Control of Crystal Structure and Its Defect of ε-HNIW prepared by Evaporation Crystallization

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ABSTRACT

In the evaporation crystallization, the structural defect and density of ε-hexanitrohexaazaisowurtzitane (HNIW) crystals were controlled by operating parameters of evaporation rate, initial concentration of HNIW and temperature. The density change of the crystal was counted as the variation of the crystal structural defect because the crystal defect in the structure reduced the apparent crystal density. Due to formation of crystal defects during the crystal growth, the operating condition promoting the growth rate brought about increasing the crystal defects and decreasing crystal density. Thereby, the crystal density was significantly reduced with increasing the evaporation rate and initial concentration of HNIW. The influence of the evaporation rate on the crystal density change was much higher than that of the initial concentration. However, the crystal density was enhanced as increasing the temperature because the crystal growth process was retarded at high temperature. It was interesting to find that the crystal structure of ε-form was changed to β-form one by high evaporation rate above 0.125 ml/hr at 70 ℃.

Keywords : crystal defect, crystal density, evaporation crystallization, operating conditions, structural transformation.

1. INTRODUCTION

The high density and stable structure of crystals are essentially required physical properties of high energetic materials (HEMs) used as propellants and explosives because they predominantly dictate the detonation velocity, stability (shelf life time) and sensitivity of materials, which are the uppermost characteristics determining the quality and performance of HEMs. As such, 2,4,6,8,10,12-hexanitrohexaazaisowurtzitane crystal (HNIW) composed of nitramine group containing high oxygen content and no halogen component in the molecular formula is highest in crystal density (>2g/cm^3) at ε-form of structure, exhibiting the highest detonation velocity (9800m/s) among the HEMs, as shown in Table 1. So, the control of the crystal density and structure of HNIW is of great attention in crystallization studies to produce high performance HEM [1, 2].

Among four structural isomers of α, β, γ and ε-form of HNIW crystal, the crystal of ε-form is thermodynamically and mechanically most stable due to its high symmetric configuration of molecules in the structure. Therefore, it has much advantages of density, solubility, thermal stability etc to those of the other forms (α, β and γ) [3, 4]. According to Foltz et al [1994], it was shown that the β-form of crystals could be transformed to γ-one and then finally to ε-one by adjusting solvent and temperature for re-crystallization. Correspondingly, the crystal density is also shifted from 1.98 g/cm3 (β-form) to 2.044 (ε-form) as with the structural transformation. Hoffman [5] had measured the influence of the synthetic method of HNIW on the crystal density of HNIW. As such, HNIW prepared from tetraacetyldiamina hexaazaisowurtzitane (TADA) provided lower crystal density of ε-form than one prepared from tetraformyldiamino hexaazaisowurtzitane (TADF) due to different by-product of synthesis.

In crystallization of RDX, Borne and Patedoye [6] have observed the void defects included in the crystal structure during the crystallization by using polarized optical microscope and insisted to bring about the reduction of crystal density as well as the shock sensitivity of explosive formulation.

Although the previous studies have already implied the strong inter-relationship between the crystal density and structure with the properties of HNIW, they have barely attempted to obtain the crystals well controlled in density and structure by the crystallization yet. In the present study, thus, it is focused to investigate the influencing factors of the crystallization to control the crystal density and structure. The evaporation crystallization was adopted and the evaporation rate, concentration and temperature were considered as key influencing factors of the crystallization.

Table 1. Characteristic of high energetic materials (HEMs)

HEMs	Density (g/cm^3)	Detonation Velocity (m/sec)
HNIW	2.04$_{(max)}$	9800
HMX	1.90	9160
RDX	1.80	8754
PETN	1.78	8695
DATB	1.79	7520
Tetryl	1.70	7560

2. EXPERIMENT

2.1 Preparation of ε-HNIW

The pure HNIW was prepared by purification of raw material of HNIW powder supplied by Agency for Defense Development of Korea. At first, the raw material was highly dissolved in dimethyl carbonate (ACS grade, Fluka, Swiss) at 85 ℃ then cooled at 25 ℃ to crystallize out the HNIW and then was filtered. The purity of the crystalline powder of HNIW was examined with HPLC and was always achieved higher than 99.9 %. Here, the crystalline powder of HNIW was crystallized out in β-form by the cooling crystallization.

HNIW powder of β-form was transformed to ε-form by the drowning-out crystallization. At room temperature β-HNIW powder was dissolved in ethyl acetate solution (ACS grade, Fluka, Swiss) and then dichloro methane (ACS grade, Fluka, Swiss) was added to the solution to induce the crystallization. For the effective recovery in the drowning-out crystallization, the fraction of HNIW, ethyl acetate and dichloro methane was applied as 2 : 5 : 20, respectively. Then, the crystalline powder of ε̃-form was filtered and dried to use. The structure of the crystalline powder was confirmed by XRD and FT-Raman.

2.2 Preparation of Single Crystals

Single crystals of ε̃-HNIW were prepared by evaporation crystallization. The ethyl acetate solution of 5 ml dissolving the HNIW was loaded into a vial (20 ml of volume) and then was completely sealed with aluminum foil. For the evaporation of the solvent the pinholes were given on the foil of the vial being placed in the water bath of which the temperature was accurately controlled within ±0.1 ^{o}C of fluctuation. The evaporation rate was controlled from 0.02 to 0.15 ml/hr by varying the number of pinholes on the foil. Also, the evaporation temperature (bath temperature) was varied from 25 to 70□ and the initial concentration of HNIW in the solvent was changed from 0.03 to 0.15 g/ml. Normally, it took one day to half month to carry out an evaporation crystallization depending on the evaporation rate. The experiment system for the evaporation crystallization was set on the floor of isolated space to prevent any influence of vibration on the crystallization.

2.3 Analysis of Crystals

The single crystals obtained by the drowning-out crystallization were analyzed for the density and structure using pycnometer plus density gravity gradient column and XRD plus FT-IR, respectively. Using the density gradient column, the zinc bromide aqueous solution was used in the density range from 1.97 to 2.05 g/cm^3 at 25 ^{o}C. Again, the crystal density was finely checked with pycnometer method.

The crystal structures were confirmed with X-ray powder diffractometer (M18XHF-SRA, Mac Science, Japan) of Cu Kα radiation in the angle range of 2θ= 5° ~ 50°, and FT-IR spectrometer (FTS-60, BIO-RAD system, U.S.A.) in the wave length region of 1200~700cm^{-1}.

3. RESULTS & DISCUSSION

In general, the crystal defects of point, line, surface and volume originated from missing and mismatching the lattices result in change of physical properties including density. Obviously, the volume defect indicating the spatial void in the crystal structure reduces the apparent density of the crystal. In Fig. 1, the density change of HNIW crystals along with evaporation rate was displayed when the HNIW solution of 0.05 g/cc was evaporated at fixed temperature of 25□. At low evaporation rate of 0.02 ml/hr, the crystal density reached almost at 2.04 g/cm^3, and then was rapidly reduced as increasing the evaporation rate. The fraction of crystal defect was quantitatively estimated by comparison with ideal crystal density of HNIW ($\frac{d_{ideal}-d_{real}}{d_{ideal}}\times 100(\%)$). According to Nielsen et al. [7], it was reported that the crystal system of ε-HNIW is monoclinic (P$2_{1/n}$) having lattice parameters of a=8.852 $\overset{\circ}{\mathrm{A}}$, b=12.556 $\overset{\circ}{\mathrm{A}}$, c=13.386 $\overset{\circ}{\mathrm{A}}$, α=γ=90° and β=106.82°, and its group number is 4. Based on this information of the crystal structure, the ideal crystal density (d_{ideal}) could be calculated as 2.0446 g/ cm^3, of which the value is well consistent with the maximum density of ε-HNIW crystal suggested by Johnston and Wardle [8].

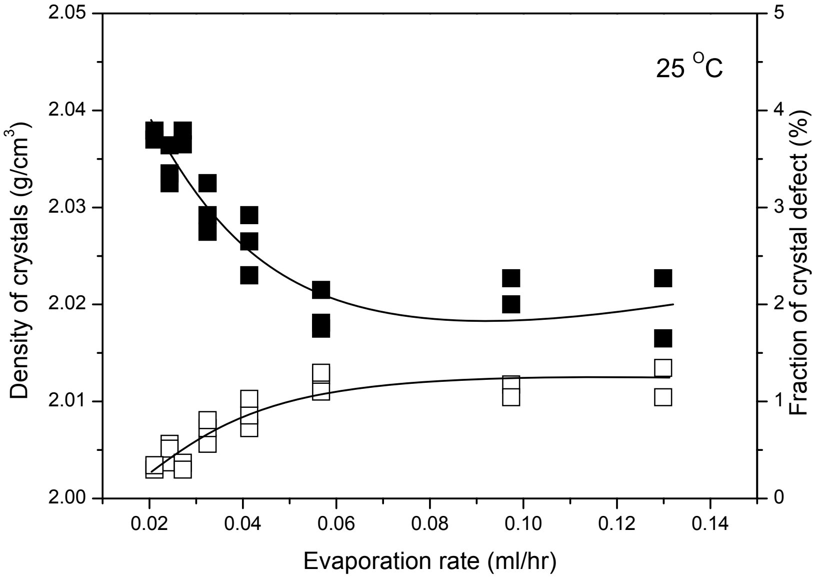


Figure 1. Influence of Evaporation rate on crystal density and structured defect of ε-HNIW crystals prepared by Evaporation Crystallization.

In the course of crystallization, the crystal defects are usually generated depending on the crystal growth conditions [9, 10]. That is, as the crystal growth rate is facilitated, the crystal defects are also promoted. In the present study, as increasing the evaporation rate, the supersaturation rate induced in the solution was enhanced to increase the crystal growth. Therefore, it resulted in increasing the crystal defects and decreasing the crystal density as increasing the evaporation rate.

In Fig. 2, the solution concentration of HNIW was varied from 0.03 – 0.13 g/cc to modify the supersaturation rate at fixed temperature of 25 □ and evaporation rate of 0.03 ml/hr. This result might confirm if the supersaturation rate contributed on the crystal defect and density, which was hypothesized above, because the supersaturation rate was expected to increase as increasing the solution concentration at fixed evaporation rate. As shown in the result, the crystal density was reduced as increasing the solution concentration, indicating the increase of the crystal defects, as consistent with above result, due to promotion of crystal growth by the enhanced supersaturation rate. It is interesting to note that the fraction of crystal defects increased slightly from 0.25 to 0.5% with increasing more than four folding times of solution concentration (Fig. 2) whereas the increase of evaporation rate in about three folding times brought about significant promotion of fraction of the crystal defects up to 1.2% (Fig. 1).

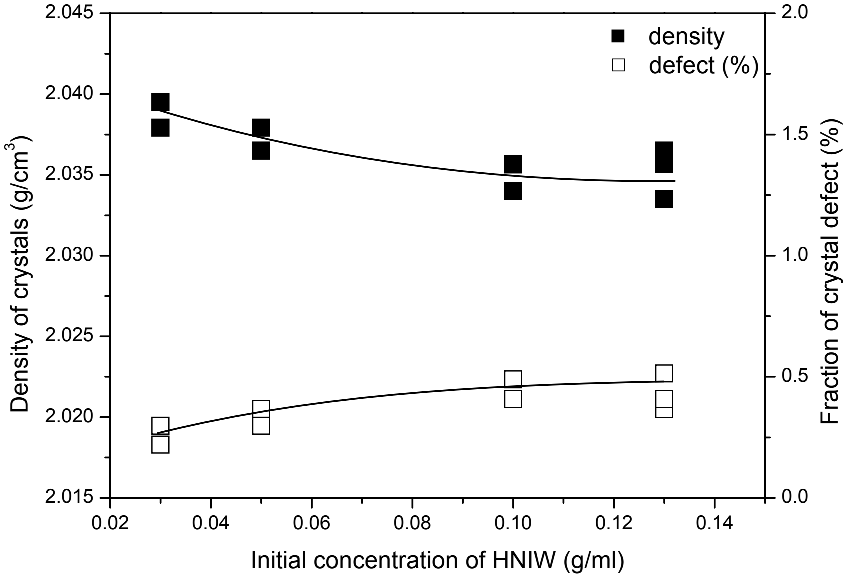


Figure 2. Influence of initial concentration of HNIW on crystal density and structured defect of ε-HNIW crystals prepared by Evaporation Crystallization.

In the present study, the influences of the both crystallization conditions of the evaporation rate and solution concentration would be described with respect to supersaturation rate defined as $\frac{dS}{dt}$, which is major driving force for the crystal growth, where S was the supersaturation ratio (C/C_s) and t was time scale. Until the crystal nucleation occurred, the material of solute in the solution ($C \cdot V$) was conserved where C is the solution concentration and V is the solution volume. In the evaporation crystallization, the reduction of solution volume was inversely related with increase of the solution concentration as,

$$V\frac{dC}{dt} = -C\frac{dV}{dt} \qquad (1)$$

If the evaporation occurred in cylindrical vial, eq. (1) could be rearranged as,

$$\frac{d\ln S}{dt} = -\frac{1}{L}\frac{dL}{dt} \qquad (2)$$

where L is the level height of the solution in the vial. Then, eq. (2) would allow to estimate the suersaturation rate at the induction point of the crystallization, if the average evaporation rate was used for *dL/dt* and the solution level at saturated concentration calculated with solubility was applied for L.

As shown in Fig. 3 based on eq. (2), it was found that the solution concentration in wide range from 0.03 to 0.13 g/cc varied the supersaturation rate only in small span of 0.006 to 0.008 [1/hr] whereas the evaporation rate (0.02 – 0.06 ml/hr) modified the superatuartion rate from 0.004 to 0.013 [1/hr]. This result might well explain the reason why the wide change of the solute concentration induced a slight modification of the crystal density and defects in contrast to the variation of evaporation rate. Also, it would be inferred that the dependency of the crystal density and defects on the crystallization conditions of evaporation rate and solution concentration were consistently described in term of the supersaturation rate.

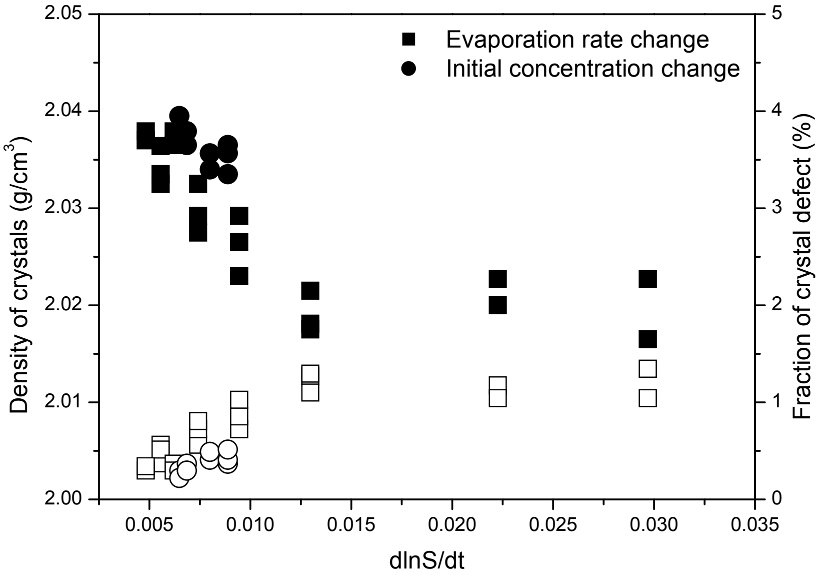


Figure 3. Correlations of crystal density and structural defect of ε-HNIW with Supersaturation rate.

Influence of crystallization temperature on the crystal density and defects were investigated at fixed crystallization conditions of evaporation rate (0.04 ml/hr) and solution concentration (0.05 g/cc), as shown in Fig. 4. The crystal structure was improved as increasing the temperature, bringing about the increase of crystal density and decrease of crystal defects.

In general, it would be considered that the temperature is involved to determine the solubility and structural isomer of crystal in the crystallization. As such, the solubility increasing with temperature would reduce the supersaturation (S), lowering crystal growth rate and the unstable crystal polymorph would be favored as increasing the temperature. Unfortunately, the present experiment result was hardly explained by above traditional concept of temperature influence on the crystallization because the solubility of HNIW was independent of temperature [9] and the ε-HNIW was most stable and dense in crystal structure [3, 4].

In the present study, a possible manner of temperature influencing on the crystal density and defects might be guessed that the molecular stacking process for the crystal growth being exothermic is retarded as increasing the temperature. Actually, the stacking probability of molecules on the growth site is reciprocally proportional to the temperature ($\propto \exp(E/k_BT)$) where T is temperature, E is binding energy between solute molecules and k_B is Boltzmann constant [12]. Also, the rough crystal surface was smoothened with increasing the temperature in case of the greater binding energy between solute molecules than between solute and solvent molecules [13, 14, 15]. Thereby, the high temperature would contribute on reducing the crystal defects and increasing the crystal density.

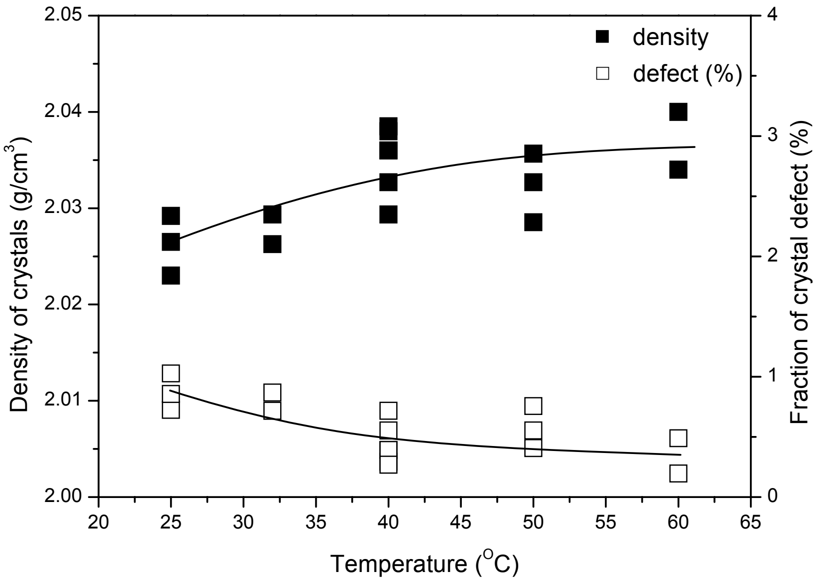
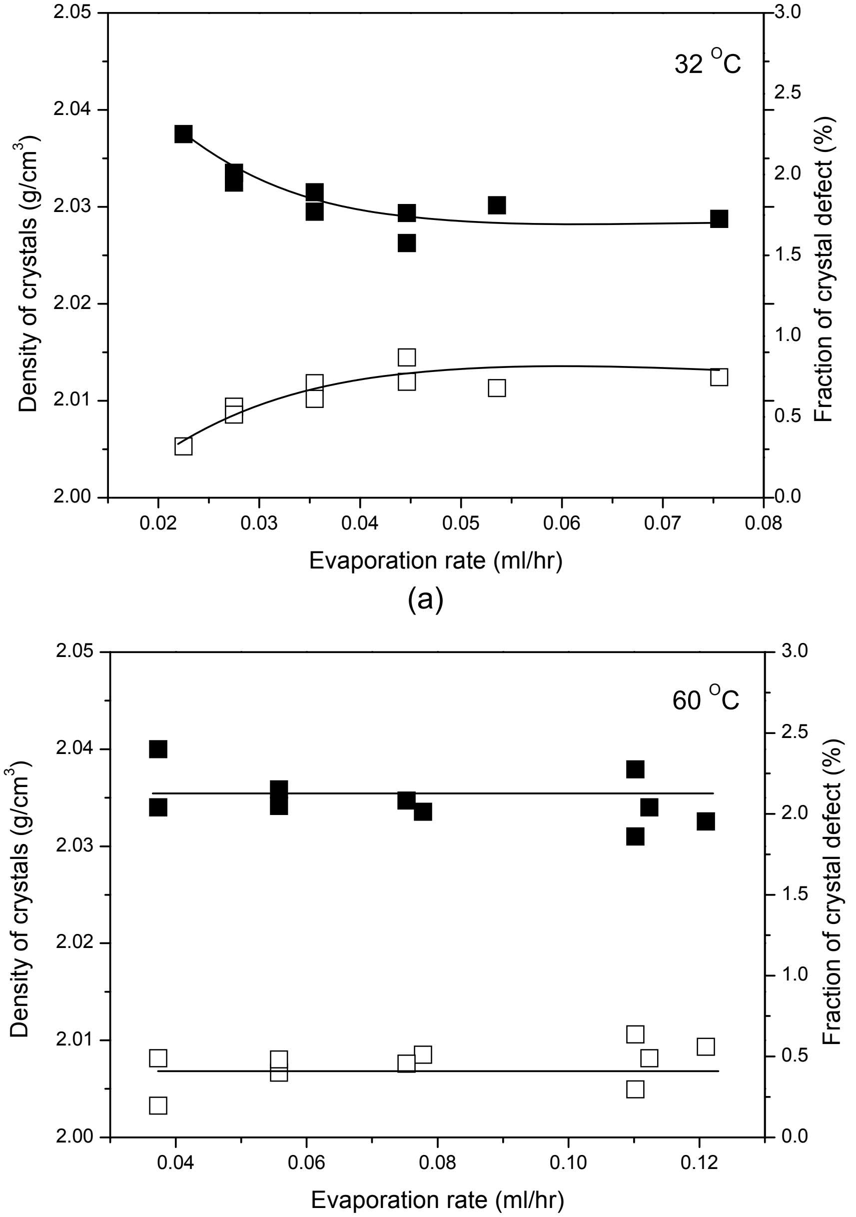


Figure 4. Influence of temperature on crystal density and structured defect of ε-HNIW crystals prepared by Evaporation Crystallization.

The influence of the temperature and evaporation rate on the crystal density and defects was compared because they oppositely contributed on the crystal density and defects, as mentioned above. At temperature of 32 ℃, as shown in Fig. 5(a), the evaporation rate still remained of impact on the crystal defects, resulting in reducing the crystal density. However, at the temperature of 40 ℃ the crystal density and defects were almost independent of the evaporation rate because the promotion of crystal growth by evaporation rate was overcome by the retardation at the high temperature. This trend appeared clearly in the quantitative description defined as the drop ratios of crystal density and defects to the span of evaporation rate causing the drops (Fig. 5(b)). The drop ratio of crystal density was about 0.5 g/hr at 25 ℃ and diminished to one tenth above 40 ℃. Actually, the drop ratios along the evaporation rate above the temperature of 40 ℃ were merely nothing more than the experimental fluctuations.

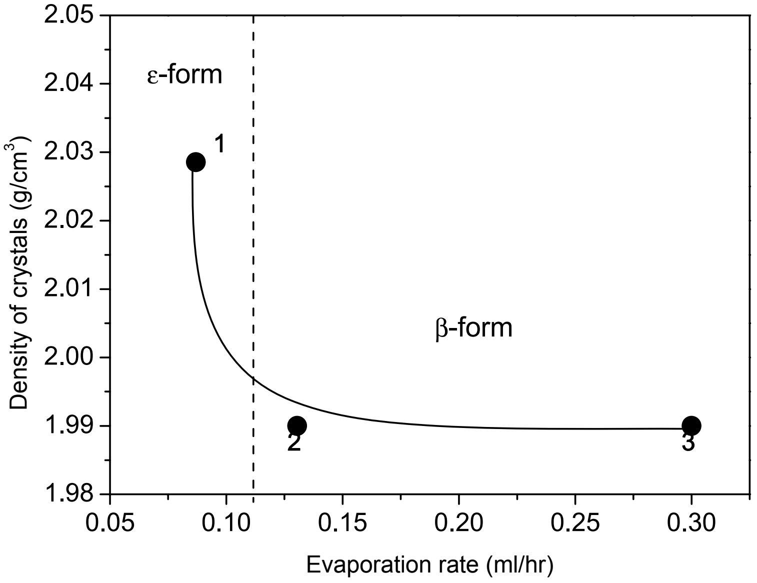


(a)

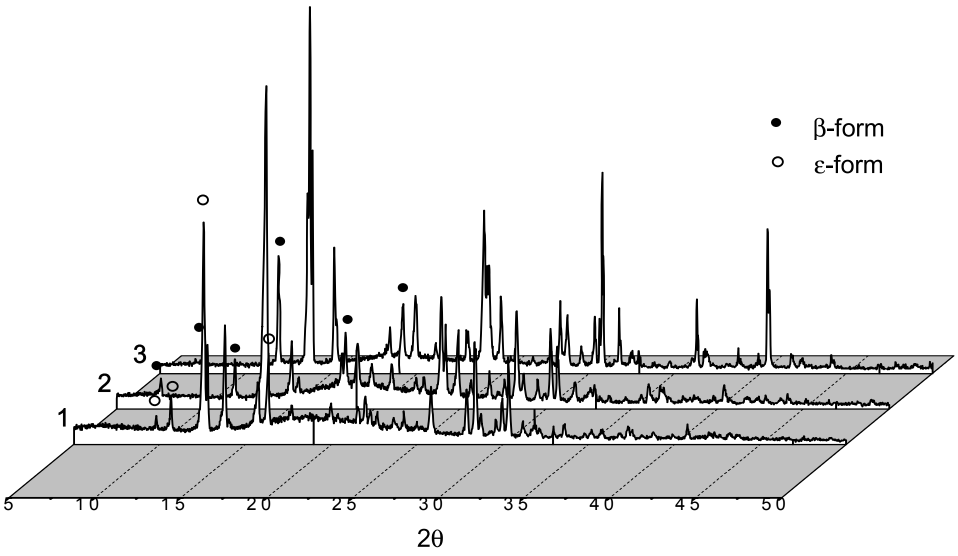
(b)

Figure 5. Influence of Evaporation rate on crystal density and structural defect of HNIW at various evaporation temperature. (a) evaporation temperature = 32℃, (b) evaporation temperature = 60℃.

However, at temperature of 70 ℃ the transformation of crystal structure from ε-form to β-one occurred as increasing the evaporation rate, as shown in Fig. 6. Due to boiling



(b)



(a)

Figure 6. Crystal Density and Structural Change with Evaporation rate at 70℃. (a) density change of crystal, (b) structural change of crystal.

point of the solvent, ethyl acetate (77.1 □), the evaporation rate below 0.07 ml/hr at 70 □ was not available in the present experiment. The high evaporation rate would generate the high supersaturation providing a condition for formation of less stable crystal structure of β-form rather than ε-one, and the high temperature would also be favored to the less stable crystal structure. As with the transformation of crystal structure from ε-form to β-one, the crystal density was suddenly dropped from about 2.03 to 1.99 g/cm^3 (Fig. 6(a)) and this structural shift was confirmed with powder pattern XRD, an shown in Fig. 6(b).

It should be mentioned that the determination of crystal structure is usually considered at the aspect of thermodynamics in crystallization. Thereupon, the temperature, pH, solution concentration, solvents, composition and additives etc, which are capable to change the chemical potential for the crystallization, have frequently been proven to modify the crystal structure. However, in the present study, the structural transformation was induced by variation of kinetic condition, the evaporation rate.

4. CONCLUSIONS

The crystal density of ε-HNIW crystals depended on the evaporation rate and temperature, which were key operating parameters in the evaporation crystallization. In the course of crystal growth, the inclusion of defects in the crystal structure might occur and it would be promoted as increasing the crystal growth rate. In the present study, thereby, as increasing the evaporation rate inducing the high crystal growth process in the evaporation crystallization, the inclusion of crystal defects were facilitated, resulting in reducing the crystal density. However, the temperature was adversary to the crystal growth process because the molecular stacking for the growth process was retarded at high temperature. Therefore, the crystal were reduced in defects of lattices and enhanced in density as increasing the temperature.

In addition, the high evaporation rate and temperature was favored to the unstable crystal structure of β-HNIW because the chemical potential of solution for the crystallization was unstably heightened. Thus, the structural transformation from ε-form to β-one of HNIW crystal occurred above the evaporation rate of 0.125 ml/hr at 70 ℃. This result would be unique at the aspect of fact that the variation of kinetic condition for crystallization induces the structural isomerism of crystal.

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