The $\text{Yb}_2\text{O}_3$–$\text{Fe}_2\text{O}_3$ system was studied to investigate the effect of oxygen partial pressure on the formation of metastable phases over a wide range of oxygen partial pressures from $10^6$ to $10^{-1}$ Pa. Two kinds of metastable phases, with space groups of $P6_3cm$ and $P6_3/mmc$, were found through rapid solidification of an undercooled YbFeO$_3$ melt in an atmosphere with reduced P$_2$O$_5$. The crystal structure of the as-solidified samples changed from orthorhombic $\text{Phmn}$ to hexagonal $P6_3cm$ and $P6_3/mmc$ with decreasing P$_2$O$_5$. X-ray diffraction and scanning electron microscopic results confirmed the existence of various phases in the as-solidified samples. The stabilities of each phase were studied by annealing the bulk sample in the thermogravimetric–differential thermal analysis (TG-DTA) furnace up to 1673 K, and the equilibrium phase diagram was constructed for the Yb–Fe–O system at 1473 K. TG analysis showed an increase of the sample mass during annealing and revealed that the existence of Fe$^{2+}$, which has an ionic radius larger than that of Fe$^{3+}$, decreases the tolerance factor and therefore destabilizes the perovskite structure.

1. Introduction

A metastable phase is a phase that does not exist under equilibrium conditions. It is not the thermodynamically most stable phase, but rather a temporarily stable phase under certain conditions. Therefore, the formation of metastable phases opens a new way of searching for novel materials. Rapid solidification methods have been successfully applied to produce metastable solids from the molten state. Recently, we investigated the effect of oxygen partial pressure (P$_2$O$_5$) on metastable phase formation from an undercooled LuFeO$_3$ melt through containerless solidification, which provides large undercooling before nucleation and leads to the formation of metastable phases. Metastable phase formation from the undercooled melt has been reported, taking into consideration novel criteria, such as an entropy-undercooling regime and thermodynamic and kinetic conditions. These criteria suggest that the phase with the smaller entropy of fusion should nucleate preferentially. In the Lu–Fe–O system, hexagonal LuFeO$_3$ ($P6_3cm$) and Fe$^{2+}$–containing phases such as Lu$_2$Fe$_3$O$_7$ (r-R3m) and new hexagonal $\text{Lu}_2\text{Fe}_2\text{O}_5$ ($P6_3/mmc$) phases were obtained metastably with decreasing P$_2$O$_5$ from $10^3$ to $10^{-1}$ Pa. This suggests that metastable phase formation occurred due to the change of valence from Fe$^{3+}$ to Fe$^{2+}$ under reduced oxygen atmosphere.

Effect of Oxygen Partial Pressure on the Formation of Metastable Phases from an Undercooled YbFeO$_3$ Melt Using an Aerodynamic Levitator

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This clearly indicates that P$_2$O$_5$ plays an important role in the formation of metastable phases. Kimizuka and Katsura$^2$ have proposed that all ternary systems Fe–Fe$_2$O$_3$–R$_2$O$_3$ (where R represents rare-earth elements) can be divided into four groups with respect to the formation of thermodynamically stable ternary compounds at a certain temperature and oxygen partial pressure. It would be interesting to know whether this classification depends only on the size of rare-earth ions. According to this classification, the Fe–Fe$_2$O$_3$–Yb$_2$O$_3$ system belongs to the D type, in which four ternary compounds, i.e., YbFeO$_3$, YbFe$_2$O$_5$, Yb$_2$FeO$_3$, and Yb$_2$Fe$_2$O$_5$, exist as thermodynamically stable phases. The thermodynamic stabilities of these phases have been extensively studied at elevated temperatures, and phase diagrams were constructed at 1473 K under reduced oxygen partial pressure.$^{3,8}$ In the R–Fe–O system, metastable hexagonal RFeO$_2$ and RFe$_2$O$_4$ have been reported to exhibit ferroelectricity. For the system containing iron ions, oxygen nonstoichiometry will lead to the formation of defects combined with the valence state of iron ion, because the iron valence is strongly dependent on the oxygen partial pressure.$^{19–12}$

Goldschmidt$^{13}$ discussed the stability of the perovskite structure using the tolerance factor:

$$ t = \frac{R_A + R_O}{\sqrt{2}(R_A + R_O)} \quad (1) $$

Here, $R_A$ and $R_B$ are ionic radii of the rare-earth element and iron, respectively, and $R_O$ is the ionic radius of oxygen. Goldschmidt suggested that the perovskite structure becomes unstable and other phases can be enhanced as the ionic radii of the rare-earth elements decrease with increasing atomic number from La (0.103 nm) to Lu (0.0861 nm).$^{14,15}$ Hence, in our previous experiment using LuFeO$_3$ as a model material, the metastable hexagonal phases formed, even in the sample solidified at $10^3$ Pa. This result, however, indicates that the tolerance factor of LuFeO$_3$ is too small to investigate the influence of P$_2$O$_5$ on the stability of the perovskite structure. From this point of view, YbFeO$_3$, with a tolerance factor of 0.7850, is more suited than LuFeO$_3$ for investigation of the influence of P$_2$O$_5$ on metastable phase formation and stability of YbFeO$_3$ perovskite. An average ionic radii and "r" values of YbFeO$_3$–x are listed in Table I. The ionic radius of Yb$^{3+}$, Fe$^{3+}$, Fe$^{2+}$, and O$^{2-}$ were taken from Shannon.$^{14}$

The purpose of this study was to investigate the effect of oxygen partial pressure on the stability of the perovskite and the formation of metastable phases from an undercooled YbFeO$_3$ melt in the P$_2$O$_5$ range from $10^3$ to $10^{-1}$ Pa.

II. Experimental Procedure

(1) Sample Preparation

The Yb$_2$O$_3$ and Fe$_2$O$_3$ powders were weighed in the YbFeO$_3$ composition and melted by a CO$_2$ laser on a water-cooled cop-