JASMAC
Conference of the Japan Society of Microgravity Application

P19

六方晶 DyMnO3 相における雰囲気酸素分圧とトレランス因子(*TF*)の関係

Relationship between ambient oxygen partial pressure and tolerance factor (*TF*) in hexagonal DyMnO3 phase

下村健太 [1]，栗林一彦 [2]，小澤俊平 [1]，
Kenta SHIMOMURA[1], Kazuhiko KURIBAYASHI[2], Shumpei OZAWA[1]
1 千葉工業大学，Department of Advanced Materials Science and Engineering, Chiba Institute of Technology
2 千葉工業大学附属研究，Research Liaison Centre, Chiba institute of Technology

1. Introduction

Hexagonal $DyMnO_3$ phase (*h*-$DyMnO_3$，space group: *P*6₃*cm*) is known as a functional material because of the presence of ferroelectricity and (anti) ferromagnetism in one phase. The structural stability of *h*-$DyMnO_3$ can be evaluated by the following tolerance factor (*TF*) (1) using ionic radius of composed element, r_i.

$$TF = \frac{r_{\mathrm{Dy}} + r_{\mathrm{O}}}{\sqrt{2}(r_{\mathrm{Mn}} + r_{\mathrm{O}})} \qquad (1)$$

It has been reported that the reduction in valence from Mn^{3+} to Mn^{2+} results in oxygen deficiency followed by a formation of *h*-$DyMnO_3$ when ambient oxygen partial pressure (P_{O2}) is low[1-2], though stable phase of $DyMnO_3$ is orthorhombic $DyMnO_3$ (*o*-$DyMnO_3$, space group: *Pbnm*) [3].

In this study, we aimed to clarify the relationship between the *TF* and the reason why *h*-$DyMnO_3$ tends to be formed when the oxygen partial pressure is decreased.

2. Experimental procedure

Powders of Dy_2O_3 and Mn_2O_3 mixed in an agate mortar were melted on a copper hearth by using a semiconductor laser to form a spherical $DyMnO_3$ sample with a diameter of 2 mm. The spherical sample was melted and then solidified from the undercooled melt at levitation state by an aerodynamic levitation furnace using argon and O_2 gases. The temperature and solidification process of the sample was recorded by a monochromatic pyrometer and a high-speed video camera (HSV), respectively. The solidified samples were analyzed by powder X-ray diffractometer (XRD), scanning electron microscope (SEM) and thermogravimetric differential scanning calorimeter (TG-DTA).

3. Results

Figure 1 shows a typical example of the results of TG-DTA operated under high purity oxygen gas at $P_{O2} = 10^5$ Pa an as-solidified $DyMnO_3$ sample. The weight of the sample increases from at about 500 K and saturates at about 1200 K. The weight increment during heating is regarded as an increase in oxygen due to oxidation of Mn^{2+} to Mn^{3+}, corresponding to the amount of the oxygen deficiency. Assuming that the ratio of the radius between the oxygen vacancy and the oxygen ion as 0.6, the effective oxygen ionic radius was calculated. Table 1 shows oxygen deficiency, effective ionic radii of Mn and oxygen, and calculated *TF* of $DyMnO_3$.

Figure 2 shows the relationship between P_{O2} and *TF* in $DyMnO_3$. *TF* changes in proportion to P_{O2}. **Figure 3** shows the XRD profiles of $DyMnO_3$ samples solidified at various P_{O2}. Both *h*-$DyMnO_3$ (□) and *o*-$DyMnO_3$ (△) phases are identified in the sample solidified at $P_{O2} = 10^5$ Pa. However, the diffraction peaks for the *o*-$DyMnO_3$ (△) phase disappears when the P_{O2} is lower than 3.2×10^3 Pa. Further decrease in P_{O2} induces the formation of cubic MnO (*c*-MnO，space group: Fm3-m) (○),

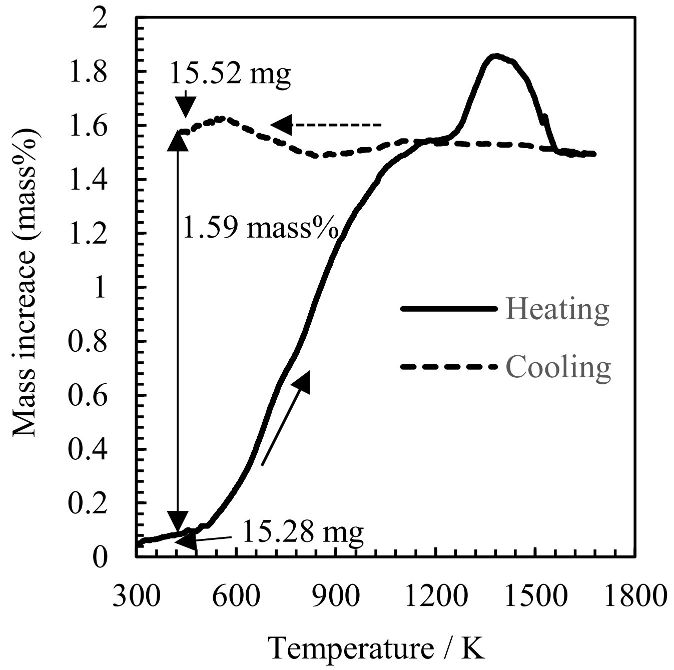

Fig. 1. TGA curve of the $DyMnO_3$ sample solidified at Po_2 of 10 Pa, carried out under high purity oxygen atmosphere

Table. 1. Oxygen deficiencies, average ionic radius, and *TF* of the as-solidified $DyMnO_3$ samples solidified under various Po_2

Po_2 (Pa)		1.0×10^5	3.2×10^3	1.0×10^3	10
O_2 deficiency (%)		0.2765	3.2020	4.5901	8.7931
Average ionic radius (nm)	**Mn**	0.0648	0.0681	0.0696	0.0743
	O_2	0.1372	0.1355	0.1344	0.1311
Tolerance Factor		0.7992	0.7875	0.7820	0.7654

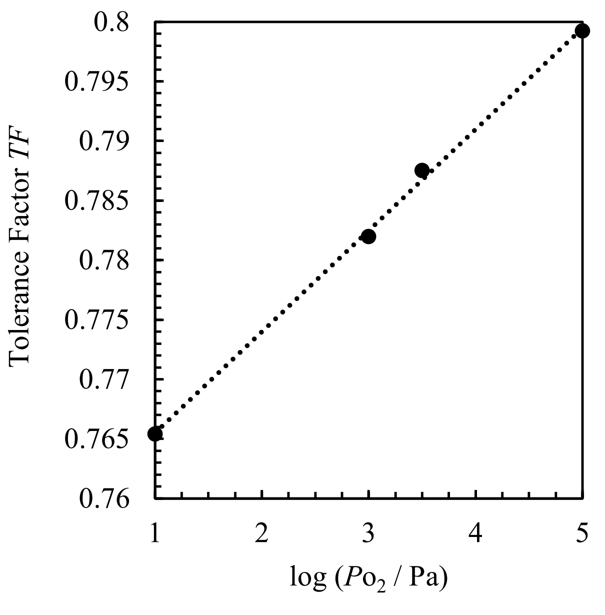

Fig. 2. TF of the as-solidified $DyMnO_3$ as a function of Po_2

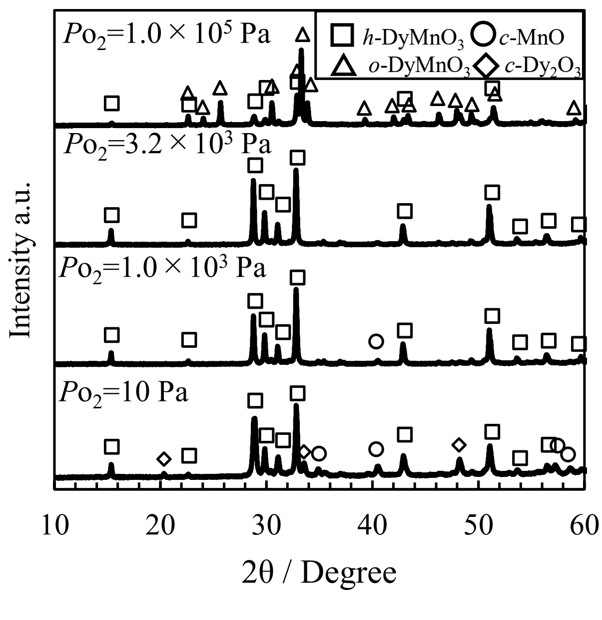

Fig. 3. XRD profiles of the as-solidified $DyMnO_3$

which would be attributed by the reduction in valence from Mn^{3+} to Mn^{2+}. When the P_{O_2} is decreased to 10^1 Pa, cubic Dy_2O_3 (c-Dy_2O_3, space group: la-3) (◇) is formed together with the h-$DyMnO_3$ and c-MnO.

Reference

1) M.S. Vijaya Kumar (2009). Formation and characterization of metastable phases in the R-M-O (R=La to Lu and Y; M=Fe and Mn) system under controlled oxygen partial pressure using containerless technique, Tokyo Metropolitan University Dissertation.
2) S. Harikrishnan, S. Rombler, C. M. N. Kumar, H. L. Bhat, U. K. Robler, S. Wirth, F. Steglich, S. Elizabeth: J. Phys. Condens. Matter, 21 (2009) 096002
3) A. A. Bosak, C. Dubourdieu, J. P. Senateur, O. Yu. Gorbenko and A.R. Kaul: *Crys. Eng.*, 5 (2002) 355-364.