Solubility and solid phase of trivalent lanthanide hydroxides and oxides

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An undersaturation approach was adopted to reveal the solubility and solubility-limiting solid phase of La, Eu and Tm in the sample solutions with the ionic strength (I) of 0.1 mol/L (M) and the hydrogen ion concentration range (pH, $=-\log[H^+]$) of 6 to 12 after aging at 25 to 90°C for certain periods up to 12 weeks. Solubility and solubility-limiting solid phases were discussed with the aid of X-ray diffraction (XRD) patterns of the solid phases and temperature dependence of solubility products (log $K_p^*$) values. The XRD patterns of the solid phases indicated that the initial solid phase of La$_2$O$_3$(cr) transformed to La(OH)$_3$(cr) after aging at 25 °C and 90 °C. On the other hand, Eu$_2$O$_3$(cr) remained stable after aging at 25 °C, but after 90 °C, converted to Eu(OH)$_3$(cr). It was observed that Tm$_2$O$_3$(cr) was not transformed after aging at both 25 °C or 90 °C. Thermodynamic properties obtained from the temperature dependence of the solubility products agreed well with the observations in the XRD patterns.

1. Introduction

For the safety assessment of radioactive waste disposal, it is necessary to predict the migration behavior of actinide elements under relevant geochemical conditions, as they are included in the waste as alpha-emitting radionuclides with long half-lives. Actinide elements of thorium, uranium, neptunium, and plutonium can exist in a tetravalent oxidation state under reducing geochemical conditions, deep underground and easily precipitate as a sparingly soluble amorphous hydroxide solid phase (An(IV)(OH)$_4$(am)) under neutral to alkaline pH conditions of the waste repository systems [1-4]. The solubilities of An(IV)(OH)$_4$(am), hence, play an important role in understanding their migration behavior. It is known that a crystalline oxide solid phase as An(IV)O$_2$(cr) is thermodynamically more stable and has been reported that the crystallization of An(IV)(OH)$_4$(am) towards An(IV)O$_2$(cr) proceeded under certain solution conditions such as strong alkaline pH or elevated temperatures [5-7]. The solubilities of An(IV)O$_2$(cr) have been reported to several orders of magnitude lower than those of An(IV)(OH)$_4$(am) [1-7].

Trivalent actinide elements of americium and curium also exhibit a strong hydrolysis reactions under neutral to alkaline pH conditions to precipitate the sparingly soluble amorphous hydroxide solid phase (An(III)(OH)$_3$(am)) [8-11]. In contrast to the tetravalent actinide elements, no crystalline oxide solid phase (An(III)O$_2$(cr)) was observed in the solubility experiments [2,12]. A few literatures have observed crystalline hydroxide solid phase (An(III)(OH)$_3$(cr)) from X-ray diffraction patterns instead of An(III)O$_2$(cr) and showed an order of magnitude lower solubility values than those of An(III)(OH)$_3$(am) [13,14]. This can be explained by thermodynamic data of An(III)O$_2$(cr). For example, the standard enthalpy (Δr$\Delta H^\circ$) and entropy (Δr$\Delta S^\circ$) of An$_2$O$_3$(cr) have been reported to be Δr$\Delta H^\circ$ = −1690.4±8.0 kJ/mol and Δr$\Delta S^\circ$ = 133.6±6.0 J/K/mol resulted in the standard formation Gibbs energy of Δr$\Delta G^\circ$ = −1605.449±8.284 [2]. Combined with the thermodynamic data for An$^{3+}$ and H$_2$O [2], the standard reaction Gibbs energy (Δr$\Delta G^\circ$) for 1/2 An$_2$O$_3$(cr) + 3H$^+$ $\rightarrow$ An$^{3+}$ + 3/2 H$_2$O was calculated to be Δr$\Delta G^\circ$ = −151.59 kJ/mol, leading to the solubility product ($K_p^*$) of log $K_p^* = 26.56$. This value is approximately 10 orders of magnitude higher than those reported for Am(OH)$_3$(am) and Am(OH)$_3$(cr) [2,4], hinting the oxide solid phase is less stable in aqueous systems. However, due to experimental limitations for handling macro amounts of trivalent actinide elements, only few studies have investigated the An(III) solubility with a definite solid phase characterization [8,11,13] and the stability of An(III)O$_2$(cr) in aqueous systems has not been well experimentally clarified.

Trivalent lanthanide elements are often used as analogues of trivalent actinide elements. A number of literatures have investigated the hydrolysis behavior, solubilities and solid phases of lighter to heavier lanthanide elements and reported their thermodynamic data [15-24]. Several works occasionally summarized the state of knowledge on the solubilities of trivalent lanthanide elements [25-28]. Most recently, Brown and Ekberg [4] have compiled the literature data on the hydrolysis of lanthanide elements and selected the recommended values for the solubility product of hydroxide solid phase (Ln(III)(OH)$_3$(s)) and related thermodynamic data. It is noted that the solubility product of amorphous hydroxide solid phase (Ln(III)(OH)$_3$(am)) obtained after short aging periods was excluded in the review due to poor identification of the solid phase [4]. Konings et al. [29] conducted a comprehensive review on the thermodynamic properties of lanthanide and actinide oxides, where recommended values of Δr$\Delta H^\circ$ and Δr$\Delta S^\circ$ for the lanthanide oxide solid phase (Ln(III)O$_2$(cr)) were selected. For example, the values of Δr$\Delta H^\circ = −1791.6±2.0$ kJ/mol and Δr$\Delta S^\circ = 127.32±0.84$ J/K/mol, based on the reported results by solution calorimetry and heat capacity measurements [29]. The calculated Δr$\Delta G^\circ$ and subsequently Δr$\Delta G^\circ$ for 1/2 La$_2$O$_3$(cr) + 3H$^+$ $\rightarrow$ La$^{3+}$ + 3/2 H$_2$O was −192.33 kJ/mol, leading to $log K_p^* = 33.70$, which is much larger than the selected $K_p^*$ value for La(OH)$_3$(s) (log $K_p^* = 19.72$) [4]. The transformation of Ln(III)(OH)$_3$(cr) to Ln(III)(OH)$_3$(cr) in aqueous systems was observed in a few literatures [30-32]. The formation of Ln(III)(OH)$_3$(cr) was observed by precipitating Ln(III) solutions with NaOH, after complete dissolution of initial Ln(III)O$_2$(cr) with a hot nitrate solution [31]. Neckel et al. [32] observed that the initial material of Nd$_2$O$_3$(cr) was converted to Nd(OH)$_3$(cr) in a purified water at 25 °C after a few months, prior to the their solubility experiment of

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N\textsubscript{(OH)}\textsubscript{2}(cr). However, not many literatures have investigated the solid phase transformation from lighter to heavier lanthanide elements with a combination of definite solid phase characterization and solubility measurement. It is evident that, clarifying the “solubility-limiting solid phase” is essential for the reliable prediction of the solubility limits of trivalent radio-nuclides.

The present study focuses on the solubilities and solid phases of trivalent lanthanum (La), europium (Eu) and thulium (Tm), in neutral to alkaline pH region, for the sample solutions containing Eu\textsubscript{2}O\textsubscript{3} and Tm\textsubscript{2}O\textsubscript{3} at certain pH conditions were prepared for the solid phase analysis. After the preparation, caps of the sample tubes were tightly closed, and the tubes were taken from the Ar glove box. The sample tubes were placed and stored in temperature chambers controlled at the aging temperatures (T\textsubscript{meas}) at 25, 40, 50, 60, and 90 °C for up to 12 weeks (TAITEC BIOShaker BR-43F2 for 25 °C and ETTAS E0450B for 40 to 90 °C). The sample tubes were shaken by a shaker equipped with the temperature chamber during the aging at 25 °C, and shaken by hand occasionally for a few minutes during the aging at 40 to 90 °C.

2.2. Solid phase analysis. After aging at 25 and 90 °C for given periods, selected sample tubes were taken from the temperature chamber and kept at room temperature for 1 day. The pH of the sample solution was measured and the solid phase was separated by centrifuging at 5,000 rpm (H-103N, Kokusan) for 5 min under atmospheric conditions, and dried in a vacuum desiccator for several hours. The diffraction patterns of the solid phase were then collected using XRD (Miniflex, RIGAKU), with Cu-Kα (λ = 0.154 nm) in the range of scattering angle 2θ = 10 to 60°, and a scan rate of 20 °/min. The solid phase samples of La\textsubscript{2}O\textsubscript{3}, Eu\textsubscript{2}O\textsubscript{3}, and Tm\textsubscript{2}O\textsubscript{3} prior to and after aging were used to determine the solubility products.

2.3. Solubility measurement. After aging the sample solution at 25, 40, 50, 60, and 90 °C for certain weeks, the sample tubes were taken out from the temperature chambers. The sample solutions were filtrated through ultrafiltration membranes (Microcon, nominal molecular weight limit (NMWL) of 3,000 (3 kDa), corresponding to pore sizes of approximately 2 nm, Millipore). Filter units and membranes were equilibrated at each T\textsubscript{meas} prior to the ultrafiltration, and the T\textsubscript{meas} values during the ultrafiltration were monitored by the thermostat equipped with the centrifuge device (CF15R, Hitachi Koki Co. Ltd.) run at 13,000 rpm for 20 minutes in the case of T\textsubscript{meas} = 25 or 40 °C. A desktop centrifuge (FB-4000, Kurabo) introduced in a temperature chamber was used to filtrate the sample solutions at T\textsubscript{meas} in the case of T\textsubscript{meas} = 50 and 60 °C. After the pH measurement and ultrafiltration at each T\textsubscript{meas}, the sample solutions were returned to the temperature chambers. A few of the sample solutions were kept at T\textsubscript{meas}, longer than 1 day and pH measurement and ultrafiltration at the T\textsubscript{meas} were repeated to confirm the steady state was achieved at the T\textsubscript{meas}. The whole solubility measurements were repeated several times for different aging times up to 12 weeks. After the ultrafiltration at each T\textsubscript{meas}, 0.3 mL of filtrate was taken and acidified with 2.0 mL of 0.1 M HNO\textsubscript{3}. The La, Eu, and Tm concentrations were then measured by ICP-MS (ELANDRC II, PerkinElmer). The added solid phase completely dissolved. The Eu and Tm stock suspensions were prepared by adding 17.6 g and 19.3 g of Eu\textsubscript{2}O\textsubscript{3} and Tm\textsubscript{2}O\textsubscript{3}, respectively in 50 mL of pure waters and the sample solutions containing Eu\textsubscript{2}O\textsubscript{3} and Tm\textsubscript{2}O\textsubscript{3} were prepared in the same method as those of La\textsubscript{2}O\textsubscript{3}. For the solid phase analysis, aliquots of 10 mL of the La stock suspension, containing approximately 3.3 g of La\textsubscript{2}O\textsubscript{3}, was added in 100 mL of sample solutions. The La concentration would be 0.2 M if the added solid phase completely dissolved. Similarly, 100 mL of sample solutions containing 3.5 g of Eu\textsubscript{2}O\textsubscript{3} and 3.8 g of Tm\textsubscript{2}O\textsubscript{3} at certain pH conditions were prepared for the solid phase analysis. After the preparation, caps of the sample tubes were tightly closed, and the tubes were taken from the Ar glove box. The sample tubes were placed and stored in temperature chambers controlled at the aging temperatures (T\textsubscript{meas}) at 25, 40, 50, 60, and 90 °C for up to 12 weeks (TAITEC BIOShaker BR-43F2 for 25 °C and ETTAS E0450B for 40 to 90 °C). The sample tubes were shaken by a shaker equipped with the temperature chamber during the aging at 25 °C, and shaken by hand occasionally for a few minutes during the aging at 40 to 90 °C.

2. Materials and sample preparation. Reagent grades of sodium perchlorate monohydrate (NaClO\textsubscript{4}·H\textsubscript{2}O, 98%), perchloric acid (HClO\textsubscript{4}, 60%), sodium hydroxide (NaOH, 97%), were purchased from WAKO Pure Chem. HEPES (C\textsubscript{2}H\textsubscript{4}N\textsubscript{2}O\textsubscript{4}·S, 99.0%, Dojindo) was used to adjust pH of sample solutions to the neutral pH region. Lanthanum oxide (La\textsubscript{2}O\textsubscript{3}, 99.99%), europium oxide (Eu\textsubscript{2}O\textsubscript{3}, 99.9%), and thulium oxide (Tm\textsubscript{2}O\textsubscript{3}, 99.9%) were also purchased from WAKO Pure Chem., and were used without any prior treatments. The appearance of these initial oxides was investigated using a desktop scanning electron microscope (JCM-6000 NeoScope, JEOL) and the particles size of these oxides were found to be 1-3 μm. Deionized purified water (Milli-Q, Millipore) was used in the preparation of all solutions. The solution preparation was conducted in a CO\textsubscript{2} free, argon gas filled glove box, at 25 °C and 1 atm to prevent entering CO\textsubscript{2} in the sample solutions. The pH values of the samples were measured by a pH meter (D-72, Horiba Ltd.) with a combined glass electrode (9615-10D, Horiba Ltd.). The reference electrode was filled with 3.89 M NaCl and 0.41 M NaClO\textsubscript{4} (Wako Pure Chem.). The electrode was calibrated against standard HCIO\textsubscript{4} and NaOH solutions (pH, 1, 2, 3, 11, 12, and 13; Wako Pure Chem.) at T = 0.1 M using NaClO\textsubscript{4} at 25, 40, 50, and 60 °C to correct the experimentally measured pH\textsubscript{exp} values, to the pH values at different temperatures. Sample solutions were prepared by an undersaturation approach. A certain amount of 0.1 M NaClO\textsubscript{4} solution was prepared as an initial solution. Then, 0.1 M HCIO\textsubscript{4} or 0.1 M NaOH was added to the initial solution to adjust the pH, so that the ionic strength (I) of the initial solution kept constant at I = 0.1 M. Each 10 mL of aliquot was withdrawn at fixed pH levels ranging from pH 7 to 12 and put into polypropylene tubes. For the sample solutions in the neutral pH region, an appropriate amount of 0.1 M HEPES solution was added to stabilize the pH. The concentration of HEPES was 10\textsuperscript{-3} M for each sample solution. The La stock suspension was prepared by adding 16.3 g of La\textsubscript{2}O\textsubscript{3} in 50 mL of pure water. If the La\textsubscript{2}O\textsubscript{3} solid phase totally dissolved, the concentration would correspond to 2.0 M. An aliquot of 50 μL stock suspension was then added to each 10 mL of sample solution, so that the La concentration of the sample solution would be 0.01 M, if the added solid phase completely dissolved. The Eu and Tm stock suspensions were prepared by adding 17.6 g and 19.3 g of Eu\textsubscript{2}O\textsubscript{3} and Tm\textsubscript{2}O\textsubscript{3}, respectively in 50 mL of pure waters and the sample solutions containing Eu\textsubscript{2}O\textsubscript{3} and Tm\textsubscript{2}O\textsubscript{3} were prepared in the same method as those of La\textsubscript{2}O\textsubscript{3}. For the solid phase analysis, aliquots of 10 mL of the La stock suspension, containing approximately 3.3 g of La\textsubscript{2}O\textsubscript{3}, was added in 100 mL of sample solutions. The La concentration would be 0.2 M if the added solid phase completely dissolved. Similarly, 100 mL of sample solutions containing 3.5 g of Eu\textsubscript{2}O\textsubscript{3} and 3.8 g of Tm\textsubscript{2}O\textsubscript{3} at certain pH conditions were prepared for the solid phase analysis. After the preparation, caps of the sample tubes were tightly closed, and the tubes were taken from the Ar glove box. The sample tubes were placed and stored in temperature chambers controlled at the aging temperatures (T\textsubscript{meas}) at 25, 40, 50, 60, and 90 °C for up to 12 weeks (TAITEC BIOShaker BR-43F2 for 25 °C and ETTAS E0450B for 40 to 90 °C). The sample tubes were shaken by a shaker equipped with the temperature chamber during the aging at 25 °C, and shaken by hand occasionally for a few minutes during the aging at 40 to 90 °C.
3. Results and discussion

3.1. Solid phases after aging at 25 and 90 °C

3.1.1. La solid phases after aging at 25 and 90 °C. Figure 1 shows the XRD patterns for La solid phases after aging of the sample solutions at 25 and 90 °C, in the neutral to alkaline pH region for 4 weeks. The XRD pattern of La₂O₃(cr) was measured at its initial state and shown in Fig. 1 for comparison. After aging the sample solutions under the above-mentioned conditions, the XRD patterns showed that, the peaks corresponding to the initial La₂O₃(cr) showing the hexagonal antiprismatic structure disappeared, whereas those corresponding to La(OH)₃(cr) as the UCl₃-type structure (trigonal prismatic) (ICSD No. 31584) appeared. This indicates that the initial La₂O₃(s) transformed to La(OH)₃(cr), by aging of the sample solutions at 25 and 90 °C for 4 weeks. It was in fact noted from the XRD patterns, that the transformation of La₂O₃(cr) to La(OH)₃(cr) already took place after aging at 25 and 90 °C for 1 week, suggesting that the solid phase transformation has rather fast kinetics under the investigative experimental conditions. This confirms that the solid phase of La₂O₃(cr) is unstable and it transforms to La(OH)₃(cr) in aqueous solutions, as has been pointed out in previous literature, where La₂O₃(cr) was dissolved in a heated nitrate solution [31]. Similar transformation was observed for Nd₂O₃(cr), where Nd₂O₃(cr) converted to Nd(OH)₃(cr) after aging in pure water at 25 °C for 3 months [32]. It can also be observed from Fig. 1, that there is no significant difference between the XRD patterns of the La solid phases, aged at different pHc conditions and aging temperatures.

3.1.2. Eu solid phases after aging at 25 and 90 °C. In Fig. 2, the XRD patterns of Eu solid phases, derived after aging of the sample solutions at 25 and 90 °C in neutral to alkaline pH region for 4 weeks, were compared with those of the initial state of Eu₂O₃(cr) which exhibited cubic structure (ICSD No. 27997). After aging at 25 °C, the XRD patterns corresponded to that of the initial Eu₂O₃(cr) solid phase, indicating that no phase transformation occurred at 25 °C. On the other hand, after aging at 90 °C, the peak positions of the samples changed, and were identified as those of Eu(OH)₃(cr), that had UCl₃-type structure (ICSD No. 200488). This suggests that Eu₂O₃(cr) transformed to Eu(OH)₃(cr) during the aging at 90 °C, whereas no solid phase transformation occurred at 25 °C. It is further noted, that the solid phase transformation from Eu₂O₃(cr) to Eu(OH)₃(cr) at 90 °C in fact occurs after aging for just 1 week. This difference in trend between the solid phase transformations for Eu₂O₃(cr) and La₂O₃(cr), Nd₂O₃(cr), may be related to the difference in their crystal structures; La₂O₃(cr) and Nd₂O₃(cr) have the hexagonal phase, whereas Eu₂O₃(cr) has the cubic phase.

3.1.3. Tm solid phases after aging at 25 and 90 °C. In Fig. 3, the XRD patterns of Tm solid phases, after aging at 25 and 90 °C in the neutral to alkaline pH region for 4 weeks, were presented together with that of the initial Tm₂O₃(cr) solid phase exhibiting cubic structure. The XRD patterns did not change after aging at both temperatures and remained stable as the initial Tm₂O₃(cr) (ICSD No. 33657). The same peak patterns were obtained for samples aged at 25 °C and 90 °C for 1 week.

The results of the solid phase analysis are summarized in Table 1, together with the aging temperature conditions.

3.2. Solubilities measured at 25 °C after aging at 25 to 90 °C

3.2.1. La Solubilities measured at 25 °C after aging at 25 to 90 °C. The XRD patterns of the La solid phase indicated that the initial La₂O₃(cr) converted to La(OH)₃(cr) after aging of its sample solutions, at 25 and 90 °C for more than 1 week. As described above, the reported values of $\Delta H_f^\circ = -1791.6 \pm 2.0$ kJ/mol and $S_2^\circ = 127.32 \pm 0.84$ J/K/mol for La₂O₃(cr) [29] resulted in $\Delta G_f^\circ = -192.33$ kJ/mol, and log $K^\circ = 33.70$ at 25 °C for 1/2 La₂O₃(cr) + 3H²⁺ + 3H₂O combined with the $\Delta H_f^\circ$ and $S_2^\circ$ for La²⁺ and H₂O [2,4]. Larger log $K^\circ$ value for La₂O₃(cr) possibly leads the transformation of initial La₂O₃(cr)
to La(OH)$_3$(cr) in the present study. Figure 4 shows the solubility of La(OH)$_3$(cr) measured at $T_{\text{meas}} = 25$ °C after aging at $T_{\text{age}} = 25, 40, 50, 60$ and 90 °C for 8 to 12 weeks. Since no significant change in the solubility values was observed after different aging periods, it was considered that the solubility reached a steady state after 8 weeks. It is noted that after aging at 60 °C, the sample solutions kept at 25 °C for longer days prior to the solubility measurement at 25 °C. No significant change was observed between different periods at 25 °C, also suggesting that a steady state has been achieved at 25 °C after the solid phase transformation at 60 °C. After aging at 25 °C, the La solubility at around pHc 7, was observed to be near 2 × 10$^{-1}$ M, which corresponded to the total dissolution of the added La$_2$O$_3$(cr) in the initial solid phase. The solubility then rapidly decreased with increasing pH, and was almost constant at 10$^{-9}$ M above pHc 10, which is close to the detection limit of ICP-MS. After aging at $T_{\text{age}} = 40, 50$, and 60 °C, the solubility values measured at 25 °C were observed to be similar to those aged at 25 °C, suggesting that no significant effect of the $T_{\text{age}}$ on the La(OH)$_3$(cr) solid phases below $T_{\text{age}} = 60$ °C, as summarized in Table 1.

On the other hand, after aging at $T_{\text{age}} = 90$ °C, the obtained solubility values at pH 8−9 measured at $T_{\text{meas}} = 25$ °C were found to be lower by about 2 orders of magnitude than those obtained after aging at 25 to 60 °C. As seen in Fig. 1, the XRD patterns of the La(OH)$_3$(cr) solid phase after aging at 90 °C, were similar to those obtained after aging at 25 °C. This indicated that there is no significant difference between the bulk structures of the solid phases aged at both temperatures. However, here we assumed a different solubility-limit-

![Figure 3](image3.png)

**Figure 3.** XRD patterns of the Tm solid phases after aging for 4 weeks at pHc 7.30, 7.88, and 12.52 at 25 °C and pHc 7.53, 8.05, and 12.52 at 90 °C, together with that of Tm$_2$O$_3$(cr) as the initial solid phase. Filled circles (●) represent the peaks from ICSD pattern of Tm$_2$O$_3$ (No. 33657).

![Figure 4](image4.png)

**Figure 4.** La solubilities measured at $T_{\text{meas}} = 25$ °C after aging at $T_{\text{age}} = 25, 40, 50, 60$, and 90 °C for 8 and 12 weeks. The ionic strength was maintained at $I = 0.1$ M, and the solubilities were obtained after filtration through 3 kDa membranes. The solid lines with blue and red colors represent the calculated solubility of La(OH)$_3$(cr) and La(OH)$_3$(cr,90), respectively. The broken lines with blue and red colors represent the contributions of La$^{3+}$ and first hydrolysis species; LaOH$^+$. A gray field in the figure indicated the detection limit level of the ICP-MS.

### Table 1: Summary of the solid phases investigated in the present study

| Aging Temp, $T_{\text{age}}$ | Measurement temp, $T_{\text{meas}}$ |
|-----------------------------|----------------------------------|
|                             | 25 °C                             |
|                             | La(OH)$_3$(cr)$^a$                |
|                             | Eu$_2$O$_3$(cr)$^a$               |
|                             | Tm$_2$O$_3$(cr)$^a$               |
| 40 °C                       | La(OH)$_3$(cr)$^b$                |
|                             | Eu$_2$O$_3$(cr)$^b$               |
|                             | Tm$_2$O$_3$(cr)$^b$               |
| 50 °C                       | La(OH)$_3$(cr)$^b$                |
|                             | Eu$_2$O$_3$(cr)$^b$               |
|                             | Tm$_2$O$_3$(cr)$^b$               |
| 60 °C                       | La(OH)$_3$(cr)$^b$                |
|                             | Eu$_2$O$_3$(cr)$^b$               |
|                             | Tm$_2$O$_3$(cr)$^b$               |
| 90 °C                       | La(OH)$_3$(cr, 90 °C)$^a$         |
|                             | Eu(OH)$_3$(cr)$^a$                |
|                             | Tm$_2$O$_3$(cr)$^a$               |

a) The solid phase was confirmed by the XRD patterns.
b) The solid phase was assumed from the observed solubilities.
The solubility of Eu(OH)₃(s) has been investigated in several literatures [4, 15, 16, 18, 24, 25, 39-42]. Akselrud and Ermolenko [18] observed starting points of precipitation by adding NaOH solutions to Eu solution in certain concentrations. The pH of these sample solutions starting to precipitate was measured several times for up to 150 days, to determine the solubility product values [18]. Moeller et al. also investigated the solubility limit of Eu(OH)₃(s) by measuring the starting points of precipitations [15, 16]. The Eu concentrations against pH of starting points for precipitation after 50 days [18] were plotted in Fig. 5 for comparison. Although the pH range of the present study and the literature do not overlap, the estimated trends from the measured solubility values of Eu(OH)₃(s) seem to be in agreement with those seen in previous studies.

3.2.3. Tm solubilities measured at 25 °C after aging at 25 to 90 °C. The XRD patterns of the Tm solid phases after aging at 25 and 90 °C suggested that the solid phases remained Tm₂O₃(cr) during the investigated periods. The reported values of ΔH°ₘₜ = −1889.3±5.7 kJ/mol and S°ₘₜ = 139.7±0.4 J/K·mol for Tm₂O₃(cr) [29] resulted in ΔrG°ₘₜ = −129.39 kJ/mol, hence log K°ₘₜ = 22.67 for 1/2 Tm₂O₃(cr) + 3H²⁺ = Tm³⁺ + 3/2 H₂O, combined with the ΔH°ₘₜ and S°ₘₜ for Tm(OH)₃ and H₂O [2,4]. Although the calculated K°ₘₜ value was less than those for Eu₂O₃(cr) and La₂O₃(cr), the value was found to be still orders of magnitude larger than those of reported log K°₁/₂ for Tm(OH)₃(cr) [4]. However, similarly to the case of Eu₂O₃(cr), the solid phase transformation was thought to be kinetically hindered under the experimental condition in the present study. In Fig. 6, the Tm solubilities measured at Tₘₜ = 25 °C after aging at Tₐge = 25, 40, 50, 60, and 90 °C up to 8 weeks were plotted. No significant difference was observed after aging different aging temperatures, indicating that the initial
Tm$_2$O$_3$(cr) was stable up to \( T_{\text{age}} = 90 \) °C. The solubility of Tm$_2$O$_3$(cr) measured at 25 °C was approximately 10\(^{-5}\) M at pHc 7, after which it gradually decreased with an increase in pHc. In the region where pHc > 10, solubility plots were observed close to 10\(^{-9}\) M of the detection limit.

In literature, only one study has reported the experimental solubility data for Tm(OH)$_3$(s) [15]. Moeller and Kremers [15] measured the starting point for precipitation by adding NaOH to Tm solutions, and assumed that the precipitate was Tm(OH)$_3$(s). On the other hand, the solubility experiment in the present study started from Tm$_2$O$_3$(cr), by adding Tm$_2$O$_3$(cr) into the sample solutions as an initial solid phase. Further discussions on this are given in the following sections.

### 3.3. Solubilities measured at 25 to 60 °C

After aging the La, Eu, and Tm sample solutions at \( T_{\text{age}} = 25, 40, 50, \) and 60 °C for 4 to 12 weeks, their solubilities were investigated under different measurement temperature (\( T_{\text{meas}} \)) conditions at 25, 40, 50, and 60 °C (See Table 1). As described above, the sample tubes after aging at a certain temperature were kept in thermostatted baths at 25, 40, 50, and 60 °C for 1 day, then pHc was measured and the supernatant of the sample solutions were ultrafiltrated at a fixed \( T_{\text{meas}} \) condition. The obtained La, Eu, and Tm solubilities are presented in Fig. 7. Contrary to the effect of aging temperature, the La, Eu, and Tm solubilities decreased with increasing \( T_{\text{meas}} \) at the same pH conditions. In Fig. 7(a), the solubilities of La(OH)$_3$(s) measured at 40, 60, 90, and 150 °C by Deberdt et al. [23] were plotted for comparison. The solubility values in the present study were in agreement with the reported results at the same \( T_{\text{meas}} \) condition. Since no significant difference by the aging temperatures up to 60 °C.
was observed for each element, we assumed that the solid phases in Fig. 7 were La(OH)₃(cr), Eu₂O₃(cr), and Tm₂O₃(cr), regardless of the aging temperatures. The solubilities at each T meas are analyzed to determine the K° values at respective temperatures, to discuss their temperature dependences in the following section.

### 3.4. Thermodynamic analysis of the solubility data.

#### 3.4.1. Thermodynamic model for the solubility of Ln₂O₃(cr) and Ln(OH)₃(cr).
In the systems for La, Eu, and Tm solubilities in neutral to alkaline pH region after aging at T meas = 25 to 90 °C, oxide (Ln₂O₃(cr)) or hydroxide (Ln(OH)₃(cr)) (Ln = La, Eu, Tm) solid phases were observed depending on the elements and aging temperatures. The dissolution and precipitation reactions of Ln₂O₃(cr) and Ln(OH)₃(cr) can be described respectively by the following equations:

\[
\frac{1}{2} \text{Ln}_2\text{O}_3(\text{cr}) + 3\text{H}^+ \rightleftharpoons \text{Ln}^{3+} + \frac{3}{2} \text{H}_2\text{O} \tag{1}
\]

\[
K_s(\text{Ln}_2\text{O}_3(\text{cr})) = \frac{[\text{Ln}^{3+}][\text{H}^+]^3}{[\text{H}_2\text{O}]} \tag{2}
\]

\[
\text{Ln(OH)}_3(\text{cr}) + 3\text{H}^+ \rightleftharpoons \text{Ln}^{3+} + 3\text{H}_2\text{O} \tag{3}
\]

\[
K_s(\text{Ln(OH)}_3(\text{cr})) = \frac{[\text{Ln}^{3+}][\text{H}^+]^3}{[\text{H}_2\text{O}]} \tag{4}
\]

where \(K_s(\text{Ln}_2\text{O}_3(\text{cr}))\) and \(K_s(\text{Ln(OH)}_3(\text{cr}))\) represent the solubility products of Ln₂O₃(cr) and Ln(OH)₃(cr), respectively.

In the aqueous phase, the hydrolysis reactions and the hydrolysis constants (βₙ; n = 1–3) were given as follows:

\[
\text{Ln}^{3+} + n\text{H}_2\text{O} \rightleftharpoons \text{Ln(OH)}_{n\text{–}3}^{3\text{–}n\text{+}+} + n\text{H}^+ \tag{5}
\]

\[
\beta_n = \frac{[\text{Ln(OH)}_{n\text{–}3}^{3\text{–}n\text{+}+}][\text{H}^+]^n}{[\text{Ln}^{3+}]} \tag{6}
\]

The solubility as a total Ln concentration ([Ln] tot) can be described as:

\[
[\text{Ln}]_{\text{tot}} = [\text{Ln}^{3+}] + [\text{Ln(OH)}_{3\text{–}n\text{+}+}] + [\text{Ln(OH)}_{3\text{–}n\text{+}+}][\text{H}^+]^n
\]

\[
= [\text{Ln}^{3+}] + [\beta_3[\text{H}^+]^3 + \beta_2[\text{H}^+]^2 + \beta_1[\text{H}^+] + \beta] \tag{7}
\]

According to the specific ion interaction theory (SIT) method, the solubility product (\(K_s\)) and hydrolysis constants (\(\beta_n\)) can be corrected to I = 0 by the following equations;

\[
\log K_s = \log K_s^\circ + 6D - J_{\text{meas}} \left[ \varepsilon(\text{Ln}^{3+}, \text{ClO}_4^-) - 3\varepsilon(\text{H}^+, \text{ClO}_4^-) \right] \tag{8}
\]

\[
\log \beta_n = \log \beta_n^\circ + \left[ (3-n)\varepsilon-n \right] + m \log a_{\text{H}_2\text{O}} - I_{\text{meas}} \left[ \varepsilon(\text{Ln(OH)}_{3\text{–}n\text{+}+}, \text{ClO}_4^-) + n\varepsilon(\text{H}^+, \text{ClO}_4^-) - \varepsilon(\text{Ln}^{3+}, \text{ClO}_4^-) \right] \tag{9}
\]

where \(K_s^\circ, \beta_n^\circ, D, I_{\text{meas}}, a_{\text{H}_2\text{O}}, m\) and \(D\) are the solubility product, hydrolysis constant at I = 0, the ionic strength, activity of water, and the Debye-Hückel term at 25 °C, respectively. \(\varepsilon(\text{Ln(OH)}_{3\text{–}n\text{+}+}, \text{ClO}_4^-), \varepsilon(\text{Ln}^{3+}, \text{ClO}_4^-), \) and \(\varepsilon(\text{H}^+, \text{ClO}_4^-)\) represent ion interaction coefficients for each species.

Based on the integrated van’t Hoff equation, the \(K_s\) and \(\beta_n\) can be expressed as a function of \(T_{\text{meas}}\):

\[
\log K_s(T_{\text{meas}}) = \log K_s(T_0) + \frac{\Delta H_s(\text{Ln}_2\text{O}_3(\text{cr}) \text{ or Ln(OH)}_3(\text{cr}))}{R \ln 10} \left[ \frac{1}{T_0} - \frac{1}{T_{\text{meas}}} \right] \tag{10}
\]

\[
\log \beta_n(T_{\text{meas}}) = \log \beta_n(T_0) + \frac{\Delta H_s(\text{Ln(OH)}_{3\text{–}n\text{+}+})}{R \ln 10} \left[ \frac{1}{T_0} - \frac{1}{T_{\text{meas}}} \right] \tag{11}
\]

where \(R\) and \(T_0\) are the universal gas constant, and 298 K (25 °C), respectively.

#### 3.4.2. Solubility product of Ln₂O₃(cr) and Ln(OH)₃(cr) at \(T_{\text{meas}} = 25\) to 60 °C.
The solubility data for La, Eu, and Tm in 0.1 M NaClO₄ solution at T meas = 25 to 60 °C were analyzed based on Eq. (7) with a combination of the ionic strength correction by SIT shown in Eqs. (8) and (9) to determine the solubility product of Ln₂O₃(cr) or Ln(OH)₃(cr) at respective T meas. Since the solubility values at pH > 10 were close to the detection limit of ICP-MS, the solubility data used in the analysis were limited at pH < 10. Therefore, only Ln³⁺ and first hydrolysis species of LnOH²⁻ in Eq. (7) was taken into account in the analysis. It is noted that the ion interaction coefficient values were fixed as \(\varepsilon(\text{Ln(OH)}_{3\text{–}n\text{+}+}, \text{ClO}_4^-) = 0.39\) and \(\varepsilon(\text{Ln}^{3+}, \text{ClO}_4^-) = 0.47\) [4] for La, Eu, and Tm, and \(\varepsilon(\text{H}^+, \text{ClO}_4^-) = 0.14\) [2]. These values were assumed constant against T meas due to the lacking data on their temperature dependence, while the D value was corrected based on the temperature correction in [2]. No polynuclear species was taken into account in the analysis of the solubility data. The sample solutions were prepared by an undersaturation method, and the measured solubility values were mostly limited to lower than 10⁻⁴ M, where contribution of polynuclear species was considered to be negligible.

In the present analysis, the \(\beta_1\) value was treated as a fixed parameter. The \(\beta_1\) values for lanthanide elements have been reported in many literatures [22,38,39,43-52] and summarized in [4, 25-28]. Although some scatterings were found in the literatures, the reported or re-calculated \(\beta_1\) values for 25 °C at I = 0 were relatively in good agreement and Brown and Ekberg [4] have selected the recommended \(\beta_1\) values for the lanthanide series. Hence, the \(\beta_1\) value at 25 °C was taken from [4] and used as a fixed parameter in the present analysis. Several literatures have also investigated the \(\beta_1\) value at different temperatures [47, 49, 50]. For example, Klungness and Byrne [50] determined the \(\beta_1\) values for yttrium and rare earth elements in a combination of potentiometric and spectroscopic experiments at 25 to 55 °C. The log \(\beta_1\) value for La³⁺ + H₂O ⇌ LaOH²⁺ + H⁺ increased with an increase of temperature and the enthalpy value was obtained based on the analysis using the van’t Hoff equation for lighter to heavier lanthanide elements [50]. In the present analysis, the \(\beta_1\) values for La, Eu, and Tm at 40, 50, and 60 °C were calculated from the enthalpy values reported in [50] and used as fixed parameters after the ionic strength correction.

The K₁(La(OH)(3)(cr)), K₁(Eu₂O₃(cr)), and K₁(Tm₂O₃(cr)) at T meas = 25, 40, 50, and 60 °C were determined by the least square fitting analysis of the solubility data by treating the \(\beta_1\) values as fixed parameters. The obtained values are summarized in Table 2 and the calculated solubility curves based on the values in Table 2 are shown in Figs. 4-7. The K₁(La(OH)(3)(cr)), K₁(Eu₂O₃(cr)), and K₁(Tm₂O₃(cr)) at T meas = 25, 40, 50, and 60 °C were plotted as a function of the inverse of absolute temperature in Fig. 8, together with the literature values. For La(OH)₃(cr) aged at 25 to 60 °C, the log K₁ value
TABLE 2: Solubility products and hydrolysis constants \( (I=0, \ T_{\text{meas}} = 25 \text{ to } 60 \degree \text{C}) \) for La, Eu, and Tm hydroxides and oxides obtained and used in the present study

| \( T_{\text{age}} \)  | \( T_{\text{meas}} \) | \( \log K_{\text{so}} \) | \( \log \beta_1^{\circ} \) | \( T_{\text{age}} \)  | \( T_{\text{meas}} \) | \( \log K_{\text{so}} \) | \( \log \beta_1^{\circ} \) |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 25~60 °C       | 25 °C          | 19.0±0.2       | −8.89          | 25~60 °C       | 25 °C          | 18.4±0.2       | −7.66          |
| 40~60 °C       | 40 °C          | 18.3±0.3       | −8.54          | 40~60 °C       | 40 °C          | 16.4±0.2       | −6.78          |
| 50~60 °C       | 50 °C          | 16.7±0.3       | −8.34          | 50~60 °C       | 50 °C          | 14.8±0.4       | −6.45          |
| 60 °C          | 60 °C          | 17.0±1.1       | −8.11          | 60 °C          | 60 °C          | 15.5±0.4       | −6.10          |

a) The hydrolysis constants for La, Eu, and Tm at 25 °C were taken from [4]. The values at 40 to 60 °C were calculated from the temperature dependence of the hydrolysis constants observed in [50] using the van’t Hoff equation.

Figure 8. Solubility product values of (a) La(OH)\(_3\)(cr), (b) Eu\(_2\)O\(_3\)(cr), Eu(OH)\(_3\)(cr), and (c) Tm\(_2\)O\(_3\)(cr) as a function of the inverse of measurement temperature. The broken lines in the figures represent the fitted lines in this work based on the integrated van’t Hoff equation.
terns, surface conditions of the solid phases controlling the solubility may be dependent on the aging temperature. Further studies are needed to clarify the effect arising from the bulk and surface condition of the solid phases.

The obtained log $K_r^p$ values for La(OH)$_3$(cr) at $T_{\text{meas}} = 25$ to 60 °C are plotted in Fig. 8(a). The log $K_r^p$ value linearly increased with decreasing $T_{\text{meas}}$, and the $\Delta H_m$(La(OH)$_3$(cr)) was determined to be −149.5±22.5 kJ/mol from the obtained slope based on the integrated van’t Hoff equation of Eq. (10). A few literature studies investigated the solubility of La(OH)$_3$(s) at different $T_{\text{meas}}$ from 25 °C [23, 38, 39]. Deberdt et al. [23] measured the solubility of La(OH)$_3$(s) at 40, 60, and 150 °C as shown in Fig. 7 and determined the log $K_r^p$ values at respective temperatures. The log $K_r^p$ values at the same $T_{\text{meas}}$ in both studies were found to be in an agreement as shown in Fig. 8(a). A slight difference may arise from a difference in the analysis of the solubility data. The first hydrolysis species, LaOH$^-$, was taken into consideration in the present study, while the species not included in the analysis in [23]. The slope of log $K_r^p$ against the $1/T_{\text{meas}}$ and reported $\Delta H_m$(La(OH)$_3$(cr)) = −134.570 kJ/mol [23] matched to those obtained in the present study within the measurement error. It is noted that the $\Delta H_m$(Ln(OH)$_3$(cr)) values for several lanthanide elements were determined by solution calorimetry [53, 54]. The $\Delta H_m$(La(OH)$_3$(cr)) = −150.2 kJ/mol [53] also agreed well with the obtained value in the present study. These results clearly indicate that the initial La$_2$O$_3$(cr) transformed to La(OH)$_3$(cr) at 25 °C, and control the La solubility as the solubility-limiting solid phase.

For Eu, as suggested by the XRDS patterns and the solubility data, the solid phase after aging at 25 to 60 °C was considered to be Eu$_2$O$_3$(cr), while the solid phase after aging at 90 °C was Eu(OH)$_3$(cr). The solubility products at $T_{\text{meas}} = 25$ °C were determined to be log $K_r^p$ = 18.4±0.2 for Eu$_2$O$_3$(cr), and log $K_r^p$ = 17.2±0.3 for Eu(OH)$_3$(cr). In literatures, a number of log $K_r^p$ for Eu(OH)$_3$(cr) has been reported [15, 16, 18, 25, 39–42], while no log $K_r^p$ value for Eu$_2$O$_3$(cr). The obtained log $K_r^p$ for Eu(OH)$_3$(cr) in the present study was slightly higher than the reported values and the selected one of log $K_r^p$ = 16.48±0.30 in [4].

In Fig. 8(b), the obtained log $K_r^p$ values for Eu$_2$O$_3$(cr) at $T_{\text{meas}}$ = 25 to 60 °C are plotted as a function the inverse of $T_{\text{meas}}$. The log $K_r^p$ value increased with decreasing $T_{\text{meas}}$, and the $\Delta H_m$(Eu$_2$O$_3$(cr)) was determined to be −202.8±20.1 kJ/mol from the its slope. The $\Delta H_m$(Eu$_2$O$_3$(cr)) and $\Delta H_m$(Eu(OH)$_3$(cr)) has been reported to be −209.145 kJ/mol and −143.99 kJ/mol determined by solution calorimetry of respective solid phases as summarized in [4, 25, 29]. Although the obtained $\Delta H_m$(Eu$_2$O$_3$(cr)) in the present study much relied on the log $K_r^p$ value at each $T_{\text{meas}}$, it is interesting that the obtained value was closer to that reported value for Eu$_2$O$_3$(cr). This may suggest that Eu$_2$O$_3$(cr) remained stable at 25 °C, and control the Eu solubility as the solubility-limiting solid phase, in contrast to the case of La.

For Tm, the solid phase was considered to be Tm$_2$O$_3$(cr), regardless of the aging temperature up to 90 °C. The solubility product at $T_{\text{meas}} = 25$ °C was determined to be log $K_r^p$ = 16.9±0.2. In literatures, only Moeller et al. performed the Tm solubility experiment and reported the solubility product of log $K_r^p$ = 16.0 [15] for fresh Tm(OH)$_3$(s) solid phase. The log $K_r^p$ = 16.8 was calculated from the $\Delta H_m$ and $S_r^\circ$ for Tm(OH)$_3$(s) [25, 26] was rather close to the value obtained in the present study for Tm$_2$O$_3$(cr). In Fig. 8(c), the obtained log $K_r^p$ values for Tm$_2$O$_3$(cr) at $T_{\text{meas}} = 25$ to 60 °C are plotted as a function the inverse of $T_{\text{meas}}$. The $\Delta H_m$(Tm$_2$O$_3$(cr)) was determined to be −176.2±15.7 kJ/mol from the slope using Eq. (10). The $\Delta H_m$(Tm$_2$O$_3$(cr)) and $\Delta H_m$(Tm(OH)$_3$(cr)) has been reported to be −189.295 kJ/mol and −141.59 kJ/mol determined by solution calorimetry of respective solid phases [4, 25, 29]. Similarly to the case of Eu, the obtained $\Delta H_m$(Tm$_2$O$_3$(cr)) value was also in agreement with the reported value for Tm$_2$O$_3$(cr), suggesting that Tm$_2$O$_3$(cr) remained stable at 25 °C to control the Tm solubility as the solubility-limiting solid phase.

### 4. Conclusion

Solubility and solubility limiting solid phase of La, Eu and Tm were investigated in the solutions of pH 6 to 12 after aging at $t_{\text{age}} = 25$ to 90 °C. Then, the La, Eu, and Tm solubilities were measured at $T_{\text{meas}} = 25$ to 60 °C to examine the temperature dependence of the solubility products ($K_r^p$). The XRDS patterns, the solubility values, and subsequently obtained the enthalpy of the reaction from the temperature dependence of log $K_r^p$ suggested that La$_2$O$_3$(cr) transformed to La(OH)$_3$(cr) to control the La solubility. In the case of Eu, on the other hand, the XRDS patterns showed that Eu$_2$O$_3$(cr) transformed to Eu(OH)$_3$(cr) only after the aging at 90 °C, whereas no solid phase transformation was observed at 25 °C. The solubility values and the enthalpy of the reaction suggested that Eu$_2$O$_3$(cr) remained stable at 25 °C to control the Eu solubility. For Tm, the XRDS patterns, solubility values and the enthalpy of the reaction indicated that the Tm$_2$O$_3$(cr) was stable up to $T_{\text{meas}} = 90$ °C. From lighter to heavier lanthanides (Ln), the oxides of Ln$_2$O$_3$(cr) was considered to become more stable comparing to the hydroxides of Ln(OH)$_3$(cr) and play as the solubility-limiting solid phase in the Ln-OH aqueous systems. It is note that the present study focused on the steady state of the solubility reaction after aging at certain temperatures and periods and revealed the solubility-limiting solid phase and their thermodynamic data. The reaction kinetics of solid phase transformation needs further investigations.

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