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Synthesis and properties of a new complex oxide $Dy_2MnTa_{1+x}O_{7+\delta}$ with a pyrochlore-related structure

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Abstract

A new complex oxide with a pyrochlore-related structure $Dy_2MnTa_{1+x}O_{7+\delta}$ was synthesized from the oxides Dy_2O_3, Ta_2O_5 and Mn_2O_3 at 1523 K in air. The X-ray diffraction patterns could be assigned to a hexagonal symmetry. The lattice parameters are $a = 7.3917 \pm 0.0003$Å and $c = 17.1473 \pm 0.0009$Å. It is shown by thermogravimetric analysis that the nonstoichiometric phase of $Dy_2MnTa_{1+x}O_{1+\delta}$ exists stably over the range of oxygen partial pressure $1 \sim 10^{-21}$ atm at 1273 K. A magnetic measurement shows that the quaternary oxide $Dy_2MnTa_{1+x}O_{7+\delta}$ has a paramagnetic property and the valence numbers of dysprosium and tantalum are 3^+ and 5^+ respectively, while that of manganese includes 2^+, 3^+ and 4^+ depending on the oxygen nonstoichiometry. Semiconducting property was also observed from the results of electrical conductivity in the measured temperature range.

Keywords: Synthesis; Paramagnetism; Semiconductor; Pyrochlore; Phase stability

1. Introduction

The compounds with the pyrochlore-related structure and the general formula $A_2B_{2-x}B'_xO_7$ (where A = Ln (Ln = rare earth or Y); B = V, Fe, Co, Mn; $B' = W^{6+}$, Mo^{5+}, Nb^{5+}, Ta^{5+}) have been reported by several authors [1–10]. $Ln_2M_{1-x}W_xO_7$ with $x = 2/3$ and M = V, Fe, Mn [1–5], $Ln_2M_{1-x}Mo_xO_7$ with $x = 4/3$ and M = Fe, Co, Mn [6,8–10], and $Y_2Mn_{1-x}M'_xO_7$ with $x = 4/3$ and $M'_x = Nb^{5+}$, Ta^{5+} [7] were synthesized under low oxygen partial pressure.

It is of interest to synthesize new compounds with pyrochlore-related structure with other combinations of rare earth cations in the A position and manganese and other metal cations in the B and B′ positions respectively. The complex oxide Y_2MnTaO_7 with a pyrochlore-related structure was synthesized by Bazuev et al. [7]. According to them, this Y_2MnTaO_7 phase has a dark color and rhombohedrally distorted pyrochlore structure with lattice parameters $a = 14.80$Å and $c = 17.11$Å in the hexagonal representation. They measured several properties: the temperature dependence of magnetic susceptibility χ^{-1} for Y_2MnTaO_7 obeys the Curie–Weiss law in the temperature range $160 \sim 300$ K, and has a high specific resistance at 295 K. However, the investigation of other complex oxides in this Ln_2MnTaO_7 (Ln = rare earth) family have not been reported.

In this study, several trials to synthesize single phases of complex oxides Ln_2MnTaO_7 with pyrochlore-related structure using other rare earth cations were unsuccessful for the composition ratio of Mn:Ta = 1:1, since the products always include other phases. However, in the case of a combination of dysprosium and excess tantalum, a product with a nominal composition of $Dy_2MnTa_{1+x}O_{7+\delta}$ has been obtained as a single phase under the same synthetic condition. Since the detailed structure or defect structure of this compound is not known at present, a chemical formula like $Dy_2MnTa_{1+x}O_{7+\delta}$ is tentatively adopted in this paper corresponding to the nominal composition. The present paper describes a study of the condition for the formation of the Ta-excess compound, and furthermore, powder X-ray diffraction data and electrical and magnetic properties of $Dy_2MnTa_{1+x}O_{7+\delta}$ single phase are also described. The

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stability range of $Dy_2MnTa_{1+x}O_{7+\delta}$ phase against oxygen partial pressure was also established at 1273 K.

2. Experimental details

The starting materials were Dy_2O_3 with a purity of 99.99%, and Mn_2O_3 and Ta_2O_5 with a purity of 99.9% (Rare Metallic Co. Ltd.). In order to adjust stoichiometry and to dry, all of these starting materials were used after appropriate preliminary treatments as previously described [11,12]. The powders of the starting materials were thoroughly mixed in various Mn:Ta molar ratios. The polycrystalline ceramic samples were synthesized at 1523 K in air for 24 h.

The products were identified by powder X-ray diffractometry with Cu Kα radiation using a MAC MXP[18] powder X-ray diffractometer.

The stability range of $Dy_2MnTa_{1+x}O_{7+\delta}$ compound with respect to the oxygen partial pressure was determined by thermogravimetric analysis. Mixtures of Ar and O_2 gases were used for controlling higher oxygen partial pressures ($10^5 \sim 1$ Pa), and H_2 and CO_2 gases for lower oxygen partial pressures (less than 1 Pa). The detail of the apparatus has been described previously [12–14]. The samples were maintained for 10 ~ 12 h to attain equilibrium under each oxygen partial pressure at 1273 K. The weight losses were measured with the quenched samples. The electrical conductivity of the pellet was measured by the conventional direct current four-probe method in the temperature range 750 ~ 1300 K [13,15]. The magnetic susceptibility was measured by the Faraday method in the temperature range 77 ~ 600 K [16,17].

3. Results and discussion

When the specimen was synthesized at 1523 K in air with the Mn:Ta = 1:1 molar ratio, a second phase $DyMnO_3$ was observed. Therefore, in order to obtain a single phase, synthesis was tried by incrementally increasing the tantalum content under the same calcination condition. The results demonstrate that single phase $Dy_2MnTa_{1+x}O_{7+\delta}$ could be formed for only a limited range of x (the excess composition ratio of tantalum). $DyMnO_3$ appears as the second phase when x is less than 0.24, while $DyTaO_4$ is seen in the range where x is larger than 0.27, as shown in Fig. 1. Only when x is between 0.24 and 0.27 does the single phase $Dy_2MnTa_{1+x}O_{7+\delta}$ form. The color of the synthesized $Dy_2MnTa_{1+x}O_{7+\delta}$ single phase for $0.24 \leqq x \leqq 0.27$ is black.

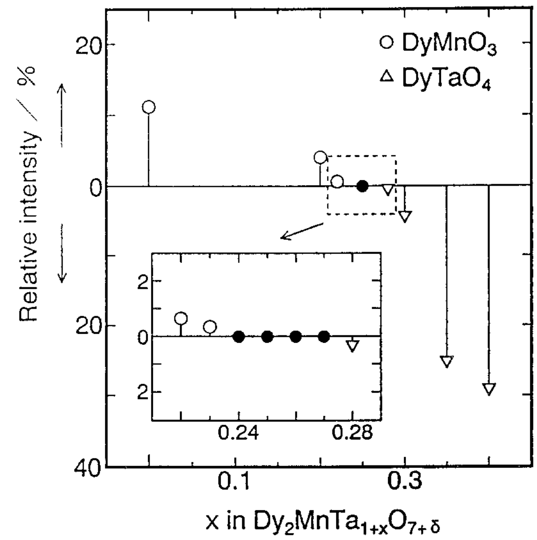

Fig. 1. Relative intensity of the peak of second phase in the powder X-ray diffraction patterns of $Dy_2MnTa_{1+x}O_{7+\delta}$ for various excess amounts x of tantalum.

The X-ray powder diffraction patterns of the synthesized $Dy_2MnTa_{1+x}O_{7+\delta}$ phase are similar to those of Y_2MnTaO_7 reported by Bazuev et al. [7]. The X-ray diffraction peaks can be indexed by hexagonal or rhombohedral symmetry, see Table 1; the lattice parameters of hexagonal crystal, calculated from the X-ray diffraction data, are $a = 7.3917 \pm 0.0003$ Å and $c = 17.1473 \pm 0.0009$ Å; for rhombohedral symmetry the lattice parameters correspond to $a = 7.1331 \pm 0.0002$ Å and $\alpha = 62.41 \pm 0.003°$. It should be noted that these lattice parameters are different from those of Y_2MnTaO_7 reported by Bazuev et al. [7]. The

Table 1
The X-ray diffraction data of $Dy_2MnTa_{1.25}O_{7.675}$ at room temperature in air

hkl		d_{obs} (Å)	d_{cal} (Å)	I/I_0 (%)
Hexagonal	(rhombohedral)			
2 0 2	(2 0 0)	2.999	2.999	100
0 0 6	(2 2 2)	2.858	2.857	28
0 2 4	(2 2 0)	2.565	2.565	39
2 2 0	($\bar{2}$ 2 0)	1.848	1.848	33
2 0 8	(4 2 2)	1.781	1.781	21
0 4 2	($\bar{2}$ 2 2)	1.574	1.573	13
2 2 6	(4 2 0)	1.552	1.552	22
0 2 10	(4 4 2)	1.512	1.512	10
4 0 4	(4 0 0)	1.500	1.499	8
0 0 12	(4 4 4)	1.429	1.429	2
0 4 8	(4 4 0)	1.282	1.282	5
4 2 2	($\bar{4}$ 2 0)	1.198	1.198	7
4 0 10	(6 2 2)	1.170	1.170	3
2 4 4	(4 $\bar{2}$ 2)	1.164	1.164	5
2 0 14	(6 4 4)	1.144	1.144	2
2 2 12	(6 4 2)	1.130	1.130	4
6 0 0	($\bar{4}$ 2 2)	1.067	1.067	3
4 2 8	(6 2 0)	1.053	1.053	4

Hexagonal parameters: $a = 7.3917 \pm 0.0003$ Å; c = 17.1473 ± 0.0009 Å; $c/a = 2.319$; $V = 811.359$ Å^3.
Rhombohedral parameters: $a = 7.1331 \pm 0.0002$ Å; $\alpha = 62.41 \pm 0.003°$; $V = 270.448$ Å^3.

lattice parameter *a* which is equal to half that of the hexagonal unit cell adopted by them, might be enough. The indices of X-ray diffraction peaks and transformation into rhombohedral crystal are also based on this kind of choice of the unit cell.

Various types of compound with pyrochlore-related structures are known, such as zirconolite [18–20], zirkelite [19–21] and others [19,20]. All these compounds possess BX_6 (B = metal cation, X = O, F) arrays arranged as hexagonal tungsten bronze (HTB) motifs. These structures were distinguished by the difference of the interlayer stacking vector and the intermodular stacking angle for HTB layers [18–23]. The *a* size of the unit of $Dy_2MnTa_{1+x}O_{7+\delta}$, especially, is nearly equal to those of zirkelite with trigonal symmetry. Therefore, trigonal symmetry should be considered as a possible structure in $Dy_2MnTa_{1+x}O_{7+\delta}$. Further study on the crystal structure of $Dy_2MnTa_{1+x}O_{7+\delta}$ phase is necessary.

To investigate the stability range of this phase, thermogravimetric analysis was carried out at 1273 K as a function of oxygen partial pressure as shown in Fig. 2. $Dy_2MnTa_{1.25}O_{7+\delta}$ phases did not decompose and existed stably over the range of oxygen partial pressure $1 \sim 10^{-21}$ atm (or even in H_2). The powder X-ray diffraction patterns of quenched samples of $Dy_2MnTa_{1.25}O_{7+\delta}$ after annealing under various oxygen partial pressures at 1273 K are shown in Fig.3. All the diffraction patterns show the isostructure and little change of the lattice parameters with oxygen partial pressure, which suggests that $Dy_2MnTa_{1.25}O_{7+\delta}$ phase has a wide range of oxygen nonstoichiometry. The lattice parameter *a* in the hexagonal settings slightly increases in the range $0.21 \sim 10^{-1.5}$ atm and then keeps almost constant with decreasing oxygen partial pressure; the lattice parameter *c* increases with decreasing oxygen partial pressure below 0.21 atm. Thus, *c*/*a* decreases in the range $0.21 \sim 10^{-1.5}$ atm and then an increasing tendency was seen with decreasing oxygen partial pressure. The volume of the unit cell increases slightly with decreasing oxygen partial pressure until 10^{-21} atm (Fig.4).

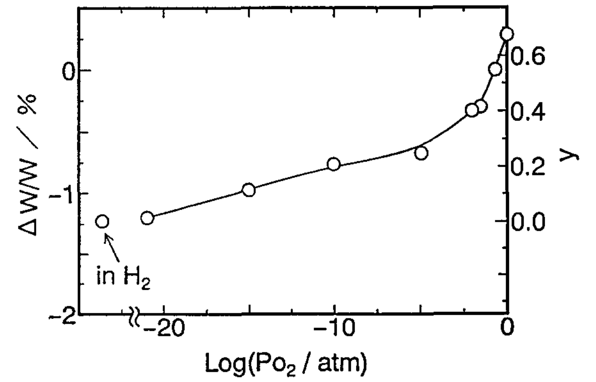

Fig. 2. Dependence of weight change of $Dy_2MnTa_{1.25}O_{7.125+y}$ on oxygen partial pressure at 1273 K and oxygen nonstoichiometry *y*.

From the weight change ($\Delta W/W_0$) and variation of the lattice parameters of $Dy_2MnTa_{1.25}O_{7+\delta}$ with oxygen partial pressure (Figs. 2–4), it is considered that a considerably wide range of oxygen nonstoichiometry exists in the $Dy_2MnTa_{1.25}O_{7+\delta}$ phase. In the present experiment, the standard point of stoichiometry is tentatively taken as the sample annealed in H_2 at 1273 K. When, under this condition, the valence of manganese is assumed to be 2^+, the oxygen nonstoichiometry of the sample annealed in air is $y = 0.55$, that is $Dy_2MnTa_{1.25}O_{7+\delta}$ can be expressed as $Dy_2MnTa_{1.25}O_{7.675}$. Thus it is considered that small amounts of Mn^{4+} are also included in this compound besides Mn^{3+}, Dy^{3+} and Ta^{5+}, although all the manganese ion in Y_2MnTaO_7 reported by Bazuev et al. was considered to be Mn^{3+} [7]. These valence states

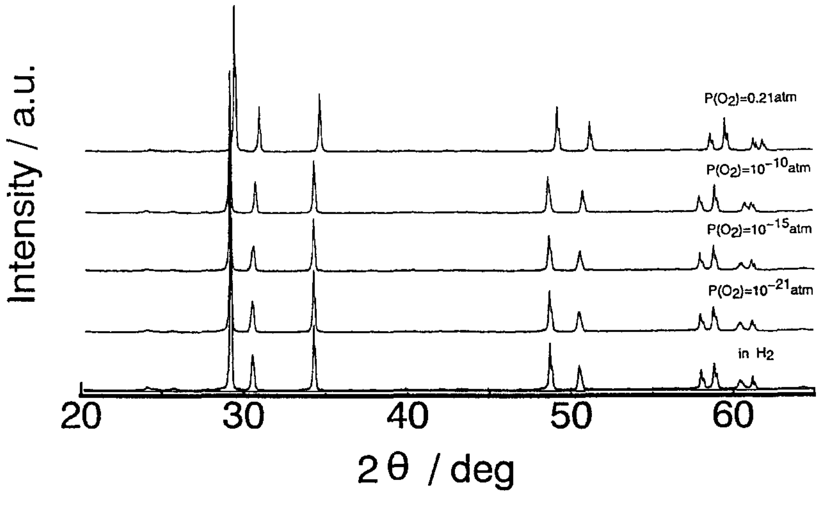

Fig. 3. Powder X-ray diffraction patterns of $Dy_2MnTa_{1+x}O_{7+\delta}$ after equilibration under various oxygen partial pressures at 1273 K.

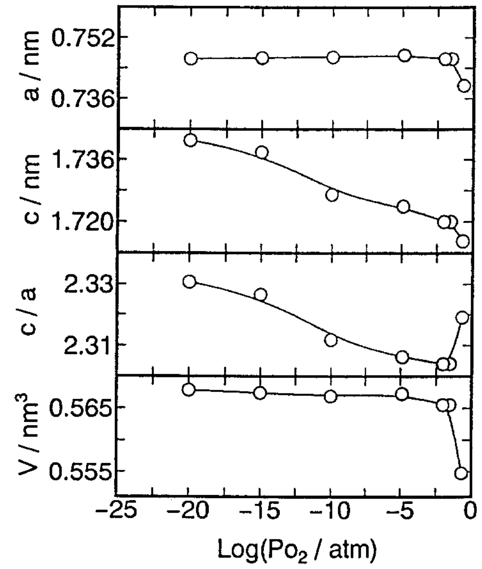

Fig. 4. Change of lattice parameter of $Dy_2MnTa_{1.25}O_{7.125+x}$, obtained in the hexagonal settings, with oxygen partial pressure at 1273 K.

in the composition $Dy_2MnTa_{1.25}O_{7.675}$ can be further supported from the magnetic measurement. The inverse magnetic susceptibility of $Dy_2MnTa_{1.25}O_{7.675}$ is given in Fig. 5 as a function of temperature. This figure shows that the linear relationship gives the Curie–Weiss law, and so this phase has paramagnetic behavior in the measured temperature range. The experimental value of the effective magnetic moment derived from the slope of the straight line in Fig. 5 is $\mu_{obs} = 15.70\ \mu_B$, and the theoretical value of the effective magnetic moment calculated by assuming Dy^{3+}, Ta^{5+}, Mn^{3+} (90%) and small amounts of Mn^{4+} (10%) in $Dy_2MnTa_{1.25}O_{7.675}$ is $\mu_{cal} = 15.78\ \mu_B$. The calculated and observed values are in fair agreement. Therefore, the assumption of the valence states of Dy^{3+}, Ta^{5+}, Mn^{3+} and small amounts of Mn^{4+} in $Dy_2MnTa_{1.25}O_{7.675}$ is reasonable.

Thus, the nonstoichiometric range extends from $Dy_2MnTa_{1.25}O_{7.802}$ under the highest oxygen partial pressure to $Dy_2MnTa_{1.25}O_{7.140}$ under the lowest oxygen partial pressure at 1273 K (derived from Fig. 2). These results show that the valence state of manganese ion in $Dy_2MnTa_{1+x}O_{7+\delta}$ phase varies continuously from divalent to trivalent or tetravalent, keeping Dy^{3+} and Ta^{5+} constant. The composition ratio of $Dy_2MnTa_{1.25}O_{7.675}$ in air can be expressed as $Dy_{1.824}Mn_{0.912}Ta_{1.140}O_7$ or $Dy_{1.778}Mn_{0.889}Ta_{1.111}O_{6.822}$, both of which show the defect-type pyrochlore structure. The former case also gives the possibility of $(Dy_{1.824}Ta_{0.052})(Mn_{0.912}Ta_{1.088})O_7$ with an A site defect type, while the latter gives A site and O site vacancies. As the difference in ionic size between dysprosium and tantalum is comparatively large, it is considered that the possibility that $Dy_2MnTa_{1+x}O_{7+\delta}$ phase is expressed in the latter is higher. According to this expression, the present compound is expressed as $Dy_{1.778}Mn_{0.889}Ta_{1.111}O_{6.346}$ under $P_{O_2} = 10^{-21}$ atm at 1273 K. This kind of large amount of oxygen defect is often observed in pyrochlore-related structures, such as $Sn_{2-2x}(Sn_xB_{2-x})O_{7-(5/2)x}$ [24], $Pb_{1+x}M_2O_{6+x}$ [25,26] and AB_2O_6 [27]. The dependence of isothermal electrical conductivity on oxygen partial pressure was also measured at 1273 K, see Fig. 6. A small positive dependence on oxygen partial pressure (the slope is about 1/32) is seen, which suggests a p-type character in this compound. The detailed defect structure from the above results should be resolved after the determination of the crystal structure of this phase.

The dependence of electrical conductivity of $Dy_2MnTa_{1.25}O_{7.625}$ on the reciprocal temperature is shown in Fig. 7. The electrical conductivity σ increases almost linearly with rising temperature in the range

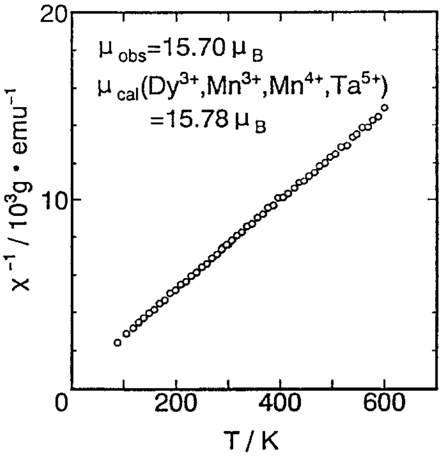

Fig. 5. Temperature dependence of the inverse magnetic susceptibility of $Dy_2MnTa_{1.25}O_{7.675}$ in air.

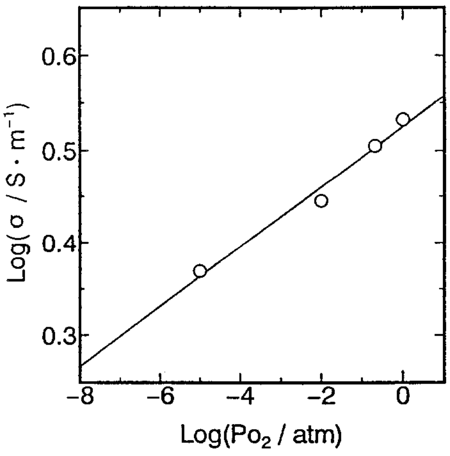

Fig. 6. Isothermal electrical conductivity of $Dy_2MnTa_{1.25}O_{7+\delta}$ as a function of oxygen partial pressure.

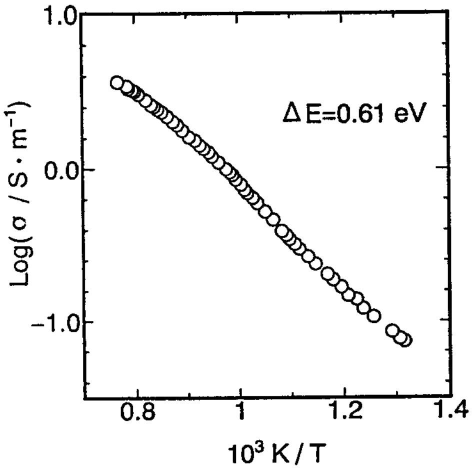

Fig. 7. Electrical conductivity of $Dy_2MnTa_{1.25}O_{7.675}$ as a function of reciprocal temperature in air.

750 ~ 1300 K. It is considered from this result that the compound $Dy_2MnTa_{1+x}O_{7+\delta}$ has semiconducting properties in the measured temperature range. The activation energy of the electrical conductivity calculated from Fig. 7 is 0.61 eV.

4. Conclusions

A single phase complex oxide $Dy_2MnTa_{1+x}O_{7+\delta}$ with a pyrochlore-related structure was synthesized in the range $x = 0.24 \sim 0.27$ of excess amount (mole) of tantalum in air at 1523 K. This new compound exists stably in a wide range of oxygen partial pressure at 1273 K. The electrical properties of $Dy_2MnTa_{1+x}O_{7+\delta}$ phase show semiconducting behavior in the temperature range 750 ~ 1300 K. The magnetic properties show paramagnetic behavior in the temperature range 77 ~ 660 K.

With regard to the structure of $Dy_2MnTa_{1+x}O_{7+\delta}$ phases, it is considered that there is a possibility of one of the polymorphic structures being related to the pyrochlore-type structure which includes stacking of the hexagonal tungsten bronze layer.

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