

P08

無容器溶融凝固法による LnFeO₃-ScFeO₃系における
共晶凝固挙動の解明と準安定状態図の構築

Eutectic Solidification Process of LnFeO₃-ScFeO₃ System
by Containerless Processing and Construction of
Metastable Phase Diagram

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1. Introduction

The metastable phase diagram of the LnFeO₃-ScFeO₃ system deduced by containerless processing is basically a eutectic system consisting of *h*-LnFeO₃, *o*-LnFeO₃ and ScFeO₃. The relationship between *h*-LnFeO₃ and *o*-LnFeO₃ depends on the ionic radius of Ln³⁺, and as the ionic radius of Ln³⁺ increases, the range of *h*-LnFeO₃ formation decreases, and disappears in the DyFeO₃-ScFeO₃ system. If *h*-LnFeO₃ is frozen, the recalescence behavior is sluggish, but if it is not frozen, it shows a so-called double recalescence. These phenomena are peculiar to the formation of *h*-LnFeO₃, but in the DyFeO₃-ScFeO₃ system, as shown in Fig. 1, two-step recalescence appears near the eutectic composition. Furthermore, although there is no signal for formation of garnet phase on the liquidus temperature, XRD shows the presence of garnet phase in samples where approximately 30% of Ln³⁺ was substituted with Sc³⁺. The objective of the present investigation is to elucidate the details of eutectic solidification including the formation of garnet phase in the LnFeO₃-ScFeO₃ system by studying this two-step recalescence behavior.

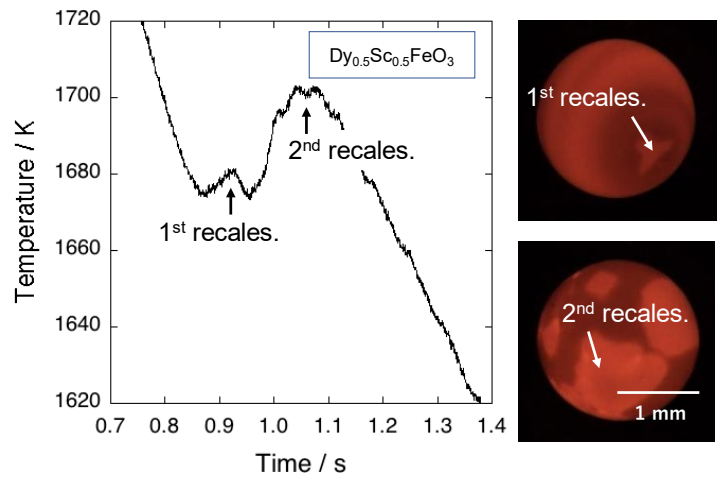


Fig. 1. Cooling curve the Dy_{0.5}Sc_{0.5}FeO₃ sample showing two-step recalescence: the 1st and 2nd recalescence correspond to the nucleation of ScFeO₃ and *o*-LnFeO₃ phases, respectively

2. Experimental procedure

Since the two-step recalescence behavior does not appear in systems where the ionic radius of Ln³⁺ is smaller than that of Dy³⁺, the TbFeO₃-ScFeO₃ and GdFeO₃-ScFeO₃ systems, in which this behavior is expected to be more pronounced than that in the DyFeO₃-ScFeO₃ system, were chosen as samples. The sample which was prepared by melting the weighed

mixed powder into a spherical shape with a diameter of 2 mm was processed in an aerodynamic levitation furnace (ADL) using oxygen gas as the levitating gas. The temperature of the sample was measured by a monochromatic pyrometer and the solidification process were monitored by a high-speed video camera (HSV). The phase constitution and the microstructure of the as-solidified sample were analyzed by a powder X-ray diffraction (XRD) and a scanning electron microscope (SEM).

3. Results and discussion

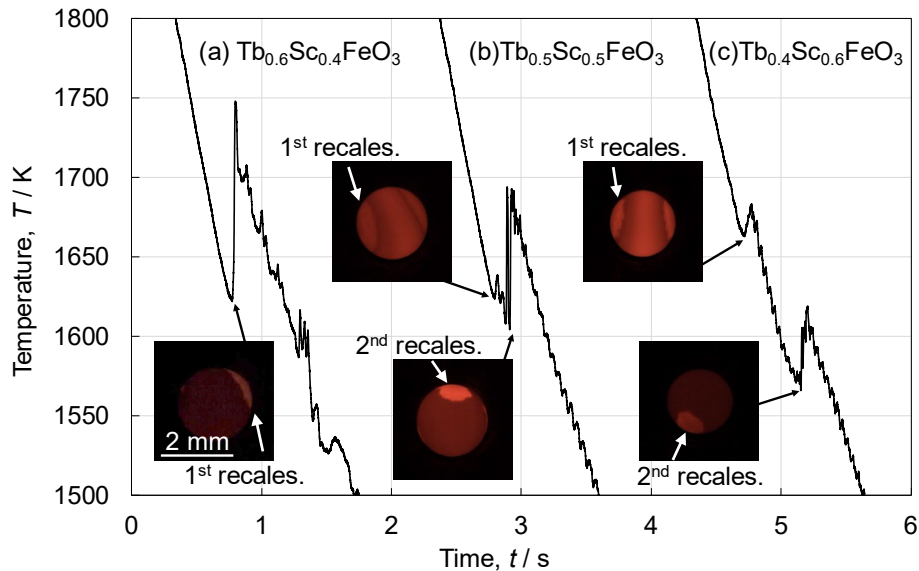


Fig. 2. Typical cooling curve and corresponding HSV image of $Tb_{1-x}Sc_xFeO_3$ sample. a: single recalescence, b and c: two-stage recalescence.

Figure 2 shows the temperature *vs.* time during recalescence. The molar ratios x of $ScFeO_3$ in each sample are 0.4, 0.5 and 0.6, respectively. As shown in this figure, single recalescence was observed in the sample of $x = 0.4$, whereas two-step recalescence was observed in the samples of $x = 0.5$ and $x = 0.6$.

Figure 3 shows the XRD results for as-solidified samples with x greater than 0.5. The phase is mainly composed of o - $LnFeO_3$ and $ScFeO_3$, but the garnet phase was formed in the samples with $x = 0.8$ and 0.85.

Figure 4 shows the nucleation and post-recalescence temperatures as a function of x . Post-recalescence temperature was assumed to be the liquidus temperature of related phase. Two-step recalescence which was observed in the samples at $0.5 \leq x \leq 0.75$ consists of two kinds of recalescence: The first and the second recalescences correspond to the nucleation of $ScFeO_3$ phase and the o - $TbFeO_3$ phase, respectively. As shown in this figure, the undercooling required for nucleation of the o - $LnFeO_3$ phase in the hypoeutectic region decreases with increasing x competing with that for nucleation of the $ScFeO_3$ phase at $x=0.5$. In the region of $x > 0.5$, the nucleation of the $ScFeO_3$ phase precedes, and the temperature at which the o - $LnFeO_3$ phase nucleates decreases along the hypothetically elongated liquidus line, forming a skewed eutectic zone.

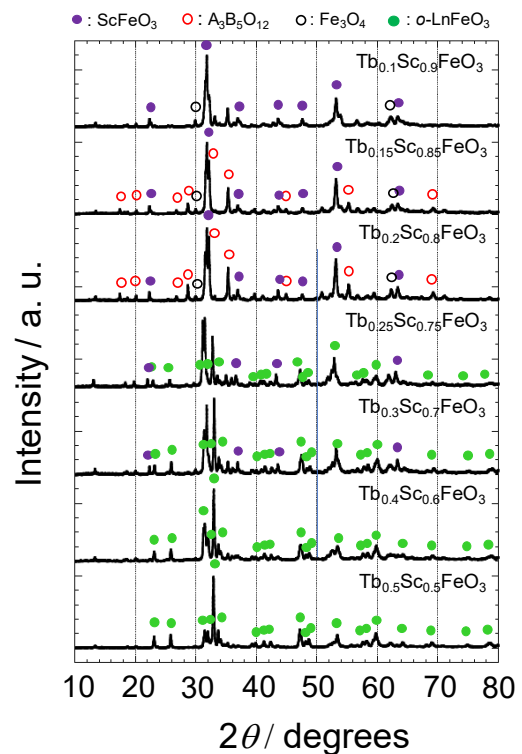


Fig. 3. XRD of as-solidified $Tb_{1-x}Sc_xFeO_3$ sample

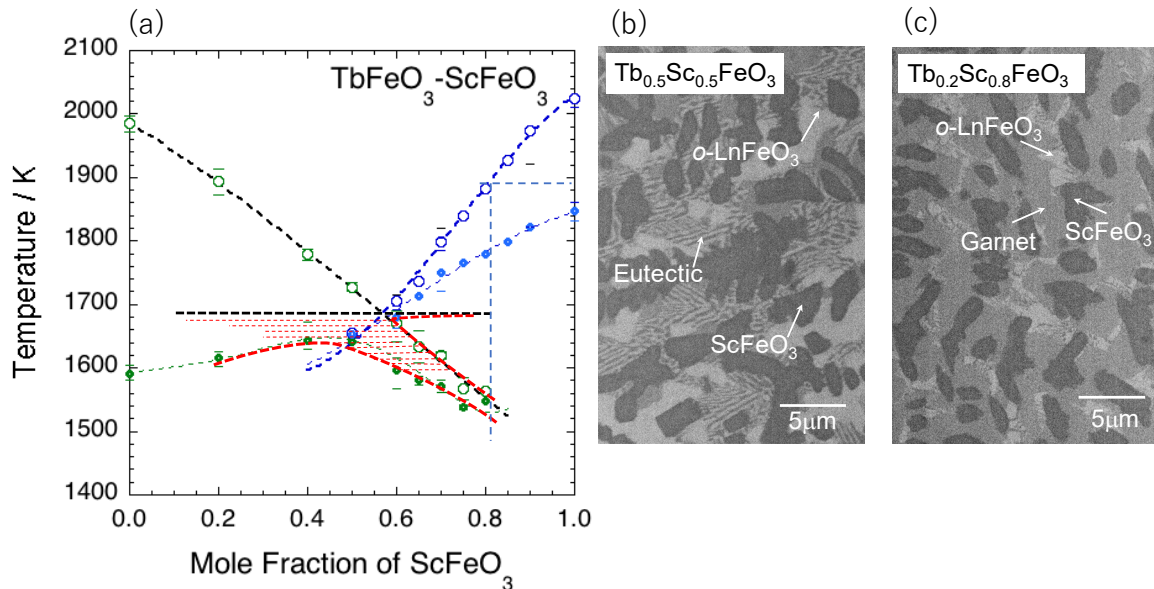


Fig. 3. Metastable phase diagram of TbFeO_3 and ScFeO_3 system, and the microstructure of as-solidified sample. **a:** The lined area is the eutectic region. Since the activation energy for forming acritical nucleus of $o\text{-LnFeO}_3$ phase is larger, the eutectic region is largely skewed to the ScFeO_3 side. **b:** Microstructure of the as-solidified sample of $\text{Tb}_{0.5}\text{Sc}_{0.5}\text{FeO}_3$. The $o\text{-LnFeO}_3$ phase is formed adjacent the primary ScFeO_3 phase, indicating that the interface between the ScFeO_3 and the liquid is the preferential nucleation site. Since the solidification rate of the $o\text{-LnFeO}_3$ phase is lower than that of the ScFeO_3 phase, the eutectic structure is underdeveloped, and thus the area becomes smaller.

Furthermore, although there is no signal for formation of garnet phase on the liquidus temperature, XRD shows the presence of garnet phase in samples where approximately 30% of Ln^{3+} was substituted with Sc^{3+} . In fact, it is observed from the microstructure that the garnet phase is formed so as to envelope the primary phase ScFeO_3 . These results suggest that the garnet phase is a peritectic phase with an incongruent melting point.



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