

# METASTABLE PHASE FORMATION FROM UNDERCOOLED MELT OF $\text{REFeO}_3$ (RE: RARE-EARTH ELEMENT)

Kazuhiko Kuribayashi<sup>1</sup>, Kosuke Nagashio<sup>1</sup>, Kenji Niwata<sup>2</sup>, M. S. Vijaya Kumar<sup>2</sup> and Taketoshi Hibiya<sup>2</sup>

<sup>1</sup>Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, 3-1-1, Yoshinodai, Sagami-hara, Kanagawa 229-8510, Japan

<sup>2</sup>Department of Aerospace Engineering, Tokyo Metropolitan University 6-6, Asahigaoka, Hino 191-0065, Japan

Received: March 29, 2008

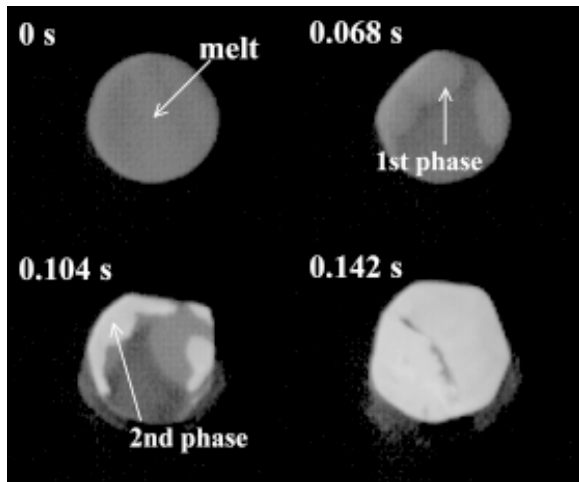
**Abstract.** For phase selection at rapid solidification into undercooled melts, the entropy-undercooling regime criterion in which a phase with a lower entropy of fusion preferentially nucleates has been proposed. To verify this criterion, real-time X-ray diffraction during rapid solidification of a deeply undercooled melt was performed on  $\text{REFeO}_3$  (RE: rare-earth element) using synchrotron radiation. The result shows that for  $\text{YFeO}_3$  the crystal structure of the phase formed at the first recalescence is hexagonal, and that at the second recalescence is orthorhombic. Thermogravimetry analysis shows that the hexagonal phase contains high deficit amounts of oxygen. Since the oxygen vacancies on the oxygen sub-lattice increase configurational entropy as well as vibrational entropy due to weighed phonon density of states in the acoustic region, the entropy of the hexagonal phase is concluded to be higher than that of the orthorhombic phase. This result is consistent with the prediction that the hexagonal phase with a lower entropy of fusion preferentially nucleates as a metastable phase at high undercooling.

## 1. INTRODUCTION

A metastable phase is not the most thermodynamically stable phase, but rather a temporary stable phase which can exist under certain conditions. In 1897, Ostwald [1] formulated a rule that the crystal phase nucleated from the melt is the phase closest in free energy to the liquid phase. Stranksi and Totomanov [2] reformulated this rule by stating that the phase initially formed is the one that has the lowest free-energy barrier of formation. In regards to free-energy barrier, classic nucleation theory [3] states that the activation energy to form a critical nucleus can be critically controlled by the interfacial free energy  $\gamma$  between the liquid and solid phases. Turnbull [4] first pointed out that the origin of  $\gamma$  is the entropy loss associated with the short-

range order that is built up in the liquid at the interface region. For simple liquids such as a monoatomic melt, Spaepen [5], and Spaepen and Meyer [6], based on the hard-sphere model, derived that  $\gamma$  is expressed in terms of a temperature-independent quantity  $\alpha$ , which is a scaling factor between the configuration entropy of the interface and the entropy of fusion  $\Delta S_f$ . In fact, recent numerical simulations of interfacial free energy using the Monte-Carlo or molecular dynamics techniques [7,8] predict that at the crystal-liquid interface, the atomic density profile continuously transforms from a periodic oscillation in a crystalline state to uniform density in the liquid state. However, in ionic crystals showing a faceted interface, the density profiles will be different from those of metallic

Corresponding author: Kazuhiko Kuribayashi, e-mail: kuribayashi@iasa.jaxa.jp



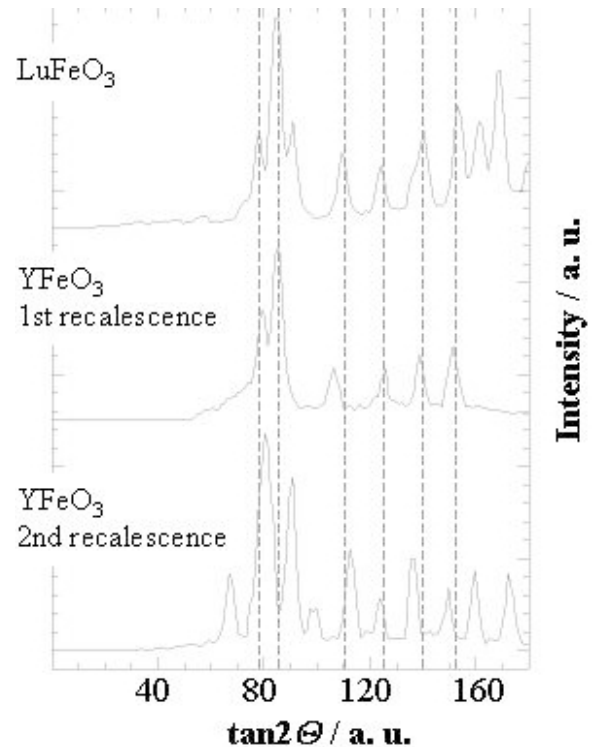
**Fig. 1.** Sequence of photographs taken at appropriate intervals during recrystallization in a sample of  $\text{YFeO}_3$  showing the so-called “double recrystallization”. The solid phase with a polyhedral shape that appears during the first recrystallization is the metastable phase. The second phase with a high contrast is the stable phase.

materials. They will steeply change to a uniform density of a liquid within a few layers. In this case,  $\alpha$  will be relatively small and insensitive to the crystal structure, where  $\gamma$  is induced to directly relate to  $\Delta S_f$  itself.

In accordance with this idea, Kuribayashi *et al.* [9] proposed the entropy-undercooling regime criterion for a metastable phase to directly nucleate in the undercooled melt. That is, the critical factor for forming a metastable phase is the ratio of  $\Delta S_f$  of a metastable phase to that of a stable phase; the smaller  $\Delta S_f$  facilitates the metastable phase to preferentially nucleate even at low undercooling. They performed the *in-situ* observation that the metastable phase nucleates in the undercooled melt of  $\text{REFeO}_3$ , where RE denotes rare-earth elements [10]. However, the crystal structure of the metastable phase was not identified. Hence, in the present study, real-time X-ray diffraction using 50 keV synchrotron radiation of SPring-8 is addressed and the criterion for the formation of the metastable phase is discussed.

## 2. EXPERIMENTAL

Spherical samples with a chemical composition of  $\text{YFeO}_3$  were levitated in an aerodynamic levitator



**Fig. 2.** X-ray diffraction profiles measured *in-situ* during first and the second recrystallization. The diffraction profile of  $\text{LuFeO}_3$  measured during the recrystallization is also shown for comparison. Each profile was linearly converted from the concentric 2D pattern.

(ADL) and heated by a continuous-wave  $\text{CO}_2$  laser. Oxygen was used as the levitation gas in order to reduce the deoxidization of  $\text{Fe}^{+3}$ . X-ray diffraction was performed at BL11XU in SPring 8, the size of the collimated monochromatic beam was  $\sim 1 \times 1 \text{ mm}^2$ . The details of the ADL and the X-ray diffraction system have been shown elsewhere [11–12].

The diffraction pattern was imaged by a 2D detector that consists of an X-ray image intensifier and a high-speed video camera (HSV) with  $512 \times 480$  spatial resolution operated at a sampling rate of 250 Hz.

## 3. RESULTS

Fig. 1 shows a sequence of photographs taken by HSV during the recrystallization, showing the so-called “double recrystallization”. During the first recrystallization, a solid phase with a polyhedral shape



**Fig. 3.** Result of thermogravimetry analysis (TGA) on the as-solidified sample of  $\text{LuFeO}_3$ . The initial mass of the sample is approximately 20 mg. Therefore, the fractional concentration vacancies on the oxygen sub-lattice in the as-solidified sample approximately amounts to 7% if the change of mass can be attributed to the oxidation of  $\text{Fe}^{+2}$  to  $\text{Fe}^{+3}$ .

appeared. The low contrast at the solid-liquid interface indicates that the net undercooling of the first phase is small. During second recalescence, however, another solid phase with high contrast appeared as if it replaces the first phase. The high contrast implies that the melting temperature of the second phase is much higher than that of the first phase. As previously reported [13], the first phase is the metastable phase that appears at undercoolings larger than the critical one.

Fig. 2 shows diffraction profiles of the samples measured during the first and second recalescences. For comparison, the diffraction profile of  $\text{LuFeO}_3$  measured during the recalescence in the deeply undercooled melt is also shown. Each diffraction profile was synthesized by integrating the intensities of the diffraction spots as a function of  $\delta$ , which is the distance between the spot and the centre of the diffraction pattern on the 2D detector. Since the spatial resolution of the 2D detector is too poor to absolutely determine the crystal structure, the phase identification was carried out comparing the synthesized profile with that of  $\text{LuFeO}_3$ . Furthermore, the profile at high diffraction angles of the metastable  $\text{YFeO}_3$  was omitted, because the time-interval between the first and the second recalescences was too short to integrate a sufficient number of diffraction spots at high diffraction

angles. The unit of the horizontal axis of the synthesized profile is expressed by  $\tan 2\theta$  ( $=\delta/L$ ,  $L$  - distance from the sample to the 2D detector).

During the first recalescence in  $\text{YFeO}_3$ , as indicated by the broken lines, the diffraction peaks at particularly low diffraction angles agree well with those of  $\text{LuFeO}_3$ . As already reported in the previous paper [10], the recalescences in  $\text{LuFeO}_3$  occur almost as a single step and the crystal structure of the sample solidified from the deeply undercooled melt is a metastable hexagonal one. Therefore the first recalescence of  $\text{YFeO}_3$  implies the formation of the metastable hexagonal phase.

#### 4. DISCUSSION

As shown in the previous section, the solid phase formed during the first recalescence in  $\text{YFeO}_3$  is the metastable hexagonal phase. According to the entropy-undercooling regime criterion, the entropy of the hexagonal phase must be higher than that of the equilibrium orthorhombic phase. In order to confirm this presupposition, thermogravimetry analysis (TGA) was carried out on the metastable hexagonal phase of  $\text{LuFeO}_3$ . During TGA measurements samples were heated at a heating rate of 20 K/s under an oxygen-rich environment. After the temperature reached 1623K, the heating power

was cut to allow samples spontaneously to cool to ambient temperature. Fig. 3 shows the relation between the change of mass and the temperature at heating and cooling stages. If the change of mass can be attributed to the oxidation of Fe<sup>+2</sup> to Fe<sup>+3</sup>, it can be deduced that the as-solidified sample contains oxygen vacancies on the oxygen sub-lattice. Since the mass of the sample is approximately 20 mg, the fractional concentration of the oxygen vacancies in the oxygen sub-lattice of the as-solidified sample is evaluated as approximately 7%. This amount is high enough for the configurational entropy of the system to increase. Furthermore, the deficit of light elements such as oxygen increases the fraction of the phonon density of states in the acoustic region [14], resulting in an increase in vibrational entropy.

## 5. CONCLUSIONS

Phase selection during rapid solidification from an undercooled melt, particularly in ionic materials showing a faceted interface, is controlled by the entropy-undercooling regime criterion. In order to verify this criterion, real-time X-ray diffraction using synchrotron radiation was carried out on REFeO<sub>3</sub> (RE: rare-earth element). In YFeO<sub>3</sub> showing double recalescence, the first recalescence corresponds to the formation of a metastable phase, the crystal structure of which is hexagonal, while the second recalescence corresponds to the equilibrium orthorhombic phase. Thermogravimetry analysis shows that the metastable phase contains high amounts of vacancies on the oxygen sub-lattice. The oxygen deficit increases configurational entropy and vibrational entropy due to the random distribution of vacancies on the oxygen sub-lattice, and increased phonon density of states in the

acoustic region, respectively. This is in good agreement with the entropy-undercooling regime criterion: the entropy of the metastable phase is higher than that of the one at equilibrium.

## REFERENCES

- [1] W. Ostwald // *Z. Phys. Chem.* **22** (1897) 282.
- [2] I. Stranski and D. Totomanov // *Z. Phys. Chem. A* **163** (1933) 399.
- [3] K. F. Kelton // *Solid State Physics* **45**, (1991) 75.
- [4] D. Turnbull, In: *Physics of Non-Crystalline Solids*, ed by J. A. Pines (North-Holland, Amsterdam, 1964), p. 41.
- [5] F. Spaepen // *Acta Metall.* **23** (1975) 729.
- [6] F. Spaepen and P. B. Meyer // *Scripta Metall.* **10** (1976) 257.
- [7] R. L. Davidchack and B. B. Laird // *Phys. Rev. Lett.* **85** (2000) 4751.
- [8] J. J. Hoyt, M. Asta and A. Karma // *Phys. Rev. Lett.* **86** (2001) 5530.
- [9] K. Kuribayashi and S. Ozawa // *J. Alloy Compd.* **408-412** (2006) 266.
- [10] K. Kuribayashi, K. Nagashio, K. Niwata, M. S. Vijaya Kumar and T. Hibiya // *Mat. Sci. Eng. A* **449-510** (2007) 675.
- [11] K. Nagashio, M. Adachi, A. Mizuno, M. Watanabe, K. Kuribayashi and Y. Katayama // *J. Appl. Phys.* **100** (2006) 033524.
- [12] K. Nagashio, K. Kuribayashi, M. S. Vijaya Kumar, K. Niwata, T. Hibiya and Y. Katayama // *Appl. Phys. Lett.* **89** (2006) 241923.
- [13] K. Nagashio and K. Kuribayashi // *J. Am. Ceram. Soc.* **80** (1997) 2550.
- [14] P. D. Bogdanoff and B. Fultz // *Phil. Mag. B* **79** (1999) 753.