Constitution of Stable and Metastable Phase Diagrams for TmFeO$_3$-ScFeO$_3$ System by Undercooling Solidification Using the Containerless Technique$^{*1}$

Junya Takasaki$^{1,*2}$, Kazuhiko Kuribayashi$^2$ and Shumpei Ozawa$^3$

$^1$Graduate School of Engineering, Chiba Institute of Technology, Narashino 275–0016, Japan
$^2$Research Liaison Centre, Chiba Institute of Technology, Narashino 275–0016, Japan
$^3$Department of Advanced Materials Science and Engineering, Chiba Institute of Technology, Narashino 275–0016, Japan

Spherical samples of Tm$_{1-x}$Sc$_x$FeO$_3$ were solidified from the undercooled melt under the containerless state using an aerodynamic levitation (ADL) furnace. The change of solidification behavior from double recalescence to single recalescence and powder X-ray diffraction (XRD) analysis of as-solidified samples revealed that metastable hexagonal LnFeO$_3$ ($h$-LnFeO$_3$) stabilizes with increasing of mole fraction of Sc. The reason for this stabilization was ascribed to the decrease of the difference in the liquidus temperatures of stable orthorhombic LnFeO$_3$ ($o$-LnFeO$_3$) and metastable $h$-LnFeO$_3$ phases. Annealing the as-solidified samples at 1473 K for 1 hour resulted in the two-phase coexistent states of of $o$–LnFeO$_3$ and garnet ($c$-A$_3$B$_5$O$_{12}$) at $0 < x < 0.3$, $c$-A$_3$B$_5$O$_{12}$ and $h$-LnFeO$_3$ at $0.3 < x < 0.5$ and $h$-LnFeO$_3$ and $c$-ScFeO$_3$ at $0.5 < x < 1.0$. Based on these results, we proposed the phase diagram between TmFeO$_3$ and ScFeO$_3$. [doi:10.2320/matertrans.M2017359]

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1. Introduction

Hexagonal LnFeO$_3$ ($h$-LnFeO$_3$, Ln: Eu–Lu) is attracting attention as a multi-ferroic material having both ferroelectric and (anti) ferromagnetic properties. However, the production method of a bulk sample is restricted to rapid solidification into undercooled melt since $h$-LnFeO$_3$ is a metastable phase. In fact, it is reported that $h$-LnFeO$_3$ is formed from the undercooled melt by a containerless solidification method. However, when other lanthanide ions, the ionic radii of which are larger than that of Lu$^{3+}$, are used, $h$-LnFeO$_3$ is rarely formed. The reason for this rarity is due to the melting temperature of the orthorhombic LnFeO$_3$ phase ($o$-LnFeO$_3$) except LuFeO$_3$ being much higher than that of the $h$-LnFeO$_3$ phase. That is, the degree of undercooling for $o$-LnFeO$_3$ is much larger than that for $h$-LnFeO$_3$. For this reason, even if the metastable $h$-LnFeO$_3$ phase is formed initially, $o$-LnFeO$_3$ that is nucleated heterogeneously on the interface between $h$-LnFeO$_3$ and the residual melt is crystallized with re-melting the $h$-LnFeO$_3$ phase. Therefore, in order to obtain the $h$-LnFeO$_3$ phase from the undercooled melt by using the containerless solidification method, it is indispensable for $h$-LnFeO$_3$ to be thermodynamically stabilized. Regarding the stability of $h$-LnFeO$_3$, Masuno et al.$^5$ recently reported that substituting a part of Lu$^{3+}$ by Sc$^{3+}$ stabilizes $h$-LnFeO$_3$. This result suggests that decreasing the apparent ionic radius of Ln$^{3+}$ stabilizes the $h$-LnFeO$_3$ phase. However, it was also reported that substituting Ln$^{3+}$ by Sc$^{3+}$ facilitates other phases such as garnet and bixbyite to be formed.$^5$ Therefore, to optimize the chemical composition at which $h$-LnFeO$_3$ may be stabilized, it is required to establish the stable and the metastable phase-diagrams between LnFeO$_3$ and ScFeO$_3$.

In the present investigation, using TmFeO$_3$ as a model material, in which typical double recalescence is observed and therefore $h$-LnFeO$_3$ is never frozen, we aimed to elucidate the influence of Sc substitution on the stabilization of $h$-LnFeO$_3$.

2. Experimental Procedure

The mixed powder of high purity (99.9%) Tm$_2$O$_3$, Sc$_2$O$_3$ and Fe$_2$O$_3$ that were weighed to be Tm$_{1-x}$Sc$_x$FeO$_3$ of approximately 100 mg were melted on a water-cooled copper hearth using a LD power-laser. Then, pulverizing the solidified ingot we melted and again solidified the powdered ingot on a water-cooled copper hearth into spherical samples, the diameter and mass of which are approximately 2 mm and 20 mg, respectively. These samples were processed by using an aero-dynamic levitation (ADL) furnace. As a levitating gas, high-purity oxygen was used. The temperature of the sample was monitored by a pyrometer, the measured wavelength and the sampling rate of which are 0.8–1.6 μm and 1 millisecond, respectively. The emissivity of samples was assumed to be 1.0, on the basis of the black-body approximation. The sample, after being completely melted, was solidified in a containerless state. A high-speed video (HSV, FASTCAM MC-MP, Photron) with a sampling rate of 2000 frames/s was used to record solidification process and surface conditions.

After grinding the solidified samples into 10 μm$^3$ pieces, we investigated the crystal structure via X-ray diffraction (XRD, MiniFlex 600, Rigaku) using the CoK$_{α}$ line. The cross-sectional microstructure of the sample was observed using a scanning electron microscope (SEM, JSM-6010LA, JEOL). Furthermore, in order to investigate the thermal stability of the phase, we carried out annealing treatment for 1 hr at 1473 K in an electric furnace. The present investigation also aims to elucidate the relation among the stable phase, the metastable phase and their liquidus temperature. In achieving this aim, the post-recalescence technique is indispensable for stable and metastable phase diagrams of LnFeO$_3$. Further, the use of ADL furnace is indispensable for rare earth compounds. In the present investigation, the as-solidified samples were annealed at 1473 K for 1 hour. We investigated the phase diagram between TmFeO$_3$ and ScFeO$_3$.
ence temperature, $T_{Pr}$, is assumed to be the liquidus temperature of a related phase (Fig. 1(a)). In the case when this assumption is applied to the sample showing double recalescence, the spot-size (1 mm$^2$) of the pyrometer is too large to evaluate $T_{Pr}$ of the phase formed at the first recalescence (Fig. 1(b)). Therefore, based on the measured relation between the luminance and temperature at the liquid state, we regarded $T_{Lum}$, which is the temperature evaluated from the luminescence of the area corresponding the first recalescence, as the liquidus temperature of the metastable phase (Fig. 1(c)).

3. Experimental Results

3.1 As-solidified sample

Figure 2 shows a sequence of HSV images taken during recalescences in samples of (a) $x = 0.2$, (b) $x = 0.3$ and (c) $x = 0.5$, which are selected as typical examples showing characteristic surface patterns: That is, (a) Similar to YFeO$_3$ that was solidified from undercooled melt, a phase with higher luminance was formed subsequent to discoidal crystals, showing double recalescence; (b) The recalescence was single although discoidal crystals were formed in a similar process to (a); (c) The surface pattern changed to a spherical pattern, indicating the primary phase changed to a bixbyite-type crystal ($c$-ScFeO$_3$). Figure 3 shows the XRD
pattern of as-solidified samples. In the sample of $0 \leq x \leq 0.2$, in which double recalescence was observed, the XRD pattern showed the peak profile of only $o$-LnFeO$_3$. In the sample of $0.3 \leq x \leq 0.4$, on the other hand, double recalescence was not confirmed, and the peak profile showed only $h$-LnFeO$_3$ was formed. These results suggest that increasing the $x$ value up to 0.3 stabilizes the $h$-LnFeO$_3$ phase. For the sample of $x = 0.5$ that showed a spherical surface, $c$-ScFeO$_3$ was identified in addition to $h$-LnFeO$_3$. Increasing the $x$ value further, the peak-intensity of $h$-LnFeO$_3$ reduced and that of $c$-ScFeO$_3$ increased. In the sample of LnFeO$_3$, when $h$-LnFeO$_3$ is formed from the undercooled melt, the surface pattern shows polyhedral irrespective the number of recalescence.\(^3\) In the samples of $x \geq 0.5$, however, although the XRD pattern shows the formation of $h$-LnFeO$_3$, the surface of solidifying sample shapes was spherical. Considering that $c$-ScFeO$_3$ was confirmed in the samples of $x \geq 0.5$, the change of surface patterns suggests the primary phase changed to $c$-ScFeO$_3$ having a spherical surface from $h$-LnFeO$_3$ with polyhedral surface.

In order to clarify this point, using SEM we observed the microstructures of the as-solidified samples of $x = 0.3$ and $x = 0.5$, the surfaces of which are the polyhedral shape and spherical shape, respectively. Figure 4 shows the compositional image in backscattered electrons. In the sample of $x = 0.3$, the faceted microstructure (Fig. 4(a)) substantiates the formation of $h$-LnFeO$_3$. In the sample of $x = 0.5$, on the other hand, a dark dendritic pattern that corresponds to $c$-ScFeO$_3$ (Fig. 4(b)) verifies the primary phase changed to $c$-ScFeO$_3$.

As stated above, in the sample of $x = 0.3$, double recalescence did not occur, and the XRD pattern showed the formation of $h$-LnFeO$_3$. This is a proof for $h$-LnFeO$_3$ to be stabilized by Sc substitution.

Kuribayashi et al.\(^7\) reported that when the difference of melting temperatures between $o$-LnFeO$_3$ and $h$-LnFeO$_3$ is larger than 2%, double recalescence occurs. In fact, this criterion is satisfied in samples where Ln$^{3+}$’s other than Lu$^{3+}$ were used. According to their report, the reason for double recalescence not to occur in the sample of $0.3 \leq x \leq 0.4$ may be ascribed to the difference of liquidus temperatures between $o$-LnFeO$_3$ and $h$-LnFeO$_3$ reducing by less than 2%. Figure 5 shows $T_{Pr}$ and $T_{Lumi}$ as a function of $x$ for samples solidified from undercooled melt, indicating that increasing the $x$ value up to 0.3 stabilizes the $h$-LnFeO$_3$ by reducing the difference between $T_{Pr}$ and $T_{Lumi}$. Namely, the liquidus temperature of $o$-LnFeO$_3$, crystallized at the second recalescence, decreases with the increase of the $x$ value. On the other hand, $T_{Lumi}$, which corresponds to the liquidus temperature of the metastable $h$-LnFeO$_3$ phase, increases. As a result, in samples of $x \geq 0.2$, the difference of the liquidus temperatures between $o$-LnFeO$_3$ and $h$-LnFeO$_3$ decreases to below 2%.

3.2 Annealed samples

In order to investigate the thermal stability of the phase, as-solidified samples were annealed for 1 hr at 1473 K. Figure 6 shows the XRD pattern of the annealed samples. In
samples with \( x \) values of 0.1 and 0.2, not only \( o\text{-}LnFeO_3 \) but also the cubic garnet phase \((c\text{-}A_3B_5O_{12})\) was identified. Furthermore, in samples with \( x = 0.3 \), it was suggested that a large proportion of \( h\text{-}LnFeO_3 \) formed from the undercooled melt was transformed to \( c\text{-}A_3B_5O_{12} \) in the annealing process. Furthermore, in samples of \( 0.4 \leq x \leq 0.6 \), \( c\text{-}A_3B_5O_{12} \) coexisted with \( h\text{-}LnFeO_3 \), and in the samples of \( 0.6 \leq x \leq 0.7 \), \( c\text{-}A_3B_5O_{12} \) coexisted with not only \( h\text{-}LnFeO_3 \) but also \( c\text{-}ScFeO_3 \). On the other hand, in samples of \( 0.8 \leq x \), \( c\text{-}A_3B_5O_{12} \) was not verified and \( h\text{-}LnFeO_3 \) coexisted with \( c\text{-}ScFeO_3 \).

Summarizing these data, increasing the substituting amount of \( Sc^{3+} \), the liquidus temperature of \( o\text{-}LnFeO_3 \) falls, yet the liquidus temperature of \( h\text{-}LnFeO_3 \) rises, and, as a result, \( h\text{-}LnFeO_3 \) stabilizes. Therefore, with the increase of the \( x \) value, the phase constitution of this system changed as shown follows:

\[
o\text{-}LnFeO_3 \Rightarrow o\text{-}LnFeO_3 \Rightarrow o\text{-}LnFeO_3 + c\text{-}ScFeO_3 \Rightarrow c\text{-}ScFeO_3, \text{ in as-solidified samples.}
\]

On the other hand, the phase constituent in annealed samples is as follows:

\[
o\text{-}LnFeO_3 \Rightarrow o\text{-}LnFeO_3 + c\text{-}A_3B_5O_{12} \Rightarrow c\text{-}A_3B_5O_{12} + h\text{-}LnFeO_3 \Rightarrow h\text{-}LnFeO_3 + c\text{-}ScFeO_3 \Rightarrow c\text{-}ScFeO_3.
\]

Table 1 shows the relation between the \( x \) values and the phase constitutions for as-solidified samples and annealed samples. In the next chapter, we will consider the stable and metastable phase diagrams of the \( TmFeO_3\text{-}ScFeO_3 \) system along with the cause for \( c\text{-}A_3B_5O_{12} \) to appear.

![Fig. 5](image)

**Fig. 5** Estimated liquidus temperature of stable and metastable phase for \( Tm_{1-x}\text{-}ScFeO_3 \) samples that crystallized at the first and second recensions, in which \( T_{Lumi} \) that is the temperature estimated from the luminescence of the sample is assumed to corresponds to the liquidus temperature of the metastable phase.

![Fig. 6](image)

**Fig. 6** Powder X-ray diffraction patterns of the \( Tm_{1-x}\text{-}ScFeO_3 \) samples annealed at 1473 K for 1 hr.

### Discussion

The garnet structure that is a compact cubic structure represented by \( [A_3](C_2)(B_3)O_{12} \) consists of three 8-coordination sites \([ \] \), two 6-coordination sites \([ ] \) and three 4-coordination sites \(( \) \). If the garnet structure appears in \( Tm_{1-x}\text{-}ScFeO_3 \), it should be \( [L_{3(1-x)}\text{-}Sc_{3x}][Sc_2\text{-}Fe_2]O_{12} \) where Fe and Sc are equally coordinated in \([ \] \), since \( Fe^{3+} \) that has the smallest ionic radius is considered to occupy the 4-coordination site and \( Ln^{3+} \) that has the largest ionic radius will occupy 8-coordination site. Therefore, for the sample of \( x = 0.25 \), we predict the existence of \( [Lm_{0.75}][Sc_{0.25}Fe_{0.75}]O_{12} \) as the ideal garnet structure. In fact, the XRD pattern shows a garnet single phase in the annealed sample of \( x = 0.3 \). On the other hand, for samples of \( x < 0.25 \), the microstructure consists of \( o\text{-}LnFeO_3 \) and garnet. For example, when \( x = 0.2 \), the phase constitution of the sample is two phases of orthorhombic perovskite and garnet according to the equation:

\[
Ln_8Sc_2FeO_3=4/5Ln_{0.75}Sc_{0.25}Fe_{0.75}O_3+1/5LnFeO_3.
\]

When \( Sc^{3+} \) having an ionic radius smaller than \( Ln^{3+} \) increases, the mean ionic radius of \( Ln^{3+} \) that is partially substi-

<table>
<thead>
<tr>
<th>composition</th>
<th>phase constitution</th>
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<tbody>
<tr>
<td>( x )</td>
<td>as-solidified sample</td>
</tr>
<tr>
<td>0.0</td>
<td>( o\text{-}LnFeO_3 )</td>
</tr>
<tr>
<td>0.1</td>
<td>( o\text{-}LnFeO_3 )</td>
</tr>
<tr>
<td>0.2</td>
<td>( o\text{-}LnFeO_3 + c\text{-}A_3B_5O_{12} )</td>
</tr>
<tr>
<td>0.3</td>
<td>( h\text{-}LnFeO_3 )</td>
</tr>
<tr>
<td>0.4</td>
<td>( c\text{-}A_3B_5O_{12} )</td>
</tr>
<tr>
<td>0.5</td>
<td>( c\text{-}A_3B_5O_{12} + h\text{-}LnFeO_3 )</td>
</tr>
<tr>
<td>0.6</td>
<td>( c\text{-}ScFeO_3 + h\text{-}LnFeO_3 + c\text{-}A_3B_5O_{12} )</td>
</tr>
<tr>
<td>0.7</td>
<td>( h\text{-}LnFeO_3 + c\text{-}ScFeO_3 )</td>
</tr>
<tr>
<td>0.8</td>
<td>( h\text{-}LnFeO_3 + c\text{-}ScFeO_3 )</td>
</tr>
<tr>
<td>0.9</td>
<td>( c\text{-}ScFeO_3 )</td>
</tr>
<tr>
<td>1.0</td>
<td>( c\text{-}ScFeO_3 )</td>
</tr>
</tbody>
</table>
tuted by Sc$^{3+}$ becomes too small to fit in the 8-coordination site. Therefore, the 8-coordination site destabilizes and Ln$^{3+}$ and Sc$^{3+}$ will occupy 7-coordination sites, forming $h$-LnFeO$_3$. Further increasing the substitution by Sc$^{3+}$ also destabilizes the 7-coordination site, and Ln$^{3+}$ and Sc$^{3+}$ will occupy 6-coordination sites, generating c-ScFeO$_3$. The XRD analysis well supports this interpretation.

Figure 7 shows stable and meta-stable phase diagrams of the TmFeO$_3$-ScFeO$_3$ system predicted on the basis of these results: That is, in the metastable phase-diagram (Fig. 7(a)), the regions of $0 < x < 0.3$ and $0.3 < x < 0.5$ are represented as the single-phase regions of $o$-LnFeO$_3$ and $h$-LnFeO$_3$, respectively. The region of $x > 0.5$, however, is represented as a two-phase region of $h$-LnFeO$_3$ and c-ScFeO$_3$. On the other hand, in the annealed state, XRD shows the regions of $o$-LnFeO$_3$ and $h$-LnFeO$_3$ are reduced due to the formation of the garnet phase.

When the phase diagram of the representative garnet phases of Y$_3$Al$_5$O$_{12}$ and Y$_3$Fe$_5$O$_{12}$ are compared, the different point is whether the melting temperature is congruent or incongruent: the former has a congruent melting temperature, while the latter shows an incongruent melting temperature.

The melting temperature of the garnet phase is congruent and incongruent.

Fig. 7 Hypothetical phase diagrams of TmFeO$_3$-ScFeO$_3$ system. (a) metastable state; (b) stable state assuming that $c$-Tm$_3$ScFe$_4$O$_{12}$ has a congruent melting point; (c) stable state assuming that $c$-Tm$_3$ScFe$_4$O$_{12}$ has an incongruent melting point.

5. Conclusion

In order to elucidate the influence of substitution of Ln$^{3+}$ by Sc$^{3+}$ on the stability of $h$-LnFeO$_3$, we carried out the experiment of rapid solidification from undercooled melt using ADL. In this experiment, we used Tm$_{1-x}$Sc$_x$FeO$_3$ as a model material.

In samples of $x = 0.1$ and 0.2, similar to the sample of $x = 0.0$, after the metastable hexagonal LnFeO$_3$ phase ($h$-LnFeO$_3$) nucleated as the primary phase, the stable orthorhombic LnFeO$_3$ phase (o-LnFeO$_3$) nucleated through double recalescence. Increasing the $x$ value more than 0.2, the double recombination disappeared and $h$-LnFeO$_3$ was frozen as the stable phase. The reason for this stabilizing of $h$-LnFeO$_3$ is attributed to the decrease of the difference between the liquidus temperature of o-LnFeO$_3$ and that of h-LnFeO$_3$. Further increase of the $x$ value changed the primary phase to bixbyite-type ScFeO$_3$. Annealing the as-solidified samples, the c-A$_3$B$_5$O$_{12}$ garnet phase appeared at the region of $x < 0.5$. In particular at $x = 0.3$, the microstructure of the sample consisted of the single phase of the garnet phase. Furthermore, a meta-stable phase diagram and stable phase diagram for the TmFeO$_3$-ScFeO$_3$ system were estimated based on these experimental results and interpretations.

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