecipitation method.
3.3 Simulation results with the species and content of the substitutional element

From the MD simulations, the calculated Young’s modulus of MgO is 176 GPa, which is between the literature values of 130 GPa \cite{40} and 300 GPa using a nanoindentation test \cite{41}. In the doped MgO compounds, Young’s moduli for Ni-doped MgO, or Mg\(_{1-x}\)Ni\(_x\)O, where \(x = 0.03, 0.06, \) and \(0.12\), are 171 GPa, 164 GPa, and 149 GPa, respectively. In comparison, Young’s moduli for Mn-doped MgO, or Mg\(_{1-x}\)Mn\(_x\)O, where \(x = 0.03, 0.06, \) and \(0.12\), are 166 GPa, 157 GPa, and 141 GPa, respectively.

The results showed that the Young’s moduli values decrease with increasing doping level. Because both Ni and Mn are transition metals, they have multiple valences, which introduce oxygen vacancies in the compound. The presence of vacancies decreases the strength of chemical bonds, essentially making the bonds “weaker.” Therefore, higher doping levels reduce Young’s modulus further. The difference between the doping elements Ni and Mn can be explained by the chemical strain effect \cite{42}. As Ni\(^{2+}\) or Mn\(^{2+}\) ions substitute Mg\(^{2+}\), the surrounding Mg\(^{2+}\) ions become distorted, causing strains in the compound. The ionic radii of Mg\(^{2+}\), Ni\(^{2+}\), and Mn\(^{2+}\) are 86, 83, and 97 pm, respectively \cite{43}. Because the ionic radius difference between Mg\(^{2+}\) and Ni\(^{2+}\) is smaller than that between Mg\(^{2+}\) and Mn\(^{2+}\), it is expected that the chemical strain in the Ni-doped MgO is less than that in the Mn-doped MgO. Therefore, the reduction in Young’s modulus in the Ni-doped MgO is smaller than the case of Mn.

Regarding the simulations for XRD patterns, they were performed with the content of the substitutional element as 1.5, 3, 6, and 12\% in the Mg\(_{1-x}\)Ni\(_x\)O structure, which is shown in Fig. 10(A). The diffraction patterns of relative intensity against the angle of diffraction show a peak backward shift, as well as an increased intensity in the doped structures accordingly. The Mg\(_{1-x}\)Mn\(_x\)O structures with the content of the substitutional element as 1.5, 3, 6, and 12\% were also obtained as shown in Fig. 10(B). The peaks were shifted to a greater degree than
that for the Mg$_{1-x}$Ni$_x$O structures as shown in Fig. 10(A). It is shown that the ion radius of Mn is shifted to the left because that of Mn is larger than that of Mg, and Ni is shifted to the right because the atomic radius of Ni is smaller than that of Mg, as mentioned in Section 3.1. The XRD patterns obtained with the simulation correspond quite well to those with experimental results shown in Figs. 2 and 4. Therefore, it can be confirmed that Mn and Ni, which are substitutional elements, were synthesized as a solid solution.

3.4 Reactivity with the species and content of the substitutional element

The XRD results before and after the reaction between Mg$_{1-x}$M$_x$O powders and SiO$_2$ are shown in Figs. 11 and 12, with the species and content of the substitutional element. The MgO and amorphous SiO$_2$ peaks were detected before heat treatment. When only MgO was used, Mg$_2$SiO$_4$ and unreacted SiO$_2$ (cristobalite) were detected (Figs. 11(B-1) and 12(B-1)). In the reaction between the Mg–Ni binary powders and SiO$_2$, unreacted Ni was detected with Mg$_2$SiO$_4$ and unreacted SiO$_2$ (Fig. 11(B-3)). As the content of Ni was decreased, the peak intensity of Ni was reduced without unreacted SiO$_2$. However, in the case of Mg–Mn binary oxides, only Mg$_2$SiO$_4$ was synthesized by completely reacting with SiO$_2$ (Fig. 12(B-2) and 12(B-3)), independent of the content of Mn. This is because the electronegativity of Mn is higher than that of Ni, which is due to the strength of the ionic bonding force [44], which can be seen to correspond to the above simulation results. Therefore, MnO, which has a strong binding force, was not reduced to Mn, but NiO is considered to be precipitated as Ni because the bond with oxygen ions is broken.

The microstructure and element analysis results after the reactivity test for each composition are shown in Fig. 13. The Mg–Ni binary powders showed better reactivity than the MgO powder, enhancing the reactivity with increasing content of Ni. However, as the content of Ni was increased, the Ni element was precipitated as shown in Fig. 13(B) and
13(C), which was verified as Ni element in the element analysis and Fig. 11. On the other hand, in the Mg–Mn binary powders, as the content of Mn increased, the reaction layer around SiO$_2$ became thick. As can be seen from the XRD results in Fig. 12, it was confirmed that Mn was not precipitated and fully dissolved in MgO, showing a core–shell structure. Through this, it was found that the substitution by Mn element in MgO powder could make a stable binary composition and reaction layer rather than the Ni element for synthesizing Mg$_2$SiO$_4$.

Through the results above, it was possible to synthesize large quantities of powder with a uniform composition by the coprecipitation synthesis method, which is economically cheaper than the existing sol–gel process [45,46]. In addition, in the synthesis of Mg$_2$SiO$_4$, the MgO-based binary powder with a substitutional element doped into MgO would react completely to obtain a uniform Mg$_2$SiO$_4$. Furthermore, the nonuniform reactivity, which is a problem of the conventional solid-phase reaction method [47], could be improved by controlling processing parameters in the coprecipitation process.

4. Conclusions

Mg$_{1-x}$M$_x$O (M = Ni and Mn) binary powders with improved reactivity were prepared by doping substitutional metal ions into MgO using the coprecipitation method. As the content of the substitutional element was increased, the diffraction patterns were shifted to higher and lower angles continuously in the Mg$_{1-x}$Ni$_x$O and Mg$_{1-x}$Mn$_x$O powders, respectively, showing a greater degree in the Mg$_{1-x}$Mn$_x$O powder, owing to the difference of ion radius. The most suitable heat-treatment temperature was considered to be 800 °C for preparing the binary powder in both cases, based on the particle size and crystallinity, even though the particle size was dependent on the species of substitutional element and the Mn-doped binary powder showed a larger particle size than the Ni-doped one. The crystallinity and crystal size
increased as the heat-treatment temperature increased, especially in the case of Mg$_{1-x}$Mn$_x$O binary composition, showing an effect of the heat-treatment atmosphere. The pH value of slurry and the concentration of catalyst did not significantly affect crystallinity, but the particle size tended to be finer as the pH value increased, indicating again that the heat-treatment atmosphere had a great influence on the grain growth behavior of the Mg$_{0.7}$M$_{0.3}$O powders synthesized by the coprecipitation method. The simulation results with the species and content of the substitutional element indicated that the Mn and Ni, which are substitutional elements, were synthesized as a solid solution. The X-ray patterns obtained with the simulation corresponded quite well to those of the experimental results. As a result of analyzing the reactivity with SiO$_2$, unreacted SiO$_2$ was detected when the MgO and Mg$_{1-x}$Ni$_x$O powders were applied, and Ni was precipitated in the Mg$_{1-x}$Ni$_x$O binary powder. On the other hand, when the Mg$_{1-x}$Mn$_x$O powder was applied for the reaction with SiO$_2$, only forsterite (Mg$_2$SiO$_4$) was synthesized by reacting uniformly with SiO$_2$. Finally, the processing parameters for synthesizing the Mg$_{1-x}$M$_x$O binary powders were optimized in the coprecipitation method and the reactivity was confirmed to form Mg$_2$SiO$_4$ using the binary powders.

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Table captions

Table 1. Mole ratio of precursors for preparing Mg$_{1-x}$Ni$_x$O and Mg$_{1-x}$Mn$_x$O powders

Table 2. Average crystallite size of Mg$_{1-x}$M$_x$O powders according to the content of M (M = Ni, Mn) and heat-treatment temperature
Figure captions

Fig. 1. Schematic diagram for preparing the binary powders of Mg$_{1-x}$Ni$_x$O and Mg$_{1-x}$Mn$_x$O using the precursors of metal chlorides.

Fig. 2. XRD results for the synthesized MgO, Mg$_{1-x}$Ni$_x$O, and NiO powders with heat-treatment temperature: (A) before heat treatment, (B) 600 °C, (D) 800 °C, (C) 1000 °C, and (E) 1200 °C. Each number indicates the composition of powders shown in Table 1.

Fig. 3. Particle size and morphology of synthesized powders after heat treatment: (A) 600 °C, (B) 800 °C, (C) 1000 °C, and (D) 1200 °C. Each number indicates the MgO, Mg$_{0.7}$Ni$_{0.3}$O, and NiO powders.

Fig. 4. XRD results for the synthesized MgO, Mg$_{1-x}$Mn$_x$O, and MnO powders with heat-treatment temperature: (A) before heat treatment, (B) 600 °C, (D) 800 °C, (C) 1000 °C, and (E) 1200 °C. Each number indicates the composition of powders shown in Table 1.

Fig. 5. Particle size and morphology of synthesized powders after heat treatment: (A) 600 °C, (B) 800 °C, (C) 1000 °C, and (D) 1200 °C. Each number indicates the MgO, Mg$_{0.7}$Mn$_{0.3}$O, and MnO powders.

Fig. 6. Variation of XRD results for Mg$_{0.7}$M$_{0.3}$O powder with the pH value: (A) Mg$_{0.7}$Ni$_{0.3}$O and (B) Mg$_{0.7}$Mn$_{0.3}$O. Each number indicates the pH values of 9, 11, and 13.

Fig. 7. Particle size and morphology for Mg$_{0.7}$M$_{0.3}$O powder synthesized with the pH value: (A) Mg$_{0.7}$Ni$_{0.3}$O and (B) Mg$_{0.7}$Mn$_{0.3}$O. Each number indicates the pH values of 9, 11, and 13.

Fig. 8. XRD results for Mg$_{0.7}$M$_{0.3}$O powder synthesized with the concentration of catalyst: (A) Mg$_{0.7}$Ni$_{0.3}$O and (B) Mg$_{0.7}$Mn$_{0.3}$O. Each number indicates 0.1, 0.5, and 1.0 M.

Fig. 9. Particle size and morphology for Mg$_{0.7}$M$_{0.3}$O powder synthesized with the concentration of catalyst: (A) Mg$_{0.7}$Ni$_{0.3}$O and (B) Mg$_{0.7}$Mn$_{0.3}$O. Each number indicates 0.1, 0.5, and 1.0 M.

Fig. 10. XRD results obtained from simulation for MgO-based binary powders: (A) Mg$_{1-x}$Ni$_x$O and (B) Mg$_{1-x}$Mn$_x$O. The red, black, green, blue, and yellow patterns in each figure indicate MgO, Mg$_{0.985}$M$_{0.015}$O, Mg$_{0.97}$M$_{0.03}$O, Mg$_{0.94}$M$_{0.06}$O, and Mg$_{0.88}$M$_{0.12}$O, respectively.
**Fig. 11.** XRD results before and after the reaction between Mg$_{1-x}$Ni$_x$O and SiO$_2$: (A) before reaction and (B) after reaction. Each number indicates MgO + SiO$_2$, Mg$_{0.9}$Ni$_{0.1}$O + SiO$_2$, and Mg$_{0.7}$Ni$_{0.3}$O + SiO$_2$.

**Fig. 12.** XRD results before and after the reaction between Mg$_{1-x}$Mn$_x$O and SiO$_2$: (A) before reaction and (B) after reaction. Each number indicates MgO + SiO$_2$, Mg$_{0.9}$Mn$_{0.1}$O + SiO$_2$, and Mg$_{0.7}$Mn$_{0.3}$O + SiO$_2$.

**Fig. 13.** Microstructure and element analysis after the reaction between Mg$_{1-x}$M$_x$O powders and SiO$_2$: (A) MgO + SiO$_2$, (B) Mg$_{0.9}$Ni$_{0.1}$O + SiO$_2$, (C) Mg$_{0.7}$Ni$_{0.3}$O + SiO$_2$, (D) Mg$_{0.9}$Mn$_{0.1}$O + SiO$_2$, and (E) Mg$_{0.7}$Mn$_{0.3}$O + SiO$_2$. 