Metastable Phase Formation from Undercooled Melt of Oxide Material

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Abstract. Undercooling a melt often facilitates a metastable phase to nucleate preferentially. Although the classical nucleation theory shows that the most critical factor for forming a metastable phase is the interface free energy, the crystallographic stability is also indispensable for the phase to be frozen at ambient temperature. In compound materials such as oxides, authors have suggested that the decisive factors for forming a critical nucleus are not only the free energy difference but also the difference of the entropy of fusion between stable and metastable phases. In the present study, using REFeO₃ (RE: rare-earth element) as a model material, we investigate the formation of a metastable phase from undercooled melts with respect to the competitive nucleation and crystallographical stabilities of both phases.

1. Introduction
A metastable phase is a phase that does not exist in thermal equilibrium state and, although thermodynamically unstable, can temporarily exist when some conditions are fulfilled. Research on the metastable phase began with Ostwald’s prediction that a phase formed first from supersaturated liquid is not always thermodynamically stable but is close to liquid in energy [1]. This prediction is called “step rule”. More than thirty years later, Straniski and Totomanov [2] suggested that the step rule is a consequence of preferential formation of a critical nucleus of the metastable phase. That is, the activation energy required to form a critical nucleus, \( \Delta G^*_n \), controls the nature of the process. Regarding this point, the classical nucleation theory [3] states that \( \Delta G^*_n \) can be understood in terms of the interfacial free energy, \( \gamma \), between the liquid and solid phases. Turnbull [4] and Spaepen [5], assuming that \( \gamma \) of a simple metal is related not to the enthalpy change but to the entropy change at the solid–liquid interface, formulated the dimensionless solid-liquid interfacial energy, \( \alpha \). Furthermore, Spaepen and Meyer [6], considering the geometrical configuration of hard-spheres at the solid-liquid interface, derived \( \alpha \) as 0.86 for fcc or hcp crystals and 0.71 for bcc structures, respectively. The \( \alpha \)-factors, which strongly depend on the structure of both solid and liquid phase, are to be a critical parameter to determine \( \Delta G^*_n \). However, the recent numerical calculations of \( \alpha \) based on the molecular dynamics or density functional theory show less dependence on the structure, being scattered around 0.5 [7]. On the basis of this fact, authors proposed one hypothesis that in ionic crystals such as oxides, where the close-packed tetrahedron of anions are the structural unit both in the solid and liquid phases, an entropy of fusion is to be a dominant factor in the determination of \( \gamma \) [8, 9]. In accordance with this idea, using REFeO₃ (RE: rare-earth element) as the model material, they investigated the containerless
solidification from the undercooled melt. As a result, they elucidated that in addition to the entropy of fusion, oxygen partial pressure, $P_{O_2}$, is to be another important factor which controls phase selection: reduction of $P_{O_2}$ in RE-Fe-O system enlarges the instability of the perovskite structure and then facilitates the metastable phase to be formed [10, 11]. This result implies that the critical factor for forming a metastable phase is not only interfacial free energies but also the relative stabilities of stable and metastable phases. Then, in the present investigation, changing $P_{O_2}$ from $10^5$ to $10^3$ Pa and at Ar environment, $P_{O_2}$ of which s approximately $10^{-1}$ Pa, we carried out the rapid solidification from the undercooled melt, and discussed the criterion for formation of the metastable phase from the point of the phase stabilities.

2. Experimental

Spherical samples of REFeO$_3$ were prepared from high purity (99.99%) RE$_2$O$_3$ and Fe$_2$O$_3$ powders. Details of the sample preparation are shown elsewhere [12]. Levitation and melting of samples were carried out by an aerodynamic levitator, ADL, which was designed in order to solidify undercooled melts under the precisely controlled $P_{O_2}$, as shown in Fig. 1. The ADL chamber was initially evacuated down to $10^{-1}$ Pa and backfilled with a mixture of 6N-Ar and O$_2$ gas at a predetermined $P_{O_2}$. The $P_{O_2}$ was monitored using a ZrO$_2$ oxygen sensor, which was connected at the outlet of the ADL chamber.

![Figure 1. Schematic diagram of an aerodynamic levitation (ADL) chamber combined with a zirconia oxygen sensor. The conical nozzle angle is 60°, and orifice is 1mm.](image)

The REFeO$_3$ sphere was levitated and then completely melted by the CO$_2$ laser irradiation and held at approximately 1850 K for 5 minutes to equilibrate the melt with the chamber atmosphere. Then the sample was solidified by turning off the laser. The surface temperature of the levitated sample was measured using a two-colour pyrometer at a sampling rate of 1 kHz with central wavelengths of 0.9 and 1.55 μm and a spot size of 1 mm in diameter. The recrystallization behaviour was monitored using a colour high-speed video (HSV) camera, at a sampling rate of 1 kHz with a spatial resolution of 256 × 240 pixels.

The spontaneously solidified samples under various $P_{O_2}$ were subjected to systematic characterization. The constituent phases in as-solidified samples were identified using X-ray diffractometry (XRD). The bulk composition was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The surface morphologies and cross-sectional microstructures of
the as-solidified samples were observed by scanning electron microscopy (SEM), and the chemical compositions of the phases were analyzed by energy-dispersive spectroscopy (EDS).

3. Results

Figure 2 shows the typical cooling curves of the REFeO$_3$ (RE: (a) Lu and (b) Er) samples solidified under various $P_{O_2}$. In LuFeO$_3$, the undercooled samples spontaneously nucleated below the melting temperature $T_M$ of the LuFeO$_3$ perovskite ($\sim$1900 K) and recalescence was observed due to the release of latent heat during solidification. The nucleation ($T_N$) and post-recalescence temperatures ($T_{\text{Post-recal}}$) are commonly defined as the temperatures at the onset and at the end of the recalescence, which are approximately 1810 K and 1868 K, respectively. These temperatures decreased with decreasing $P_{O_2}$, from $10^5$ to $10^3$ Pa, showing the sudden decrease in nucleation temperatures at $P_{O_2}$=3×$10^3$ Pa. If $T_{\text{Post-recal}}$ is assumed to be nearly equal to the melting temperature of the phase formed during recalescence, the undercooling level ($T_{\text{Post-recal}} - T_N$) looks independent of $P_{O_2}$.

In ErFeO$_3$, which was used to study the effect of ionic radii of RE elements on the formation of metastable phases, because the ionic radius of Er$^{3+}$ (0.1062 nm) was slightly larger than that of Lu$^{3+}$ (0.1032 nm). In ErFeO$_3$, although $T_N$ and $T_{\text{Post-recal}}$ also gradually decreased with decreasing $P_{O_2}$ down to $10^3$ Pa, the undercooling level is quite different from those of LuFeO$_3$. That is, in LuFeO$_3$, the undercooling levels are approximately 60 K independently of $P_{O_2}$, whereas in ErFeO$_3$ the undercooling levels strongly depend on $P_{O_2}$, more than 200 K at $P_{O_2}$=1×$10^5$ and less than 60 K at $P_{O_2}$=1×$10^3$.

Figure 3 shows the XRD patterns of ErFeO$_3$ samples processed at $10^5$ Pa and $10^3$ Pa of $P_{O_2}$. The XRD patterns were recorded using monochromatic radiation with a wavelength of 0.154 nm for Cu $K\alpha$. In the sample solidified at $10^5$ Pa, the peaks of the stable orthorhombic ErFeO$_3$ (o-ErFeO$_3$) phase with a space group of $Pbnm$ were identified. However, decreasing $P_{O_2}$ to $10^3$ Pa caused the peak intensities of the o-ErFeO$_3$ to decrease, and metastable phases appeared. In our previous study on the containerless processing of LuFeO$_3$ using a similar experimental apparatus, we already reported the metastable hexagonal phase with a space group of $P6_3cm$ appeared even at $10^5$ Pa of $P_{O_2}$ [10].
ErFeO$_3$, although the most characteristic peak of the space group $P6_3cm$ at approximately 15° is absent, the secondary characteristic peak at approximately 29° is obvious, suggesting that the hexagonal metastable phase with a space group of $P6_3cm$ was formed. In addition, another metastable phase such as $h$-Er$_3$Fe$_5$O$_7$ can be appreciated though the intensity is weak.

![XRD patterns of the ErFeO$_3$ samples processed at $P0_2=10^5$ Pa and $P0_2=10^3$ Pa.](image)

Figure 3. XRD patterns of the ErFeO$_3$ samples processed at $P0_2=10^5$ Pa and $P0_2=10^3$ Pa. In the sample solidified at $10^5$ Pa, the peaks of the stable orthorhombic ErFeO$_3$ ($o$-ErFeO$_3$) phase with a space group of $Pbnm$ were identified. However, decreasing $P0_2$ to $1\times10^3$ Pa caused the peak intensities of the $o$-ErFeO$_3$ to decrease, and metastable phases appeared.

![XRD patterns of the YbFeO$_3$ samples processed at $P0_2=10^5$ Pa, $P0_2=10^4$ Pa and $P0_2=9\times10^3$ Pa, respectively.](image)

Figure 4. XRD patterns of the YbFeO$_3$ samples processed at $P0_2=10^5$ Pa, $P0_2=10^4$ Pa and $P0_2=9\times10^3$ Pa, respectively. At $10^5$ Pa of $P0_2$, the stable orthorhombic phase ($o$-YbFeO$_3$) was formed as in the case of ErFeO$_3$. At $10^4$ Pa of $P0_2$, however, the metastable hexagonal phase ($h$-REFeO$_3$) appeared, forming the dual phase with $o$-YbFeO$_3$, and at $9\times10^3$ Pa, the $o$-YbFeO$_3$ phase thoroughly disappeared.
In YbFeO$_3$, where the ionic radius of Yb$^{3+}$ is also slightly larger than that of Lu$^{3+}$ but less than that of Er$^{3+}$, the influence of $P_{O_2}$ on the phase selection between stable and metastable phases is more obvious. Figure 4 shows the XRD patterns of YbFeO$_3$ samples processed at controlled $P_{O_2}$. At $10^5$ Pa of $P_{O_2}$, the stable orthorhombic phase ($o$-YbFeO$_3$) was formed as in the case of ErFeO$_3$. At $10^4$ Pa of $P_{O_2}$, however, the metastable hexagonal phase ($h$-REFeO$_3$) appeared, forming the dual phase with $o$-YbFeO$_3$, and at $9 \times 10^3$ Pa, the $o$-YbFeO$_3$ phase thoroughly disappeared.

These results suggest that the decrease of $P_{O_2}$ facilitates the undercooled melt to solidify metastable $h$-REFeO$_3$ phase rather than the stable $o$-REFeO$_3$ phase, particularly in samples with RE$^{3+}$ of relatively small ionic radius.

![Figure 4: XRD patterns of YbFeO$_3$ samples processed at controlled $P_{O_2}$](image)

Figure 4. The XRD patterns of YbFeO$_3$ samples processed at controlled $P_{O_2}$.

Figure 5 shows the typical cooling curves of the REFeO$_3$ (RE: La and Y) samples solidified at $1 \times 10^5$ Pa and $1 \times 10^3$ Pa, respectively.

![Figure 5: Cooling curves of REFeO$_3$ samples](image)

Figure 5. The typical cooling curves of the REFeO$_3$ (RE: La and Y) samples solidified at $1 \times 10^5$ Pa and $1 \times 10^3$ Pa, respectively.

Figure 5 shows the cooling curves of the REFeO$_3$ samples having relatively larger ionic radius of RE element such as La (0.1216 nm) and Y (0.1075 nm) with $P_{O_2}$ of $10^5$ and $10^3$ Pa. As shown in this figure, the undercooling level of LaFeO$_3$ is higher than 300 K independently of $P_{O_2}$. In YFeO$_3$, however, the undercooling level is similar to that of ErFeO$_3$, that is, decreasing $P_{O_2}$, the undercooling level decreased from 235 K at $10^5$ Pa to 103 K at $10^3$ Pa.

Figure 6 shows typical images taken sequentially during recalcence in samples of LaFeO$_3$ and YFeO$_3$, each of which is processed at $P_{O_2}$ of $10^5$ Pa (Fig. 6a) and $10^3$ Pa (Fig. 6b), respectively. The elapsed time indicated in each image was set to 0 sec for one frame before the nucleation. At $10^5$ Pa, single recalcence that can be ascribed to the phase transition from undercooled melt to equilibrium perovskite phase was observed in LaFeO$_3$ samples. On the other hand, double recalcence, which could not be identified in the temperature-time profiles measured with the pyrometer, was observed in YFeO$_3$ samples. After the primary phase solidified from the undercooled melt, the secondary phase with higher brightness was initiated at the interface between melt and the primary phase. The dark and bright regions of the photograph represent the undercooled melt and the growing solid, respectively. The solid-liquid interface is clearly indicated by the large difference in brightness between the solid and liquid regions.
and liquid. The high brightness implies that the melting temperature of the secondary phase was much higher than that of the primary phase.

Previously, Nagashio et al. reported the same kind of recalescence in an undercooled YFeO$_3$ melt [13]. Later, time-resolved XRD observation on an undercooled YFeO$_3$ melt revealed that metastable hexagonal YFeO$_3$ ($P6_{3}cm$) was formed as the primary phase and this phase was subsequently transformed into the stable orthorhombic perovskite ($Pbnm$) structure during recalescence [14]. Therefore, in the present study, we conclude that the primary phase was the metastable hexagonal REFeO$_3$ ($h$-REFeO$_3$) and the secondary phase was the stable orthorhombic REFeO$_3$ ($o$-REFeO$_3$).

If we summarize the aforementioned experimental results, we can obtain the following conclusion: In REFeO$_3$ oxide system, decrease of $P_{O_2}$ facilitates the undercooled melt to solidify the metastable $h$-REFeO$_3$ phase rather than the stable $o$-REFeO$_3$ phase, particularly in samples with relatively small ionic radius of RE$^{3+}$. In LaFeO$_3$, where the ionic radius of RE$^{3+}$ is maximum in this series, the undercooling level required to form the critical nucleus of the absolutely stable $o$-REFeO$_3$ phase is as large as approximately 400 K. On the other hand, in LuFeO$_3$, where the ionic radius of RE$^{3+}$ is minimum in this series, the metastable $h$-REFeO$_3$ phase can be formed under relatively low

![Figure 6](image_url). Sequence photographs of HSV images taken during recalescences in the REFeO$_3$ ($R =\text{La and Y}$) samples processed at (a) $P_{O_2}=10^5$ Pa, and (b) $P_{O_2}=10^3$ Pa. Although single recalescence was observed even at $10^3$ Pa of $P_{O_2}$ in LaFeO$_3$, double recalescence indicating the formation of metastable phases was observed even at $10^5$ Pa of $P_{O_2}$ in YFeO$_3$. 

Previously, Nagashio et al. reported the same kind of recalescence in an undercooled YFeO$_3$ melt [13]. Later, time-resolved XRD observation on an undercooled YFeO$_3$ melt revealed that metastable hexagonal YFeO$_3$ ($P6_{3}cm$) was formed as the primary phase and this phase was subsequently transformed into the stable orthorhombic perovskite ($Pbnm$) structure during recalescence [14]. Therefore, in the present study, we conclude that the primary phase was the metastable hexagonal REFeO$_3$ ($h$-REFeO$_3$) and the secondary phase was the stable orthorhombic REFeO$_3$ ($o$-REFeO$_3$).
undercooling level, typically less than 100 K. This result means that in LuFeO$_3$, even though the thermo-equilibrium phase is $o$-LuFeO$_3$, in the deeply undercooled melt the activation energy for forming the critical nucleus of the metastable $h$-LuFeO$_3$ phase is lower than that of the stable $o$-LaFeO$_3$ phase, suggesting that the interfacial free energy of $h$-LuFeO$_3$ is lower than that of $o$-LuFeO$_3$ if the catalytic potencies for heterogeneous nucleation of both phases are assumed to be equal. In YFeO$_3$, where double recalescence was observed, the undercooling level is medium typically 200 K, suggesting that the secondary phase can be heterogeneously nucleated at the interface between primarily solidified metastable phase and the melt.

Figure 7 shows the relation between the recalescence results and $P_{O_2}$ as a function of the ionic radii of RE$^{3+}$, in which Shannon ionic radii for CN=9 were used. Decrease of $P_{O_2}$ extends the range of $TF$ for metastable $h$-REFeO$_3$ phase to be formed.

4. Discussion

Bertaut et al. [15] and Yakel et al. [16] have first reported the two hexagonal modifications in the ABO$_3$ systems, the space groups of which are $P6_3/mmc$ and $P6_3$cm, respectively. In the $h$-REMnO$_3$ system, the $P6_3$cm type modification was formed as a low temperature phase for RE$^{3+}$ with small ionic radius (Ho-Lu, Y and Sc), whereas the $P6_3/mmc$ type modification was reported as a high temperature phase [17]. In our experiment, although the space group of the metastable $h$-REFeO$_3$ phase belonged to $P6_3$cm, the high temperature phase can be deduced to belong to the $P6_3/mmc$ space group because the ionic radius of Fe$^{3+}$ is as same as that of Mn$^{3+}$ (0.0645 nm for 6 coordination). Hence, in this investigation, the geometrical analysis of the atomic configuration in $h$-REFeO$_3$ is developed on the assumption that the space group of the primary phase is $P6_3/mmc$.

The atomic configuration of the $P6_3$cm modification in ABO$_3$ system can be described as a dense oxygen-ion packing (ABCACB) with B$^{3+}$ ions having coordination number CN=5 (five-fold distorted
A trigonal bipyramidal coordination, and $A^{3+}$ with $CN=7$ (seven-fold monocapped octahedral coordination), forming a noncentrosymmetric structure. On the other hand, centrosymmetric $P6_3/mmc$ is assumed to be described simply with $B^{3+}$ ions of undistorted $CN=5$ and $A^{3+}$ of $CN=6$ (octahedral coordination).

Goldschmidt [18] discussed the stability of the perovskite structure using the tolerance factor, $TF$:

$$TF = \frac{R_A + R_{O}}{\sqrt{2(R_{Fe} + R_{O})}},$$

(1)

where $R_A$ and $R_{O}$ are ionic radii of rare-earth element and iron, respectively, and $R_{O}$ is the ionic radius of oxygen. From the systematic investigation, he summarized that the perovskite structure is stable at $TF > 0.8$ and contrary unstable at $TF < 0.8$. Using Shannon ionic radii from La (0.1216 nm) to Lu (0.1032 nm), $TF$'s for the REFeO$_3$ system were calculated to be 0.905 for LaFeO$_3$ to 0.841 for LuFeO$_3$. Therefore, the perovskite structure is expected to be stable in the REFeO$_3$ system.

Figure 8 shows the geometrical configuration among $RE^{3+}$ ($CN=6$), $Fe^{3+}$ ($CN=5$), and $O^{2-}$ in a space group of $P6_3/mmc$, in which the constituent ions are packed without any space between neighboring ions. The relation among the ionic radii of constituent ions of $h$-REFeO$_3$ is expressed as

$$R_{RE} + R_{O} = \frac{\sqrt{6}}{2}(R_{Fe} + R_{O}).$$

Therefore, the $h$-REFeO$_3$ phase will be ideal when the next equation is fulfilled,

$$TF = \frac{\sqrt{3}}{2} \approx 0.87.$$

Figure 8. Geometrical configuration among $RE^{3+}$ ($CN=6$), $Fe^{3+}$ ($CN=5$), and $O^{2-}$ in a space group of $P6_3/mmc$, in which the constituent ions are packed without any space between neighboring ions. The relation among the ionic radii of constituent ions of $h$-REFeO$_3$ is expressed as

$$R_{RE} + R_{O} = \frac{\sqrt{6}}{2}(R_{Fe} + R_{O}).$$

(2)

The $h$-REFeO$_3$ phase will be the ideal when the next equation is fulfilled,

$$TF = \frac{\sqrt{3}}{2} \approx 0.87.$$

Figure 9 shows the schematical presentation for stabilities of $o$-REFeO$_3$ and $h$-REFeO$_3$ phases. If $TF$ is deviated from the ideal value of 0.87 as expressed by Eq. 2, the stability of $h$-REFeO$_3$ phase
decreases. However, in the case that $TF < 0.87$, $h$-REFeO$_3$ can be formed as a metastable phase through a phase transition from $P6_{3}/mmc$ to $P6_{3}cm$, provided that the criterion for forming the critical nucleus is fulfilled, whereas unformed in the contrary case, because the perovskite phase is absolutely stable. This result fulfilled the criterion for forming the critical nucleus of the metastable phase. In fact, our previous experiment of real-time measurement of X-ray diffraction during rapid solidification into undercooled melt of REFeO$_3$ (RE: Y and Lu) using the synchrotron orbital radiation (SOR) showed that the diffraction peak peculiar to the $P6_{3}cm$ phase has never been observed at the recalescence stage, although the solidified phase is evidently $P6_{3}cm$ [14]. Considering that the definitive difference in XRD patterns of $P6_{3}cm$ from that of $P6_{3}/mmc$ is the existence of the diffraction peak with high intensity at $d$-0.6 nm. Therefore, the initial phase formed during recalescence is

Figure 9. Schematical presentation for stabilities of $o$-REFeO$_3$ and $h$-REFeO$_3$ phases. If $TF$ deviates from the critical value, the stability of $h$-REFeO$_3$ phase decreases. However, in the case that $TF < 0.87$, $h$-REFeO$_3$ phase can be formed, whereas unformed in the contrary case, because the perovskite phase is absolutely stable there.

Figure 10. Relation between renormalized volume of unit cell and $TF$ for both perovskite and hexagonal series [18].
expected to be not the $P6_{3}cm$ phase but the $P6_{3}/mmc$ phase. The experimental results showed that the $h$-GdFeO$_3$ phase is formed because $TF$ of which is 0.867. Whereas, the $h$-EuFeO$_3$ is not formed because of slightly high $TF$ of 0.871. This suggests that the aforementioned condition expressed by Eq. 3 is to be the criterion for the metastable $h$-REFeO$_3$ phase to be formed.

Decrease of $P_0_2$ extends the range of $TF$ for metastable $h$-REFeO$_3$ phase to be formed as shown in Fig. 7. Decrease of $P_0_2$ increases the amount of Fe$^{2+}$ (0.078 nm for CN=6) with larger ionic radius than that of Fe$^{3+}$ (0.0645 nm for CN=6), resulting in decrease of $TF$.

Figure 10 shows the relation between renormalized volume of unit cell and $TF$ for both perovskite and hexagonal series [18]. Nearly linear relationship was obtained. This means that $TF$ remains a relevant parameter for the hexagonal structures.

5. Concluding remarks
Using REFeO$_3$ (RE: rare-earth element) as a model material, containerless solidification for forming a metastable phase from undercooled melts was carried out as a function of $P_0_2$ (oxygen partial pressure). Based on the geometrical consideration on the ionic radii of constituent ion, RE$^{3+}$, Fe$^{3+}$ and O$^{2-}$, it was derived that the criterion for metastable hexagonal phase is also expressed by tolerance factor, $TF$

$$TF < 0.87.$$ 

Experimental result well agreed with this criterion under reduced $P_0_2$ as well as in ambient one.

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