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DyMnO₃ の過冷却凝固における六方晶 (*h*-LnMnO₃, Ln: Lanthanoid)と斜方晶 (*o*-LnMnO₃)の関係

Phase Selection between Hexagonal Phase and Orthorhombic Phase during Rapid Solidification from Undercooled Melt of DyMnO₃

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1. Introduction

Hexagonal LnMnO₃ (h-LnMnO₃, Ln: Lanthanoid, space group: $P6_3cm$) is known as a functional material because of the coexistence of ferroelectricity and (anti-) ferromagnetic in one phase. In LnMnO₃, it is reported[1-2] that the stable phase is h-LnMnO₃ for Ho to Lu, and orthorhombic LnMnO₃ (o-LnMnO₃, space group: $Pbnm$) for La to Dy. On the other hand, when a sample of LnMnO₃ is solidified from the undercooled melt, it is reported that in DyMnO₃, h-LnMnO₃ and o-LnMnO₃ coexist. However, the formation mechanism of the coexistence of h-LnMnO₃ and o-LnMnO₃ has not been revealed. In this study, we aimed to clarify the reason why h-LnMnO₃ and o-LnMnO₃ coexist in DyMnO₃ through establishing the phase diagram of Dy₂O₃-Mn₂O₃ system and controlling undercoolings.

2. Experimental procedure

The spherical samples of $Dy_{2(1-x)}Mn_{2x}O_3$ of 2 mm in diameter were prepared by melting mixture powders of Dy₂O₃ and Mn₂O₃ on a copper-hearth and melted using a semiconductor laser. The samples were melted and then solidified from the undercooled state by an aerodynamic levitation furnace (ADL) using oxygen gas. The temperature and the solidification process of the sample were recorded by a monocolor pyrometer and a high-speed video camera (HSV), respectively. The post-recalescence temperature was assumed to be the liquidus temperature of a related phase. The constitution phases of the sample were analyzed by a powder X-ray diffraction (XRD). The surface morphology and solidified microstructure were observed by a scanning electron microscope (SEM).

3. Results and discussion

Figure 1 shows the nucleation temperature(•) and liquidus temperature(•) of $Dy_{2(1-x)}Mn_{2x}O_3$ ($0.1 \leqq x \leqq 0.95$) nucleated spontaneously. XRD analysis identified the h-LnMnO₃ at $x = 0.4$, h-LnMnO₃ and o-LnMnO₃ at $0.45 \leq x \leq 0.5$, and o-LnMnO₃ single phase at $0.55 \leq x \leq 0.6$. **Figure 2** shows the relation between the intensity ratio of the $(002)_h$ of h-LnMnO₃ and the $(111)_o$ of o-LnMnO₃ as a function of undercooling. No single phase was obtained in samples of $x=0.5$ at any undercooling. On the other hand, in samples of $x=0.45$ h-LnMnO₃ single phase was obtained at $\Delta T < 80$ K and in samples of $x=0.55$ o-LnMnO₃ phase is predominant at $\Delta T > 150$ K. These results suggest that h-LnMnO₃ is the high temperature phase and o-LnMnO₃ is the low temperature phase. The coexistence of h-LnMnO₃ and o-LnMnO₃ in DyMnO₃ results from the

transformation of h-LnMnO$_3$ (high temperature phase) $\Leftrightarrow$ o-LnMnO$_3$ (low temperature phase). In addition, In the sample deviated toward Dy side from the stoichiometric composition, h-LnMnO$_3$ is preferentially formed due to the high eutectic temperature.
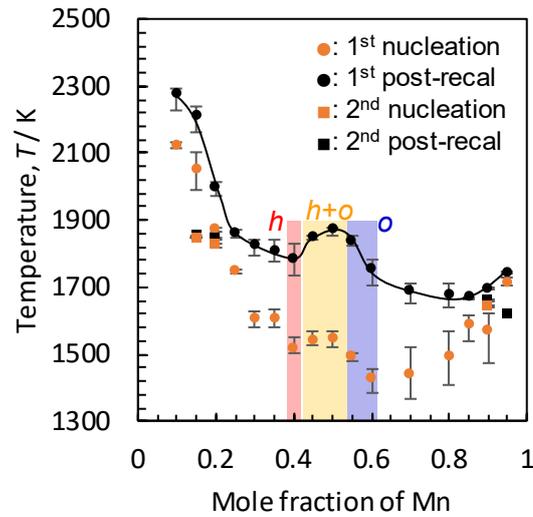
Fig. 1   Relation between liquidus temperature and nucleation temperature in Dy$_2$O$_3$-Mn$_2$O$_3$ system.
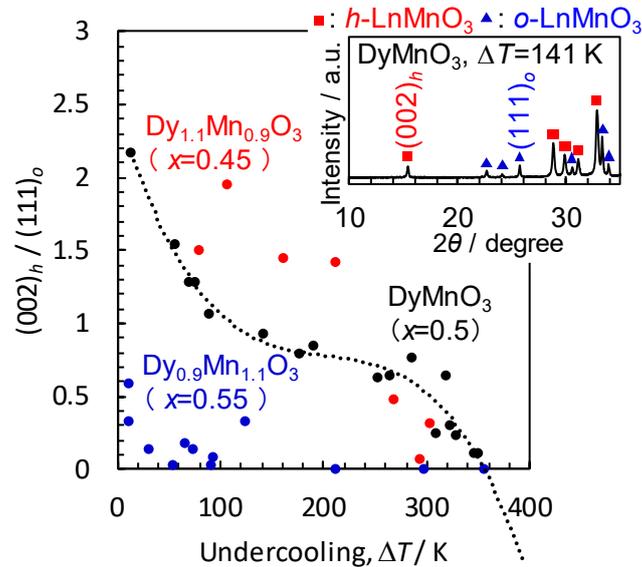
Fig. 2   Relation between undercooling and (002)h/(111)o

References

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