Changes in crystal phases and morphologies of rare earth hydroxide nitrates with ionic radius

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Rare earth hydroxide nitrates are prepared from rare earth nitrates by hydrothermal treatment. Three crystal phases, $M(\text{OH})_3$ (M1), $M_2(\text{OH})_{5.14}(\text{NO}_3)_{0.86} \cdot \text{H}_2\text{O}$ (M2), and $M_4\text{O}(\text{OH})_9\text{NO}_3$ (M4) are identified. The crystal phase systematically changes from M1 to M4 through M2 with decreasing radius of rare earth cation. Morphology of nanocrystal depends on the crystal phase. M1 and M4 phases grow to be nanorod, and M2 to nanoplate.

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1. Introduction

Rare earth hydroxide nitrates (RHNs) $M_a\text{O}_b(\text{OH})_c(\text{NO}_3)_d \cdot e\text{H}_2\text{O}$ are prepared by hydrothermal treatment of rare earth hydroxides in the presence of nitrate ion. Here, M is rare earth element. Several crystal phases of RHNs, such as $M(\text{OH})_2(\text{NO}_3) \cdot \text{H}_2\text{O}$,¹⁻⁴⁾ $M_2(\text{OH})_{5.14}(\text{NO}_3)_{0.86} \cdot \text{H}_2\text{O}$,^{5,6)} $M_2(\text{OH})_5(\text{NO}_3) \cdot 1.5\text{H}_2\text{O}$,⁷⁻¹⁰⁾ and $M_4\text{O}(\text{OH})_9\text{NO}_3$,¹⁰⁻¹²⁾ have been reported. Hereinafter, $M_2(\text{OH})_{5.14}(\text{NO}_3)_{0.86} \cdot \text{H}_2\text{O}$ is written as M2, $M_4\text{O}(\text{OH})_9\text{NO}_3$ as M4, and hexagonal rare earth hydroxide, $M(\text{OH})_3$, as M1. $M(\text{OH})_2(\text{NO}_3) \cdot \text{H}_2\text{O}$, M2, and $M_2(\text{OH})_5(\text{NO}_3) \cdot 1.5\text{H}_2\text{O}$ have layer structure. They have anion exchange ability, and interlayer distance varies with the size of exchanged anion.

Li and Yanagisawa reported that three kinds of yttrium hydroxide nitrates, $\text{Y}(\text{OH})_3$ (M1), $\text{Y}_2(\text{OH})_{5.14}(\text{NO}_3)_{0.86} \cdot \text{H}_2\text{O}$ (M2) and $\text{Y}_4\text{O}(\text{OH})_9\text{NO}_3$ (M4), were prepared by changing pH and temperature in hydrothermal treatment.¹³⁾ They also drew a pH-temperature phase diagram. According to the diagram, M1 forms at $\text{pH} > 11$ regardless of hydrothermal temperature. M2 forms at low pH and low temperature, and M4 forms at intermediate pH and high temperature.

It has also been reported that crystal particles of RHNs sometimes show anisotropic growth. From the rod and plate shape RHN crystallites, rare earth oxide nanorod and nanoplate are obtained by calcination of RHNs. In our previous work, Er_2O_3 nanorods showed excellent catalytic activity compared to Er_2O_3 nanoparticles in the dehydration of 1,4-butanediol to produce 3-buten-1-ol.¹⁴⁾ Huang et al. reported that $\text{Au}/\text{Pr}_6\text{O}_{11}$ nanorod was more active than $\text{Au}/\text{Pr}_6\text{O}_{11}$ isotropic particle in CO oxidation because Pr_6O_{11} nanorod easily released surface and lattice oxygen.¹⁵⁾ There have also been reported the catalytic advantage in CeO_2 nanorod and nanoplate.^{16,17)} Zhong et al. reported that Eu^{3+} -doped Y_2O_3 nanorod bundle showed strong red emission at around 613 nm.¹⁸⁾ Because morphology has a high impact on catalytic activity, establishment of the morphology-control method is required. However, factors of determining morphology are still not clear.

In this work, RHNs ($M = \text{Sc}, \text{Y}, \text{La-Nd}, \text{Sm-Lu}$) were prepared under three pH conditions and we investigate crystal phase, chemical composition, and morphology due to clarify factor of determining RHN morphology.

2. Experimental

In the preparation of RHNs, rare earth nitrates were used as a rare earth source. Rare earth nitrates were purchased from Sigma-Aldrich ($M = \text{Sc}, \text{Y}, \text{Ce-Nd}, \text{Sm-Tb}, \text{Er}, \text{Tm}, \text{Lu}$), Kanto Chemical Co., Inc. ($M = \text{Dy}$), and Wako Pure Chemical Industries, Ltd. ($M = \text{La}, \text{Ho}, \text{Yb}$). 25 wt % aqueous ammonia (Wako Pure Chemical Industries, Ltd.) was used as a pH adjuster. RHNs were prepared with a hydrothermal synthesis method. Rare earth nitrate (2.27–4.40 g, as 1.0 g of M_2O_3) was dissolved in 25 mL of distilled water. Then, the pH of the solution was adjusted to 7.0, 8.0 and 9.0 with 25 wt % aqueous ammonia with stirring for precipitation. No additives such as amine, fatty acid, or alcohol were added. The solution and precipitate were transferred into a 50 cm³ Teflon-lined autoclave. Hydrothermal treatment was carried out at 150°C for 24 h. We confirmed that the solution pH did not change largely during the treatment. The resulting precipitate was washed and dried at 110°C for 12 h. The prepared RHN is named as “M-pH (adjusted pH value)”.

X-ray diffraction (XRD) patterns were recorded on an XRD-7000 (Shimadzu) using $\text{Cu K}\alpha$ radiation to determine crystal phase of RHNs. The fractions of N and H in the samples were analyzed in a CHN analyzer (J-SCIENCE LAB Ltd., MICRO CORDER JM10T), where gasification temperature was 1000°C. The thermogravimetry-differential thermal analysis (TG-DTA) was performed by EXSTAR 6000 (Seiko Instruments Inc.) from 30 to 1000°C under the following conditions: nitrogen flow rate, 100 cm³ min⁻¹; heating rate, 10 °C min⁻¹; sample weight, ca. 3 mg. Scanning electron microscope (SEM) images were taken on a JEOL JSM-7001FA microscope operated at 5 and 15 kV. Fourier transform infrared (IR) spectra were measured on a Nicolet iS5 (Thermo Fisher scientific) equipped with Attenuated Total Reflection (ATR) unit. The spectra were taken in reflectance at room temperature with 32 scans accumulated at a spectral resolution of 4 cm⁻¹.

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3. Results and discussion

3.1 Crystal phase

Figure 1(a) shows XRD patterns of RHNs which were prepared at pH 7. Sm-pH 7 is identified as $\text{Sm}(\text{OH})_3$ (JCPDS 6-0117), M1, whose space group is hexagonal $P6_3/m$. La-pH 7, Pr-pH 7 and Nd-pH 7 were not obtained because no precipitation occurred. When rare earth nitrate is used as a rare earth source, light rare-earth (i.e. La, Pr and Nd) hydroxides precipitate at a pH value of higher than 7.¹⁹⁾ Scandium nitrate solution became jelly-like substance during addition of aqueous ammonia. For this reason, pH control of the scandium solution is not able. At $M = \text{Ce}$, cerium dioxide precipitated during the pH adjustment. In the pattern of Gd-pH 7, there are three peaks at 2θ value of 10.55, 21.21, and 28.07 degree corresponding to interplanar distance (d) of 0.838, 0.419, and 0.318 nm, respectively. Because 0.419 is just a half of 0.838, crystal structure of Gd-pH 7 is probably layer. The pattern of Dy-pH 7 is much like Gd-pH 7. Diffraction peaks of Er-pH 7 appear at d value of 0.908, 0.455, and 0.309 nm. The ratio of d value of the first one to the second one is 1.0 to 0.5, which suggests that Er-pH 7 is layer structure whose interlayer spacing is longer than Gd-pH 7 irrespective of the smaller cationic radius of Er than Gd. XRD patterns of Ho-pH 7 and Y-pH 7 also show layer-like structures whereas whose peak at around 10 degree is split. There are a lot of peaks in the pattern of Yb-pH 7. **Figure 1(b)** shows XRD patterns of RHNs prepared at pH 9. Sm-pH 9 and Gd-pH 9 are identified to hexagonal rare earth hydroxide. The pattern of Y-pH 9 is well accorded with

$\text{Y}_4\text{O}(\text{OH})_9\text{NO}_3$, M4, whose space group is monoclinic $P2_1$.¹¹⁾ In previous work, $\text{Y}_4\text{O}(\text{OH})_9\text{NO}_3$ was obtained at an adjusted pH value of 9 when a pH adjuster was NH_4NO_3 .¹³⁾ Our result replicated the previous work. Diffraction patterns of Ho-pH 9, Er-pH 9, and Yb-pH 9 are similar to that of Y-pH 9. The pattern of Dy-pH 9 is a cross between Gd-pH 9 and Ho-pH 9 patterns. In summary, there are three crystal phases of RHNs such as hexagonal hydroxide, layer, and monoclinic one. The diffraction patterns of these phases are similar to those of M1, M2 and M4 observed for yttrium.¹³⁾ Hereinafter, we also use these abbreviations to the RHNs.

Table 1 lists crystal phases of RHNs and ionic radius of rare earth cation (r_i) whose valence is three and coordination number is six.²⁰⁾ M1 phase is obtained when r_i is large such as La, Pr, Nd and Sm whereas M4 phase forms at small r_i . M2 phase forms at middle r_i and low pH.

Thus, it is clear that the crystal phase of RHNs systematically changes with not only temperature and pH as reported by Li and Yanagisawa¹³⁾ but also with ionic radius of rare earth cation.

3.2 Determination of chemical composition

We have identified the crystal phases of RHNs obtained in this work according to those of yttrium reported by Li and Yanagisawa based on the XRD patterns. In order to confirm the identification, ATR-IR, TG-DTA and CHN analysis were carried out.

3.2.1 ATR-IR observation

ATR-IR measurements were performed in order to clarify the

Fig. 1. XRD patterns of rare earth hydroxide nitrates prepared at pH 7 (a) and pH 9 (b).

Table 1. Crystal phases and morphologies of rare earth hydroxide nitrates

M	Lu	Yb	Tm	Er	Ho	Y	Dy	Tb	Gd	Eu	Sm	Nd	Pr	La
r_i (pm) ^{a)}	86	87	88	89	90	90	91	92	94	95	96	98	99	103
Crystal phase ^{b)}														
pH 7	M4	M4	M4	M2	M2	M2	M2	M2	M2	M1+M2	M1	—	—	—
pH 8	M4	M4	M4	M4	M4	M2	M2	M2	M1	M1	M1	M1	M1	M1
pH 9	M4	M4	M4	M4	M4	M4	M1+M4	M1	M1	M1	M1	M1	M1	M1
Morphology ^{c)}														
pH 7	R	R	B	P	P	P	P	B	B	B	R			
pH 8	R	R	R	R	R	P	P	P	R	R	R	R	R	R
pH 9	R	R	R	R	R	R	R	R	R	R	R	R	R	R

a) r_i : ionic radius of rare earth cation (valence = 3 and coordination number = 6).²⁰⁾

b) M1, $M(\text{OH})_3$; M2, $M_2(\text{OH})_{5.14}(\text{NO}_3)_{0.86} \cdot \text{H}_2\text{O}$; M4, $M_4\text{O}(\text{OH})_9\text{NO}_3$.

c) R, nanorod; B, nanobelt; P, nanoplate.

components existing in the samples. **Figure 2** shows ATR-IR spectra of Sm-pH 7, Ho-pH 7, and Yb-pH 8, with M1, M2, and M4 phases, respectively. In order to assign the absorption band of nitrate ion, spectrum of sodium nitrate anhydride is also plotted on Fig. 2. In the spectrum of Sm-pH 7, only one peak is observed at around 3600 cm^{-1} , and it is ascribed to O–H stretching vibration. There are three absorption bands in the ATR-IR spectrum of Ho-pH 7. A broad band from 3000 to 3700 cm^{-1} can be attributed to crystalline water, which is often accompanied by a weak absorption band at $1615\text{--}1640\text{ cm}^{-1}$.²¹⁾ Because the remaining peak at ca. 1350 cm^{-1} appears in the same wavenumber as the only absorption band of NaNO_3 anhydride, this peak can be ascribed to that of nitrate ion. In the spectrum of Yb-pH 8, multiplet and doublet absorption bands are observed at $3200\text{--}3700$ and $1200\text{--}1500\text{ cm}^{-1}$, corresponding to absorption of OH group and nitrate ion, respectively. Thus, it is assured that M1 phase contains only OH, and that M2 and M4 phases contain both OH and NO_3^- . It is also speculated from the broadening of OH band in M2 phase that the local structure of OH has wide variety due to hydrogen bonding. On the other hand, the sharpness and/or multiplet of OH bands in M1 and M4 phases suggest that the OH bonds in these samples are fixed at specific crystallographic positions. Additionally, the doublet and sharpness of NO_3^- bands in M4 phase suggest that NO_3^- is also fixed. These results well agree with the crystallographic structure of each phase.¹¹⁾

3.2.2 M1 phase

From the ATR-IR result, it is clear that nitrogen content of M1 phase is zero. According to CHN analysis results, nitrogen

fraction of M1 phase RHNs is less than 0.50 wt %: Pr-pH 9, 0.12; Sm-pH 9, 0.33; Gd-pH 9, 0.43; Tb-pH 9, 0.13; and Sm-pH 7, 0.21 wt %. These values can be regarded as 0 because of the experimental error. **Figure 3(a)** shows TG–DTA curves of Sm-pH 7. Experimental weight loss from 30 to 1000°C is 13.2 wt %, which is consistent with the theoretical value {13.4 wt %, $2[\text{Sm}(\text{OH})_3] \rightarrow \text{Sm}_2\text{O}_3$ }. Thus, there is little doubt that M1 phase is rare earth hydroxide $M(\text{OH})_3$. Sm-pH 7 is decomposed by two endothermic steps, and those weight losses are 8.8 wt % at around 340°C and 4.4 wt % at ca. 450°C . Possible thermal decomposition processes are as follows:

3.2.3 M2 phase

Chemical formula of M2 phase has been reported to be $\text{Y}_2(\text{OH})_{5.14}(\text{NO}_3)_{0.86} \cdot \text{H}_2\text{O}$.¹³⁾ The ATR-IR result does not contradict from this identification. **Figure 3(b)** shows TG–DTA profiles of Er-pH 7. Measured weight loss is 22.4 wt %, and it is in good harmony with the estimated loss [22.5 wt %, $\text{Er}_2(\text{OH})_{5.14}(\text{NO}_3)_{0.86} \cdot \text{H}_2\text{O} \rightarrow \text{Er}_2\text{O}_3$]. Thermal decomposition of Er-pH 7 proceeds in three endothermic steps. We estimate chemical equation of each step by reference to $\text{Y}_2(\text{OH})_{5.14}(\text{NO}_3)_{0.86} \cdot \text{H}_2\text{O}$.⁵⁾ The first and moderate weight decrease up to 270°C is 3.5% consistent with a single molecule of hydrated water (theoretical value, 3.7%). The second loss around 300°C can be ascribed to two water molecules. The final weight loss is gasification of the remaining nitrogen and hydrogen components as nitrogen oxide and water, respectively. That is, thermal decomposition steps are probably as follows:

Nitrogen content of Er-pH 7 (2.41 wt %) and Gd-pH 7 (2.75 wt %) are consistent with calculated values, 2.44 wt % of $\text{Er}_2(\text{OH})_{5.14}(\text{NO}_3)_{0.86} \cdot \text{H}_2\text{O}$ and 2.55 wt % of $\text{Gd}_2(\text{OH})_{5.14}(\text{NO}_3)_{0.86} \cdot \text{H}_2\text{O}$, respectively.

3.2.4 M4 phase

As described in Section 3.1, XRD pattern of M4-phase is similar to that of $\text{Y}_4\text{O}(\text{OH})_9\text{NO}_3$. Thus, chemical composition of M4 phase is supposed to be $M_4\text{O}(\text{OH})_9\text{NO}_3$. **Figure 3(c)** shows TG–DTA curves of Y-pH 9. Thermal decomposition of Y-pH 9 proceeds in two endothermic steps, $310\text{--}410$ and $460\text{--}550^\circ\text{C}$. This result is consistent with TGA–DSC measurement of $\text{Y}_4\text{O}(\text{OH})_9\text{NO}_3$ in the previous study.¹⁰⁾ Total experimental weight loss is 23.9%, which is slightly higher than theoretical weight

Fig. 2. ATR-IR spectra of NaNO_3 anhydride, Sm-pH 7, Ho-pH 7, and Yb-pH 8.

Fig. 3. TG–DTA curves of Sm-pH 7 (a), Er-pH 7 (b), and Y-pH 9 (c), which are M1, M2, and M4 phases, respectively.

Fig. 4. SEM images of Nd-pH 9 (a), Er-pH 9 (b), Y-pH 7 (c), Yb-pH 8 (d), Sm-pH 7 (e), and Eu-pH 7 (f).

decrease (23.0%). However, we were unable to estimate chemical equation of each step because we couldn't find any reasonable intermediate. In fact, Zhang et al. also failed to determine thermal decomposition mechanism of $Y_4O(OH)_9(NO_3)$.¹⁰ According to CHN elemental analysis, measured nitrogen content (1.56 wt% in Ho-pH 9) accords closely with theoretical one (1.57 wt%). These results suggest that chemical formula of M4 phase is $M_4O(OH)_9NO_3$.

3.3 Morphology

Figures 4(a)–4(f) show SEM images of some samples. We can categorize the morphology into 3 types, nanorod, nanobelt, and nanoplate as summarized in Table 1. Figure 4(a) shows SEM image of Nd-pH 9. This sample is nanorod with high-aspect ratio, which is ca. 1 μm long and approximate 50 nm diameter. Similar nanorod formed at $M = La$ and Pr with large cation. On the other hand, Er-pH 9 with small cation is rugged nanorod with low-aspect ratio [Fig. 4(b)]. This nanorod is similar to trilobal $Y_4O(OH)_9NO_3$ reported by Hong et al.¹² Similar nanorod is observed in Ho-pH 8 and Ho-pH 9 with M4 phase. Figure 4(c) shows SEM image of Y-pH 7, and the shape of sample is nanoplate. Nanoplate formed at low pH and middle r_i . Yb-pH 8 seems to be a bundle of many slim nanorods [Fig. 4(d)]. The bundle structure is also observed in Lu-pH 8. Sm-pH 7 is honeycomb-like hexagonal column, which is 15 μm long and ca. 10 μm wide on each side [Fig. 3(e)]. Eu-pH 7 is nanobelt, which is thinner than nanorod [Fig. 3(f)]. As listed in Table 1, morphology of RHNs is rod when the ion radius is small and large whereas plate and belt-shape particle are observed when r_i is middle. Thus, it is clear that the crystal phase of RHNs systematically changes with ionic radius of rare earth cation.

Here, the relationship between crystal phase of prepared RHN and morphology is as follows:

M1 phase	$M(OH)_3$	Rod
M2 phase	$M_2(OH)_{5.14}(NO_3)_{0.86} \cdot H_2O$	Plate and belt
M4 phase	$M_4O(OH)_9NO_3$	Rod

The relationship between crystal phase and morphology is almost one-to-one correspondence. These results indicate RHN morphology depends on crystal phase of RHN.

3.4 Possible crystal growing scheme

We can explain the origin of morphology based on crystal structure of RHN. Figure 5(a) is crystal structure of hexagonal M1 phase. Because M1 phase is six-fold symmetry, crystal growth rate along a axis can be the same as that along b axis. Morphology of Nd-pH 9 with M1 phase is nanorod as shown in

Fig. 5. Crystal structures of hexagonal $M(OH)_3$ (a) and monoclinic $M_4O(OH)_9NO_3$ (b). Green large ball, rare earth (M); gray ball, nitrogen; red ball, oxygen; bright pink ball, hydrogen. Bold black arrow represents possible crystal growth direction. These figures were drawn by VESTA.²²⁾

Fig. 4(a). This result indicates crystal growth rate along c -axis is probably faster than other axes. Figure 5(b) is crystal structure of M4 phase. There is a channel in a direction to c -axis and nitrate ions locate in the channel. Comparing length of cell edges, a , b and c , b is longer than a and c . Because of anisotropy of monoclinic structure, M4 phase seems to grow intrinsically as rod-shape crystal. In other words, crystal with M4 phase may grow along b -axis. However, morphology of M4 phase samples is not simple nanorod but trilobal-like nanorod and bundle shapes. Zhang et al. suggested that the trilobal nanorod formed by self-assembly of three rod-like nanocrystals because crystalline size might be too small to maintain single particle with stability.¹⁰ Thus, Er-pH 9 [Fig. 4(b)] is an aggregate of several nanorods. Yb-pH 8 [Fig. 4(d)] also seems to be the aggregate whereas the number of nanorods constituting Yb-pH 8 is much more than Er-pH 9. Since surface energy probably affects the stability of nanorods, narrow nanorods tend to aggregate much more than wideness. However, average width of these nanorods is unable to measure due to lose shape. Morphology of Sm-pH 7 with M1 phase is honeycomb-like hexagonal column [Fig. 4(e)]. The column seems to form by dissolution and recrystallization process of bundle. In fact, surface of the column is smooth and cross-sectional shape is hexagonal. Samarium hydroxide dissolves in aqueous solution easier than other rare earth hydroxides at the same pH.¹⁹ Additionally, Hong et al. reported dissolution and recrystallization proceeded at pH 7 whereas did not at pH 9.¹² M2 phase has layer structure although space group remains undetermined. Layer crystal is known to form nanoplate as shown in Fig. 4(c) due to a slow growing rate for direction of

stacking. Morphology of Eu-pH 7 with M2 phase is nanobelt [Fig. 4(f)]. However, layer phase is unlikely to grow uniaxially. We presume that rod-shape particles exist before hydrothermal process and these particles become thin into belt-like shape with crystal phase transition into M2 phase during hydrothermal process.

4. Conclusion

RHNs are prepared from all rare earth nitrate except $M = \text{Pm}$ under the conditions of 150°C and pH between 7 and 9. At $M = \text{Sc}$, pH control of the scandium solution is not able because of formation of jelly-like substance during addition of aqueous ammonia. At $M = \text{Ce}$, cerium dioxide precipitated during the pH adjustment. There are three crystal phases of RHNs such as hexagonal M1 phase, layer M2 phase, and monoclinic M4 phase. Crystal phase changes from M4 to M1 through M2 phase with increasing ionic radius of rare earth cation. Chemical composition of RHNs is determined by ATR-IR, TG-DTA and a CHN analysis: M1, $M(\text{OH})_3$; M2, $M_2(\text{OH})_{5.14}(\text{NO}_3)_{0.86} \cdot \text{H}_2\text{O}$; M4, $M_4\text{O}(\text{OH})_9\text{NO}_3$. Morphology of RHNs is rod when the ion radius is small and large whereas plate and belt-shape particle are observed when the ion size is middle. The relationship between crystal phase and morphology is almost one-to-one correspondence: M1 phase, rod; M2 phase, plate and belt; M4 phase, rod. These results indicate RHN morphology depends on crystal phase of RHN.

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References

- 1) M. Lundberg and A. J. Skarnulis, *Acta Crystallogr.*, B32, 2944–2947 (1976).
- 2) S. P. Newman and W. Jones, *J. Solid State Chem.*, 148, 26–40 (1999).
- 3) D. Louër, F. Deneuve, C. Herviou and C. Gourlaouen, *Powder Diffr.*, 1, 263–264 (1986).
- 4) J. M. Haschke, *Inorg. Chem.*, 13, 1812–1818 (1974).
- 5) C. E. Holcombe, Jr., *J. Am. Ceram. Soc.*, 61, 481–486 (1978).
- 6) Y. Q. Jia, J. G. Li, Y. M. Wang, L. X. Ding, X. M. Qin and X. D. Sun, *Acta Metall. Sin.*, 12, 1188–1193 (1999).
- 7) L. J. McIntyre, L. K. Jackson and A. M. Fogg, *Chem. Mater.*, 20, 335–340 (2008).
- 8) K.-H. Lee and S.-H. Byeon, *Eur. J. Inorg. Chem.*, 2009, 929–936 (2009).
- 9) S. A. Hindocha, L. J. McIntyre and A. M. Fogg, *J. Solid State Chem.*, 182, 1070–1074 (2009).
- 10) J. Zhang, Z. Liu, J. Lin and J. Fang, *Cryst. Growth Des.*, 5, 1527–1530 (2005).
- 11) A. N. Christensen, M. Nielsen, K. P. J. O'Reilly and T. Wroblewski, *Acta Chem. Scand.*, 46, 224–230 (1992).
- 12) Z. Hong, H. Guo, L. Peng and M. Wang, *Key Eng. Mat.*, 336–338, 2176–2178 (2007).
- 13) N. Li and K. Yanagisawa, *J. Solid State Chem.*, 181, 1738–1743 (2008).
- 14) F. Sato, Y. Yamada and S. Sato, *Chem. Lett.*, 41, 593–594 (2012).
- 15) P. X. Huang, F. Wu, B. L. Zhu, G. R. Li, Y. L. Wang, X. P. Gao, H. Y. Zhu, T. Y. Yan, W. P. Huang, S. M. Zhang and D. Y. Song, *J. Phys. Chem. B*, 110, 1614–1620 (2006).
- 16) K. Zhou, X. Wang, X. Sun, Q. Peng and Y. Li, *J. Catal.*, 229, 206–212 (2005).
- 17) H.-X. Mai, L.-D. Sun, Y.-W. Zhang, R. Si, W. Feng, H.-P. Zhang, H.-C. Liu and C.-H. Yan, *J. Phys. Chem. B*, 109, 24380–24385 (2005).
- 18) S. Zhong, S. Wang, H. Xu, H. Hou, Z. Wen, P. Li, S. Wang and R. Xu, *J. Mater. Sci.*, 44, 3687–3693 (2009).
- 19) T. Moeller and H. E. Kremers, *Chem. Rev.*, 37, 97–159 (1945).
- 20) R. D. Shannon, *Acta Crystallogr.*, A32, 751–767 (1976).
- 21) M. Hesse, H. Meier and B. Zeeh, "Spectroscopic Methods in Organic Chemistry 2nd Edition", Translated by R. Dunmur and M. Murray Thieme, Stuttgart (2008) pp. 49.
- 22) K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 44, 1272–1276 (2011).