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

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Spherical samples of $\text{Tm}_{1-x}\text{Sc}_x\text{FeO}_3$ 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 ($h\text{-LnFeO}_3$) 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 ($o\text{-LnFeO}_3$) and metastable $h\text{-LnFeO}_3$ phases. Annealing the as-solidified samples at 1473 K for 1 hour resulted in the two-phase coexistent states of $o\text{-LnFeO}_3$ and garnet ($c\text{-A}_3\text{B}_5\text{O}_{12}$) at $0 < x < 0.3$, $c\text{-A}_3\text{B}_5\text{O}_{12}$ and $h\text{-LnFeO}_3$ at $0.3 < x < 0.5$, and $h\text{-LnFeO}_3$ and $c\text{-ScFeO}_3$ at $0.5 < x < 1.0$. Based on these results, we proposed the quasi phase diagram between TmFeO_3 and ScFeO_3 . [doi:10.2320/matertrans.M2017359]

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1. Introduction

Hexagonal LnFeO_3 ($h\text{-LnFeO}_3$, Ln: Eu-Lu) is attracting attention as a multi-ferroic material having both ferroelectric and (anti) ferromagnetic properties.¹⁾ Nevertheless, the production method of a bulk sample is restricted to rapid solidification into undercooled melt since $h\text{-LnFeO}_3$ is a metastable phase. In fact, it is reported that $h\text{-LuFeO}_3$ is formed from the undercooled melt by a containerless solidification method.²⁾ However, when other lanthanide ions, the ionic radii of which are larger than that of Lu^{3+} , are used, $h\text{-LnFeO}_3$ is rarely formed. The reason for this rarity is due to the melting temperature of the orthorhombic LnFeO_3 phase ($o\text{-LnFeO}_3$) except LuFeO_3 being much higher than that of the $h\text{-LnFeO}_3$ phase.³⁾ That is, the degree of undercooling for $o\text{-LnFeO}_3$ is much larger than that for $h\text{-LnFeO}_3$. For this reason, even if the metastable $h\text{-LnFeO}_3$ phase is formed initially, $o\text{-LnFeO}_3$ that is nucleated heterogeneously on the interface between $h\text{-LnFeO}_3$ and the residual melt is crystallized with re-melting the $h\text{-LnFeO}_3$ phase. Therefore, in order to obtain the $h\text{-LnFeO}_3$ phase from the undercooled melt by using the containerless solidification method, it is indispensable for $h\text{-LnFeO}_3$ to be thermodynamically stabilized. Regarding the stability of $h\text{-LnFeO}_3$, Masuno *et al.*⁴⁾ recently reported that substituting a part of Lu^{3+} by Sc^{3+} stabilizes $h\text{-LnFeO}_3$. This result suggests that decreasing the apparent ionic radius of Ln^{3+} stabilizes the $h\text{-LnFeO}_3$ 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 $h\text{-LnFeO}_3$ 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 $h\text{-LnFeO}_3$ is never frozen, we aimed to elucidate the influence of Sc substitution on the stabilization of $h\text{-LnFeO}_3$.

2. Experimental Procedure

The mixed powder of high purity (99.9%) Tm_2O_3 , Sc_2O_3 and Fe_2O_3 that were weighed to be $\text{Tm}_{1-x}\text{Sc}_x\text{FeO}_3$ 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.³⁾ 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^ϕ 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-recales-

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cence 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 recalcence, the spot-size (1 mm^ϕ) of the pyrometer is too large to evaluate T_{Pr} of the phase formed at the first recalcence (Fig. 1(b)). Therefore, based on the measured relation between the luminance and temperature at the liquid state, we regarded T_{Lumi} , which is the temperature evaluated from the luminescence of the area corresponding the first recalcence, 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 recalcences 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 $\text{YFeO}_3^{(6)}$ that was solidified from undercooled melt, a phase with higher luminance was formed subsequent to discoidal crystals, showing double recalcence; (b) The recalcence 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 ($c\text{-ScFeO}_3$). Figure 3 shows the XRD

Fig. 1 Typical cooling curves and the corresponding images of $\text{Tm}_{1-x}\text{Sc}_x\text{FeO}_3$ samples when (a) single and (b) double recalcences are detected during solidification from undercooled melt, in which T_{Nu} and T_{Pr} are the nucleation temperature and the post-recalcence temperature, respectively. Also shown is (c) typical example of the relationship between temperatures measured by pyrometer and luminance of the droplet. Since the second recalcence comes into the range of pyrometer just after the first recalcence, it is difficult to distinguish T_{Pr} of the first recalcence and that of the second recalcences. Therefore, in the present experiment, the liquidus temperature of the primary phase was estimated from the luminance of the sample assuming the solid and liquid as a blackbody.

Fig. 2 Typical recalcence behavior of $\text{Tm}_{1-x}\text{Sc}_x\text{FeO}_3$ samples observed by high-speed video camera. (a) $\text{Tm}_{0.8}\text{Sc}_{0.2}\text{FeO}_3$, (b) $\text{Tm}_{0.7}\text{Sc}_{0.3}\text{FeO}_3$, and (c) $\text{Tm}_{0.5}\text{Sc}_{0.5}\text{FeO}_3$. The frames are taken at a time interval of 0.5 ms, and elapsed time indicated below each image was set at 0 ms for one frame before the nucleation.

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 $o\text{-LnFeO}_3$. 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 $h\text{-LnFeO}_3$ was formed. These results suggest that increasing the x value up to 0.3 stabilizes the $h\text{-LnFeO}_3$ phase. For the sample of $x = 0.5$ that showed a spherical surface, $c\text{-ScFeO}_3$ was identified in addition to $h\text{-LnFeO}_3$. Increasing the x value further, the peak-intensity of $h\text{-LnFeO}_3$ reduced and that of $c\text{-ScFeO}_3$ increased. In the sample of LnFeO_3 , when $h\text{-LnFeO}_3$ 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 $h\text{-LnFeO}_3$, the surface of solidifying sample shapes was spherical. Considering that $c\text{-ScFeO}_3$ was confirmed in the samples of $x \geq 0.5$, the change of surface pattern suggests the primary phase changed to $c\text{-ScFeO}_3$ having a spherical surface from $h\text{-LnFeO}_3$ 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 $h\text{-LnFeO}_3$. In the sample of $x = 0.5$, on the other hand, a dark dendritic pattern that corresponds to $c\text{-ScFeO}_3$ (Fig. 4(b)) verifies the primary phase changed to $c\text{-ScFeO}_3$.

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

Kuribayashi *et al.*⁷⁾ reported that when the difference of melting temperatures between $o\text{-LnFeO}_3$ and $h\text{-LnFeO}_3$ 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 $o\text{-LnFeO}_3$ and $h\text{-LnFeO}_3$ 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 $h\text{-LnFeO}_3$ by reducing the difference between T_{Pr} and T_{Lumi} . Namely, the liquidus temperature of $o\text{-LnFeO}_3$, 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 $h\text{-LnFeO}_3$ phase, increases. As a result, in samples of $x \geq 0.2$, the difference of the liquidus temperatures between $o\text{-LnFeO}_3$ and $h\text{-LnFeO}_3$ decreases to below 2%.

Fig. 3 Powder X-ray diffraction patterns of as-solidified $\text{Tm}_{1-x}\text{Sc}_x\text{FeO}_3$ samples.

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

(a) $x = 0.3$

20 μm

(b) $x = 0.5$

20 μm

Fig. 4 Backscattered electron images of as-solidified samples of (a) $\text{Tm}_{0.7}\text{Sc}_{0.3}\text{FeO}_3$ and (b) $\text{Tm}_{0.5}\text{Sc}_{0.5}\text{FeO}_3$.

samples with x values of 0.1 and 0.2, not only o -LnFeO₃ but also the cubic garnet phase (c -A₃B₅O₁₂) was identified. Furthermore, in samples with $x = 0.3$, it was suggested that a large proportion of h -LnFeO₃ formed from the undercooled melt was transformed to c -A₃B₅O₁₂ in the annealing process. Furthermore, in samples of $0.4 \leq x \leq 0.6$, c -A₃B₅O₁₂ coexisted with h -LnFeO₃, and in the samples of $0.6 \leq x \leq 0.7$, c -A₃B₅O₁₂ coexisted with not only h -LnFeO₃ but also c -ScFeO₃. On the other hand, in samples of $0.8 \leq x$,

c -A₃B₅O₁₂ was not verified and h -LnFeO₃ coexisted with c -ScFeO₃.

Summarizing these data, increasing the substituting amount of Sc³⁺, the liquidus temperature of o -LnFeO₃ falls, yet the liquidus temperature of h -LnFeO₃ rises, and, as a result, h -LnFeO₃ stabilizes. Therefore, with the increase of the x value, the phase constitution of this system changed as shown follows:

o -LnFeO₃ $\Rightarrow$ h -LnFeO₃ $\Rightarrow$ h -LnFeO₃ + c -ScFeO₃ $\Rightarrow$ c -ScFeO₃, in as-solidified samples.

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

o -LnFeO₃ $\Rightarrow$ o -LnFeO₃ + c -A₃B₅O₁₂ $\Rightarrow$ c -A₃B₅O₁₂ + h -LnFeO₃ $\Rightarrow$ h -LnFeO₃ + c -ScFeO₃ $\Rightarrow$ c -ScFeO₃.

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 TmFeO₃-ScFeO₃ system along with the cause for c -A₃B₅O₁₂ to appear.

4. Discussion

The garnet structure that is a compact cubic structure represented by {A₃}[C₂](B₃)O₁₂ consists of three 8-coordination sites { }, two 6-coordination sites [] and three 4-coordination sites (). If the garnet structure appears in Tm_{1-x}Sc_xFeO₃, it should be {Ln_{3(1-x)}, Sc_{3x-1}}[Sc, Fe](Fe₃)O₁₂ where Fe and Sc are equally coordinated in [], since Fe³⁺ that has the smallest ionic radius is considered to occupy the 4-coordination site and Ln³⁺ that has the largest ionic radius will occupy 8-coordination site. Therefore, for the sample of $x = 0.25$, we predict the existence of {Ln_{0.75}}[Sc_{0.25}Fe_{0.25}](Fe_{0.75})O₃ 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 -LnFeO₃ 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;

When Sc³⁺ having an ionic radius smaller than Ln³⁺ increases, the mean ionic radius of Ln³⁺ that is partially substi-

Fig. 5 Estimated liquidus temperature of stable and metastable phase for Tm_{1-x}Sc_xFeO₃ samples that crystallized at the first and second recalescences, 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 Powder X-ray diffraction patterns of the Tm_{1-x}Sc_xFeO₃ samples annealed at 1473 K for 1 hr.

Table 1 Relation between phase constitution and chemical composition.

composition		phase constitution	
x	as-solidified sample	annealed sample	
0.0		o -LnFeO ₃	
0.1	o -LnFeO ₃	o -LnFeO ₃ + c -A ₃ B ₅ O ₁₂	
0.2		c -A ₃ B ₅ O ₁₂	
0.3	h -LnFeO ₃	c -A ₃ B ₅ O ₁₂ + h -LnFeO ₃	
0.4		c -ScFeO ₃ + h -LnFeO ₃ + c -A ₃ B ₅ O ₁₂	
0.5		h -LnFeO ₃ + c -ScFeO ₃	
0.6		h -LnFeO ₃ + c -ScFeO ₃	
0.7	h -LnFeO ₃ + c -ScFeO ₃	h -LnFeO ₃ + c -ScFeO ₃	
0.8		h -LnFeO ₃ + c -ScFeO ₃	
0.9		h -LnFeO ₃ + c -ScFeO ₃	
1.0	c -ScFeO ₃	c -ScFeO ₃

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

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 $h\text{-LnFeO}_3$. 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 $c\text{-ScFeO}_3$. The XRD analysis well supports this interpretation.

Figure 7 shows stable and meta-stable phase diagrams of the $\text{TmFeO}_3\text{-ScFeO}_3$ 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 $0.3 \leq x < 0.5$ are represented as the single-phase regions of $o\text{-LnFeO}_3$ and $h\text{-LnFeO}_3$, respectively. The region of $x > 0.5$, however, is represented as a two-phase region of $h\text{-LnFeO}_3$ and $c\text{-ScFeO}_3$. On the other hand, in the annealed state, XRD shows the regions of $o\text{-LnFeO}_3$ and $h\text{-LnFeO}_3$ are reduced due to the formation of the garnet phase.

When the phase diagram of the representative garnet phases of $\text{Y}_3\text{Al}_5\text{O}_{12}$ ⁸⁾ and $\text{Y}_3\text{Fe}_5\text{O}_{12}$ ⁹⁾ 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. In order to form garnet phases for $\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{Y}_3\text{Fe}_5\text{O}_{12}$ it was reported that the cooling rate larger than 50 K/s¹⁰⁾ and the undercooling below the peritectic temperature T_{Pe} are respectively required.¹¹⁾ If these conditions are unsatisfied, the melt crystallizes to the eutectic of Al_2O_3 and YAlO_3 , and that of Fe_2O_3 and YFeO_3 . As shown in the representative temperature-time profile in Fig. 1, the cooling rate in the present experiment is approximately 450 K/s, which is much larger than the rate required to form a garnet phase for $\text{Y}_3\text{Al}_5\text{O}_{12}$. Although T_{Pe} for the present system is unknown, it is estimated to be 1760~1770 K from the analogy with Fig. 7. In other words, considering that the nucleation temperature, T_{Nu} , in this experiment is below T_{Pe} (see Fig. 1), the present system is suspected to meet both conditions for forming the garnet phase irrespective of whether the melting temperature is congruent or incongruent. Nevertheless, the lack of garnet phase in the sample solidified from undercooled melt is caused by the small activation energy of $h\text{-LnFeO}_3$ nucleation,⁷⁾ in addition to the small difference in chemical composition between $h\text{-LnFeO}_3$ and $o\text{-LnFeO}_3$. Furthermore, regarding the form of the phase di-

agram, we must consider that $\text{Ln}_3\text{Fe}_5\text{O}_{12}$ (Ln: Sm-Lu) becomes peritectic compounds.¹²⁾ Therefore, we consider that the melting temperature of the garnet phase in the system of $\text{TmFeO}_3\text{-ScFeO}_3$ is incongruent. However, as a future problem we show two cases that the melting temperature of the garnet phase is congruent and incongruent.

5. Conclusion

In order to elucidate the influence of substitution of Ln^{3+} by Sc^{3+} on the stability of $h\text{-LnFeO}_3$, we carried out the experiment of rapid solidification from undercooled melt using ADL. In this experiment, we used $\text{Tm}_{1-x}\text{Sc}_x\text{FeO}_3$ 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 ($h\text{-LnFeO}_3$) nucleated as the primary phase, the stable orthorhombic LnFeO_3 phase ($o\text{-LnFeO}_3$) nucleated through double recalescence. Increasing the x value more than 0.2, the double recombination disappeared and $h\text{-LnFeO}_3$ was frozen as the stable phase. The reason for this stabilizing of $h\text{-LnFeO}_3$ is attributed to the decrease of the difference between the liquidus temperature of $o\text{-LnFeO}_3$ and that of $h\text{-LnFeO}_3$. Further increase of the x value changed the primary phase to bixbyite-type ScFeO_3 . Annealing the as-solidified samples, the $c\text{-A}_3\text{B}_5\text{O}_{12}$ 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 $\text{TmFeO}_3\text{-ScFeO}_3$ system were estimated based on these experimental results and interpretations.

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