Abstract

The purpose of the present study was to reveal the details of the preparation of CaF₂ particles with controllable size (30-900 nm) and shape (spherical, hexagonal, and cubical forms) using a liquid-phase synthesis method, and to demonstrate that a change in the composition of the reactants and crystalline structure of the CaF₂ product could improve material performance. The particles were synthesized from the reaction of CaCl₂ and NH₄F in an aqueous solution in the absence of any additional components (e.g., chemicals, surfactants). Monodispersed particles were achieved by the optimization of the reaction condition parameters: temperature, mixing rate, and reaction time. Control of the particle size was accomplished mainly by changing the concentration of the reactants, which is qualitatively explained by the conventional nucleation theory. Flexibility of the process in controlling particle morphology, from a spherical to a hexagonal and/or a cubical form, was predominantly achieved by varying the concentration of CaCl₂. Since the identical XRD pattern was detected in particles with varying morphologies, the shape transformation was due to changes in particle growth. A theoretical background to support how the particles changed was also added and was compared with an analysis of the number of nuclei. In addition, sufficient adjustment of the reactant compositions made it possible to produce a material with an ultralow refractive index ($n_{CaF₂}$ was near to $n_{theoretical \ CaF₂}$), which was confirmed by the measurement of the refractive index and the material crystallinity.

Keywords: calcium fluoride particles, nucleation theory, particle growth, morphological control, low refractive index material, crystal size

1. Introduction

Calcium fluoride (CaF₂) is an attractive material due to its excellent properties: low refractive index, corrosion-resistance, thermal stability, and significant hardness. Excellent performance makes this material useful for applications, from catalytic support, protective-coating materials, to anti-reflective lenses.¹

Several approaches to the synthesis of this alkaline-earth metal fluoride material have been developed, which include physical and chemical methods.² Although the current synthesis methods have shown potential for industrial applications, several disadvantages have been noted: (i) most of the processes require high-temperature processing, specific and complicated synthetic equipment, and rigid conditions;³ (ii) most require the use of harmful and difficult-to-handle chemicals (e.g., hydrofluoric acid (HF)¹, trifluoroacetate (TFA)³, etc.), creating conflicts with safety and environmental regulations in industrial applications;⁴ (iii) most conduct in an anhydrous synthesis system¹ (either oil-phase, alcohol, or sol-gel synthesis), which would be inflexible for further developments; (iv) most have been applied for the production of film material only, with only a few reports published on work on the synthesis of particles;⁵ and, (v) most reports have focused on only the fabrication of the material with no emphasis on actual applications.
To circumvent the current problems described above, several alternative methods have been suggested. Methods that are conducting a reaction system in an aqueous solution and changing the type of raw materials have been suggested. Franklin reported employment of the aqueous-solution reaction system and the use of NH₄F as a fluoride source,⁵ which successfully produced CaF₂ particles with controllable size. However, no precise information exists concerning the minimum size that can be produced. Page et al.⁶ reported the synthesis of CaF₂ using alkaline metal fluoride (KF) as an F source. Particles in the range of 15 to 80 nm were effectively produced; unfortunately, the use of KF affected the production of fluoro-perovskite materials (materials with K, Ca, and F components (KCaF₃)).⁷ Further, there is no mention included on the feasibility for the control of particle morphology, as well as their material performances. Fujiwara et al.⁸ and Grob et al.⁹ reported a development in the synthesis of fluoride material. Optical properties were also reported. However, synthesis of CaF₂ was not their main focus, and the control of particle morphology was not reported. In fact, nanometer-sized particles with controllable morphology are important because the change of morphology exhibits unique properties (e.g., optical transparency).⁴,⁹ For this reason, the purpose of the present study was to reveal the details of the preparation of CaF₂ particles with controllable size and shape and to demonstrate that a change in the composition of the reactants could improve material performance (i.e., refractive index).⁴,⁹

In our initial studies, we reported the preparation of porous silica nanoparticles (namely, Hiroshima Mesoporous Materials; HMM)⁹,¹⁰ and MgF₂ nanoparticles¹⁰ with controllable size and morphology using a liquid-phase synthesis method. Experimental results in the control of particle size and morphology were investigated and compared with theoretical explanations. Besides, we also successfully developed a process for the synthesis of particles with controllable size and morphology using a spray method.¹¹⁻²⁴ Here, we report the synthesis of CaF₂ particles with controllable size and morphology using the liquid-phase synthesis method. Different from other CaF₂ synthesis methods, the synthesis was based on the reaction of Ca²⁺ and F⁻ ions in an aqueous solution in the absence of additional components (polymers, surfactants, chemicals, etc.). As the fluorine source, we used ammonium fluoride (NH₄F), which was easier to handle than either HF or TFA.⁴ Monodispersed particles could be achieved through the optimization of reaction condition parameters: temperature, mixing rate, and reaction time. The ability to control size (from 30 to 900 nm) and morphology (spherical, hexagonal, and cubical forms) was achieved by changing the NH₄F:CaCl₂ ratio, in which to the best of our knowledge, this is the first documented preparation of well-controlled particle size (from several tens nanometers) and morphology. A theoretical explanation of the control of particle size and the morphological control, as well as the particle formation phenomenon, was added to support our synthesis method. Furthermore, the relationship of particle diameter and morphology with concentration of the reactants was investigated in detail, both experimentally and theoretically. The effect of reactant composition on material performance (i.e. refractive index) was also investigated, along with an analysis of crystallinity. The results provided evidence that the present particles had a low refractive index value (approaching that of the theoretical monocrystalline CaF₂ monolayer). We believe that this information is important for further developments in the synthesis of low refractive index materials.

2. Fundamental Theory of Particle Formation

The LaMer and Dinegar theory is typically used as a qualitative model to comprehend particle-formation phenomena.²⁵ This theory describes monomer formation, the nucleation step, and the growth process. To apply this theory to the present particle formation, several conditions should be assumed: (i) The monomer is supplied only from the chemical reaction; (ii) Critical supersaturation (Ccrit) is a minimal requirement for the nucleate to be discernible; (iii) As the monomer concentration is lowered below the Ccrit level, nucleus formation ceases and the nucleus then starts to consume monomers to increase its weight (growth-step process); and, (iv) during the growth-step process, processing conditions can interfere with particle shape transformation.

An example of time-dependent particle formation illustrating the LaMer and Dinegar theory is depicted in Fig. 1. Two conditions in different monomer formation rates are selected as a comparison parameter because its discrepancies can be easily distinguished. Particle-formation models in high and low monomer formation rates are presented in Fig. 1 in condition lines 1 and 2, respectively. A high rate means the rapid progress to the step of nucleus formation, while a low rate is the low rate in the formation of monomer that makes creation of nuclei slower.
When the chemical reaction occurs, monomers are formed. This causes an increase in monomer concentrations with time. At a high rate (condition 1), the higher monomer formation rate allows the monomer concentration to get $C_{\text{crit}}$ in a short time; however, a low rate (condition 2) slows the monomer formation rate, consequently taking a longer amount of time for the monomer concentration to reach $C_{\text{crit}}$.

After $C_{\text{crit}}$ is reached, nuclei start to form. During nuclei construction, available monomers in the solution are consumed, resulting in a deceleration of monomer concentration. When there is no consumption of monomers, monomer concentration is steady (illustrated by the striped line). With a longer time period, nuclei formation causes the monomer concentration to promptly decrease. Between these two conditions, dissimilarity in the areas above $C_{\text{crit}}$ (nucleation area) can be obtained, informing different particle phenomenon characteristics (i.e., numbers of nuclei). In condition 1, a wide nucleation area (in the blue, vertical-line textured area) can be obtained. The increase in reactant conversion causes a rapid conversion of reactants into monomers, which accelerates nuclei formation but retards particle growth. Conversely, in condition 2, a narrow nucleation area (in the red, horizontal-line textured area) can be obtained. A lower monomer formation rate is found. As a consequence, a short-nucleation stage occurs, resulting in the production of fewer nuclei and allowing the nuclei to catch more monomers and increase their weight during the particle growth stage.

When the monomer concentration collapses to below $C_{\text{crit}}$, the nuclei growth stage starts. The monomers tend to coalesce with formed nuclei to increase nuclei weight, rather than forming new nuclei. The growth stage continues until the concentration of monomer reaches a stable condition ($C_{\text{stable}}$).

### 3. Experimental Method

CaF$_2$ particles were prepared using the liquid-phase synthesis method with a simple reaction between calcium and fluoride sources (CaCl$_2$ + 2 NH$_4$F $\rightarrow$ CaF$_2$ + NH$_4$Cl). Each reactant (i.e., CaCl$_2$ (Kanto Chemical Co., Inc., Japan) and NH$_4$F (Aldrich, US)) was diluted in an aqueous solution. Both diluted reactants (each fixed at 40 mL) were added into a reactor system, in which the reactor system itself was comprised a batch glass reactor (300 mL of a four-necked reactor), a magnetic stirrer, a mantle heater, a condenser, and a nitrogen gas inlet. The concentration of reactants varied from 1 to 1000 mmol/L. Detailed variations of reactant concentrations are listed in Table 1.

The mixed reactants were vigorously mixed for several minutes to reach a homogenous condition. The homogenous mixtures were then heated to a specific temperature and kept at this temperature for

![Fig. 1 Illustration of the Lamer and Dinegar theory as a function of reaction time.](image-url)
up to 4 hours under a nitrogen atmosphere. Next, the reacted solutions were cooled to room temperature. In order to collect the prepared particles and remove un-reacted reactants and impurities, the cooled solutions were purified using a centrifugation process (15,000 rpm; 30 minutes; washing by ethanol).

The purified particles were then characterized using a scanning electron microscope (SEM, Hitachi S-5000 operated at 20 kV) and a transmission electron microscope (TEM; JEM-3000F, JEOL, operated at 300 kV) to examine the size, morphology, and structure of the particles. The crystallinity of the samples was measured by an X-ray diffraction (XRD; Rigaku Denki RINT2000, with Cu Kα radiation, with angular domain between 20 and 80° (2θ)). Elemental mapping and chemical composition of the prepared particles were evaluated using a scanning transmission electron microscope (STEM) equipped with an energy-dispersive X-ray spectroscopy (EDS).

To determine the effect of reactants composition and CaF₂ particle crystallinity on material performance (i.e., refractive index), the following experimental procedure was conducted: First, the purified particles were dried at 80°C to ensure a solvent-free condition. The dried particles were then diluted by an aqueous standard solution and used as a precursor. The precursor was deposited onto a substrate (prism glass grids), which was attached to a refractive index measurement system (DR-M2, Atago Co. Ltd., Tokyo, Japan). The precursor was then measured using a visible light (589 nm) at 25°C. In addition, prior to using, the substrate was washed using an ethanol solution and left for several minutes. For a standard comparison, we prepared the precursor with no additional particles. The duration time for the measurement was no more than 1 minute to minimize the evaporation of precursor’s solvent. The measurements were repeated three times to ensure the results.

4. Results and Discussion

4.1. Synthesis of CaF₂ particles

The present work was primarily directed towards investigation of the effect of several reaction parameters on the synthesis of monodispersed CaF₂ particles. This study used a single-step process, which was performed in the absence of any additional components (e.g., chemicals, surfactants, etc). This study demonstrated the possibility of production of monodispersed particles with controllable size and morphology through suitable changes in reaction parameters: temperature, reaction time, mixing rate, and composition of reactants.

Fig. 2 shows the SEM images of prepared particles as a function of reaction time. The particles were prepared at 70°C using a ratio concentration of NH₄F:CaCl₂ of 54:450 and a mixing speed of 400 rpm. A slight difference in size was obtained with different reaction times. Particles with a size of 110 nm were formed at a relatively short reaction time (0.5 hours) (Fig. 2a). By adding longer reaction time, an increase in particle size could be obtained (Fig. 2b).

| Sample code | Reactant concentration (mmol/L) | dₚ (nm) | Stdev (nm) | Particle morphology |
|-------------|---------------------------------|---------|------------|---------------------|
| A           | 27 NH₄F 18 CaCl₂ 1.50           | 400     | 77         | Spheres             |
| B           | 54 NH₄F 18 CaCl₂ 3.00           | 222     | 32         | Spheres             |
| C           | 108 NH₄F 18 CaCl₂ 6.00          | 118     | 27         | Spheres             |
| D           | 216 NH₄F 18 CaCl₂ 12.00         | 59      | 16         | Spheres             |
| E           | 54 NH₄F 9 CaCl₂ 6.00            | 842     | 137        | Spheres             |
| F           | 27 NH₄F 36 CaCl₂ 0.75           | 305     | 89         | Hexagonal           |
| G           | 27 NH₄F 90 CaCl₂ 0.30           | 121     | 26         | Hexagonal           |
| H           | 27 NH₄F 180 CaCl₂ 0.15          | 133     | 35         | Cubes               |
| I           | 27 NH₄F 360 CaCl₂ 0.08          | 81      | 18         | Cubes               |
| J           | 54 NH₄F 900 CaCl₂ 0.06          | 62      | 15         | Cubes               |
| K           | 108 NH₄F 900 CaCl₂ 0.12         | 45      | 13         | Cubes               |
| L           | 216 NH₄F 900 CaCl₂ 0.24         | 32      | 9          | Cubes               |
| M           | 108 NH₄F 360 CaCl₂ 3.00         | 80      | 23         | Mixed spherical and cubical form |
| N           | 108 NH₄F 180 CaCl₂ 0.60         | 73      | 20         | Hexagonal           |
| O           | 108 NH₄F 360 CaCl₂ 0.30         | 70      | 20         | Mixed spherical, hexagonal, and cubical form |
A longer reaction time allows the nucleus to adsorb more monomers, gaining weight, and resulting in larger particles. However, when applying further increasing reaction time (Fig. 2c), almost no change in the particle size was detected. The size of the prepared particles at further longer reaction time (time > 2 hours) was identical. The particle size increased gradually only when the reaction time was up to 2 hours, confirming that the particle growth process occurred during this period. The particle growth would not happen when the reaction time is above the certain value, confirming the concept of $C_{\text{stable}}$ in the Lamer and Dinegar theory in Fig. 1.

Fig. 3 shows the effect of mixing speed on particle size and size distribution. Various particle sizes with different size distributions could be obtained. At a low-rate mixing speed, particles with a size of 130 nm could be produced (Fig. 3a). An increase in mixing speed caused the decreases in the particle size and the size distribution (Fig. 3b and c). However, further additional speed made no impact on the decrease of particle size. When increasing the mixing rate, a high interaction among the reactants happened, followed by a rapid conversion of the reactants into a monomer. This led to faster progress in the creation of nucleus and growth process. However, for some cases, a high interaction sometimes creates an inhomogeneous state in the particle-formation phenomenon, with the exception of the Ostwald-ripening theory. Some particles can grow and be constructed faster, while the others are still in an unstable condition (e.g. un-interacted reactant and incomplete particle growth). This condition allowed the formation of particles with a broad size distribution, which was avoided for the obtainment of monodispersed particles. From these results, an optimum mixing speed that would result in the formation of relatively monodispersed particles was 800 rpm.

Fig. 4 shows the effect of temperature on particle size and size distribution. An increase of temperature can lead to high interaction between reactants and good progress in particle formation. Nanoparticles could be obtained when processing at a temperature of 25°C (Fig. 4a). By increasing temperature, the creation of larger particles could be obtained (Fig. 4b-d). The fundamental reason for this phenomenon is that increasing temperature allows a high contact and interaction among the reactants, which results in a rapid particle formation. However, with this high contact and interaction phenomenon, increases in the particle size distribution cannot be avoided. Inhomogeneous particle growth was obtained for the case of too high temperature process, making size distribution broader. Some nuclei could catch more

![Fig. 2](image-url)  
**Fig. 2**  
SEM images of prepared particles conducted at different reaction times (0.50 (a), 2.00 (b), and 4.00 hours (c)). All samples were prepared at 70°C using NH$_4$F and CaCl$_2$ compositions of 54 and 450 mmol/L, respectively. The mixing speed used to synthesize samples was 400 rpm.
Fig. 3  SEM images of prepared particles conducted at different mixing speeds (400 (d); 800 (e); and 1000 (f)). All samples were prepared at 70 °C using NH₄F and CaCl₂ compositions of 54 and 450 mmol/L, respectively. Samples were conducted at 2 hours.

Fig. 4  SEM images of prepared particles conducted during different temperature processes: (a) 25, 50, 70, and 80 °C. All samples were prepared at 400 rpm using a NH₄F and CaCl₂ composition of 54 and 450 mmol/L, respectively.
monomers and grow faster, while the others were not. From Fig. 4a-d, an optimum temperature to gain particles with a relatively narrow size distribution was 50°C.

A reactant composition can also be selected as a comparison parameter. By varying the composition of the reactants under the optimum reaction conditions (i.e., temperature, mixing speed, and reaction time), the control of particle size and morphology can be achieved, but the process can maintain the production of particles in the monodispersed range. For this reason, the effect of the composition of reactant on the particle size and morphology was investigated.

Fig. 5 shows the effect of NH₄F concentration on particle size. Fig. 5a-c correspond to the SEM micrographs of CaF₂ particles; while Fig. 5d shows the relationship between particle diameter and reactant composition. The SEM analysis shows that spherical particles with nearly monodispersed were obtained. A strong relationship between particle diameter and reactant composition was revealed. Submicron particles were formed when a fluorine ion concentration of about 50 mmol/L was employed (Fig. 5a). The addition of anion allowed the production of smaller particles (Fig. 5b). Further increases in the anion concentration (fluorine ion concentration of more than 200 mmol/L) resulted in the formation of nanoparticles (Fig. 5c). In order to confirm the correlation between particle diameter and reactant composition, simple data regressions of final particle diameters as a function of the NH₄F concentration, when performed at CaCl₂ concentrations of 4.5; 45, 90, and 450 mmol/L, are plotted in Fig. 5d. The regressed data showed that for all variations, the final size of the particles decreased with increasing concentrations of calcium and fluoride sources.

The results of the reactant compositions in Fig. 5 were in a good agreement with the Lamer and Dinegar theory (Fig. 1). High reactant composition meant high contact and interaction among the reactants, resulted in a rapid conversion of reactants into monomers (Fig. 1, condition 1). This rapid conversion allowed the acceleration of nuclei formation but retarded particle growth, resulting in the production of smaller sized particles. Conversely, when using a low reactant composition, the condition as described in Fig. 1, condition 2 could be achieved.

To confirm our hypothetical study in the particle formation, we approximated the final particle number \(n\) from the experimental results as a quantifier of nucleation.\(^\text{6}\) The \(n\) is calculated by dividing the mass of total formed particles \(m_o\) by the mass of an apparent single particle \(m_p\). The equation of \(n\) can be

![Fig. 5](image-url)

**Fig. 5** SEM images of prepared particles with NH₄F:CaCl₂ composition ratios (in mmol/L) of 54:18 (Sample B) (a), 108:18 mmol/L (Sample C) (b), and 216:18 (Sample D) (c). Fig. (d) shows average particle size as a function of NH₄F and CaCl₂ concentrations.
derived as $n = \frac{m_o}{m_p}$. Obviously, the approximation of the value of $m_o$ came from the stoichiometrical calculation, while the value of $m_p$ was from the multiplication of particle density ($\rho$) and volume of a particle ($V_s$). The value of $\rho$ was fixed using a standard bulk density of CaF$_2$ (3,180 kg/m$^3$) to simplify the calculation of $m_p$. To simplify the calculation, the particles are assumed to be spherical particles and the $V_s$ is approximated using $V_s = \frac{1}{6} \pi d_p^3$; where $d_p$ is the apparent particle size from SEM images.

Fig. 6 shows the number of nuclei generated ($n$) as a function of NH$_4$F concentration, carried out at CaCl$_2$ concentrations of 4.50, 45.00, 90.00, and 450.00 mmol/L. The number of nuclei increased from $10^{12}$ to $10^{17}$ with the changes in reactant composition, in which the results were in a good agreement with our theoretical hypothesis. The increase in the concentrations of the reactants caused a rapid conversion of reactants into monomers. Reactants were joined to create a monomer and a nucleus rather than simply combining reactants with a formed nucleus to increase the weight. Because most of the reactants/monomers were consumed for the nucleus construction, retardation in the particle growth was found. Conversely, the decrease in reactant concentration resulted in fewer monomers. As a consequence, a short-nucleation stage occurred (resulting in the production of fewer nuclei), which allowed the nuclei to catch more monomers and increase their weight in the next step (the particle growth stage).

Fig. 7 shows the effect of various calcium ion amounts on particle morphology at a low reactant ratio. Relatively monodispersed particles with a specific morphology were examined. A strong relationship between reactant composition and particle shape was obtained. Submicrometer particles with a spherical shape were formed when a calcium amount of 9 mmol/L was employed (Fig. 7a). The increase in calcium concentration in the same concentration of a fluorine source allowed the production of smaller particles with a hexagonal shape (Fig. 7b). A further increase in calcium composition resulted in the formation of other morphologies: cubical form particles (Fig. 7c). However, in the case of changing anion concentration but in the same concentration of calcium (as resulted in Fig. 7c), the production of smaller particles with size of down to nanometer range was found (Fig. 7d). Ferret analysis showed that the particles with NH$_4$F:CaCl$_2$ molar ratios (in mmol/L) of 9:27; 90:27; 900:55; and 900:100 had sizes of 400, 305, 62, and 45 nm, respectively.

TEM images of particles with different morphologies are shown in Fig. 8. Dense particles were observed for all cases. Particles with hexagonal and cubical shapes were observed clearly in Fig. 8a and c, respectively. The low magnification of TEM images presented a group of identical particles, confirming that the morphology and dimensions of all particles

![Fig. 6](image_url)  The predicted number of nuclei ($n$) as a function of CaCl$_2$ and NH$_4$F concentrations.
under identical procedural conditions are similar. The sizes and morphologies of particles, as assessed by TEM, were in a good agreement with the SEM results (in Fig. 6c). To verify the structure of the particle, high magnification of TEM was conducted, as shown in Fig. 8b and d. This TEM analysis indicated

Fig. 7  SEM images of prepared particles with NH$_4$F/CaCl$_2$ composition ratios (in mmol/L) of 27:9 (Sample A) (a), 27:90 (Sample F) (b), 54:900 (Sample J) (c), and 108:900 (Sample K) (d).

Fig. 8  TEM images of hexagonal- (Sample G) and cubical-shaped particles (Sample K).
that the particles contained high crystallinity for both morphologies.

STEM with elemental analysis of particles with a cubical morphology is shown in Fig. 9. Dense particles with an identical shape (i.e., cubical shape) were observed (Fig. 9a). Elemental mapping analysis showed that the particles had different components: one was calcium (Fig. 9b) and the other was fluoride (Fig. 9c). Calcium and fluoride were well-distributed inside the nanoparticles as prepared, confirming that the particles consisted of calcium-fluoride compounds.

Fig. 10 presents the XRD patterns of prepared particles with different morphologies. The results showed that although different reactant ratios can possibly lead to changes in material sizes and shapes, identical patterns as a CaF$_2$ compound were detected in all cases. The main diffraction peaks of 20 were observed at 27.94, 46.68, 55.42, and 68.54. These peaks corresponded to the (110), (220), (311), (400) planes, which could be indexed to the CaF$_2$ compound. No impurity peaks were observed, indicating that the particles prepared by the present method were pure in both chemistry and in the crystalline phase. The only difference appeared to be the intensity of the peaks describing dissimilar crystal sizes. The peak intensities increased with a change in the morphology from spherical to cubical shapes. The lowest intensity was observed in the spherical particles, indicating a low degree of crystallinity. However, for the case of cubical shape particles, the highest intensity was obtained, implying that the particles had a high degree of crystallinity. This result also verified that this shape was the most stable crystal in the CaF$_2$. According to the Scherer equation, the crystal sizes of spherical- (size of 222 nm), hexagonal- (size of 114 nm), and cubical-shaped particles (size of 62 nm) were 71.22, 47.48, and 44.99 nm, respectively. These results also implied that a significant reactant ratio changed only the size of the crystalline particles (formation of a very small crystalline) but did not substantially contribute to a change in the material phase and pattern. The spherical particles had a polycrystalline structure, but the structure of the cubic particles was relatively monocrystalline.

The transformation of particle shapes from spherical into hexagonal and/or cubical form was observed (Fig. 7), but the XRD patterns for all shapes were the same (Fig. 10). This result illustrated that the fundamental reason behind the shape transformation

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**Fig. 9** STEM image (a) with elemental mapping analysis (calcium (b) and fluorine (c)) of cubical-shaped particles (Sample K).
was not changes in material patterns or chemical structures. To confirm this theoretical explanation, a modification of the Lamer and Dinegar theory should be included to describe the shape transformation phenomenon.\textsuperscript{26} This modification theory described that some conditions can change other energies (e.g., surface free energy) during particle growth formation, causing the transformation of particle shape.\textsuperscript{4} When the ratio of \text{NH}_4\text{F}:\text{CaCl}_2 was very low, a limited amount of monomer was formed. This condition caused the retardation of the particle growth rate, changing the surface potential adsorption of monomers in the nuclei, and resulting in the growth of particles into their stable and original form. This confirmed that cubical particles had a high crystallinity and was near to monocrystalline-type structure (Fig. 8). However, when the ratio was high, the number of reactants also should have been high. As the excess amount of reactants increased, monomers were rapidly produced, allowing faster nuclei and crystal formation (very small crystalline generation). This condition makes the monomer to be sufficient to change specific surface energy, enhancing particle growth from all particle surface faces. As a result, spherical particles could be formed (Fig. 7a). Evidence in the generation of very small crystallinity in the spherical particles is shown in Fig. 10. The low peak intensities were observed in the case of spherical particles, confirming that this type of particle had a low degree of crystallinity, containing polycrystalline structure. This result also implied that the pattern was nearly amorphous.

Based on all experimental results, a summary of the effect of the composition of the reactants on particle size and morphology is described in Fig. 11. The ratio of the reactants could be used as a parameter to control particle size and morphology. Some combinations of this composition resulted in the successful formation of particles with a spherical shape, while other combinations produced various morphologies (i.e., cubical and hexagonal shapes). When the ratio of \text{NH}_4\text{F}:\text{CaCl}_2 was relatively less than 0.33, cubical particles could be prepared (dark-blue-patterned area). An increase in the ratio allowed the production of hexagonal-shaped particles (sky-blue-patterned area). However, a further increase in the ratio permitted the production of spherical-shaped particles (clear-patterned area). For all shapes, particle size could be easily controlled by changing the amounts of the reactants, as illustrated by the red and dashed line (namely, the “dp trend” line). Nanoparticle synthesis lies above the dp trend line, while the submicrometer is below the line. In addition, because recognition of the present study came from the experimental results, in which the variation was within strictly specified concentrations (reactant concentration = 1–1000 mmol/L), the preparation of \text{CaF}_2 particles that are controllable for size and morphology underscores the need for further studies.

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**Fig. 10** X-ray diffraction patterns of spherical- (Sample B), hexagonal- (Sample G), and cubical-shaped particles (Sample K).
4.2. Analysis of refractive index of CaF$_2$ particles

Because the creation of the excellent properties of the material can be attained by the change of particle size and morphology,\textsuperscript{18} it should be interest to demonstrate and compare the material properties for the various particles. To characterize the properties of materials, a specific analytical measurement is typically used. However, in the present study, a refractive index based on a simple measurement system was used. Refractive index material is relatively sensitive, depending on the elemental structure and the material morphology.\textsuperscript{27,28} This reason makes that the analysis of refractive index is the best to confirm the effect of reactant composition, size, and morphology on material properties.\textsuperscript{14}

To measure the refractive index value, the conventional Lorenz-Lorentz theory is typically used:\textsuperscript{29}

\[
\frac{\phi_m}{n_{\text{tot}}^2 - 1} + \frac{\phi_p}{n_{\text{tot}}^2 + 2} = \frac{n_p^2 - 1}{n_p^2 + 2} - \frac{n_m^2 - 1}{n_m^2 + 2}
\]

where $n_{\text{tot}}$, $n_m$, and $n_p$ are the refractive index of precursor, medium, and particles, respectively. The symbols $\phi_m$ and $\phi_p$ are, respectively, the volume fractions of the medium and particles.

Table 2 shows the result of the refractive index of CaF$_2$ particles calculated using the conventional Lorenz-Lorentz theory. To simplify the investigation, samples used in this analysis contained particles with identical size and shape (cubical structures; size of about 60 nm). The solution with no additional particles showed the lowest refractive index ($n = 1.333$). Adding particles resulted in an increase in the refractive index value. Impact from the change of particle type to the material performance was confirmed.\textsuperscript{14} An increase in the calcium amount would increase the refractive index of the precursor. The particles with a Ca:F ratio of 1:2 had the lowest value of refractive index value (close to the theoretical refractive index of a single crystalline CaF$_2$ monolayer (1.433\textsuperscript{30})), while particles with a ratio of 15:1 had the highest. The size and shape of the characterized particles were almost the same, informing these factors had no effect on the change in the refractive index value. Differences in the refractive index are probably caused by differences in the crystallinity of the characterized particles. The results of the refractive index were 1.43, 1.64, and 1.89, corresponding to particles prepared from Ca: F ratios of 1:2, 5:1, and 15:1, respectively.

\textbf{Fig. 12} shows the effect of the degree of crystallinity on the refractive index. The size of the crystal ($d_{\text{crystall}}$) was measured using the Scherer method from XRD (XRD not displayed), while the particle size ($d_p$) was determined from the SEM images using the Ferret analysis. As expected, the effect of the crystallin-
ity of the material on the refractive index value was verifiable. An increase in the ratio of $d_{\text{crystal}} : d_p$ seemed to have an impact to the increase of refractive index value. When the particles with a relatively monocrystalline structure ($d_{\text{crystal}} / d_p = 100\%$) were applied, a low refractive index performance could be obtained; the particles with polycrystalline and a lower degree of crystallinity resulted in a high refractive index value.

The characterization and measurement was directly measured by the visual refractive index analysis of the dispersed particles in the solution. Therefore, there was a concern that an error might have been created by the measurement of agglomerated and precipitated particles in the suspension. The additional functionalization of particles should be the best for homogenizing particles in the standard solution; however, it can produce misleading results because some functionalization techniques use a high energy/pressure to disperse particles (e.g., ultrasonic, beads mills process, etc.) and employ other components/
chemicals as coupling agents, which doesn’t allow particles to retain their original morphology (as-synthesized shape). For this reason, additional studies are required to verify the actual material properties (e.g., refractive index). However, we believe that insights gained from this type of research will contribute to more fabrication innovation, particularly with respect to the synthesis of ultralow refractive index materials.

5. Conclusions

CaF$_2$ particles with controllable size (from 30 to 900 nm) and morphology (spherical, hexagonal, and cubic forms) were successfully prepared using a liquid-phase synthesis method. The effectiveness of this method in producing monodispersed particles relied on the optimization of several reaction parameters: temperature, mixing speed, and reaction time, which were qualitatively verified using conventional nucleation theory. The ability to create particles with various sizes and morphologies was due to changes in the NH$_4$F:CaCl$_2$ molar ratios. Particles in the size of several tens nanometer could be synthesized when a high concentration of reactants was employed, while the submicrometer particles were due to low concentrations of reactants. In the case of particle morphology, 3 types of particles could be created: spherical, hexagonal, and cubical. Cubical particles were prepared when the ratios were less than 0.33. When the ratios increased, the process led to the production of particles with a hexagonal shape. Further increases in ratio permitted to the synthesis of particles with a spherical morphology. No change in the XRD phase and pattern was found, confirming that the shape transformation was due to change in the particle growth orientation. A theoretical background to support how the particles were changing was also added, compared with an analysis of the number of nuclei. The effect of the composition and crystalline structure of particles of reactants on material performance (i.e. refractive index) was investigated in this paper, opening the door for the future synthesis of material with a low refractive index. Due to simple preparation procedures, use of relatively low-temperature processing, and employment of easy-to-handle chemicals, we believe that the present study provides important new information for the field of chemical and material science and engineering.

6. Acknowledgements

A fellowship provided for A.B.D.N. by the Japan Society for the Promotion of Science (JSPS) is gratefully acknowledged. We also thank the Hosokawa Powder Technology Foundation for providing a research support grant for A.B.D.N. This work was supported by (MEXT)-KAKENHI Grant-in-Aid for Scientific Research A (No. 22246099).

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