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Electrical conductivity of fluorite phases in the system Y_2O_3-Ta_2O_5-MgO

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Electrical conductivity of fluorite phases in the system Y_2O_3-Ta_2O_5-MgO has been studied. $Y_{0.8}Ta_{0.2}O_{1.7}$ fluorite phase, having 15 mol% oxygen ion vacancies, showed the maximum electrical conductivity. Electrical conductivity of $Y_{0.8}Ta_{0.2}O_{1.7}$ fluorite phase increased linearly with $P_{H_2O}^{1/2}$ due to the contribution of protonic conduction in water vapour. The electrical conductivity of the fluorite phase increased more remarkably at lower temperature, 700°C, than at higher temperatures, 800°C and 900°C. The obtained results imply that the protonic conduction greatly contributes to the electrical conductivity of the fluorite phases in the system Y_2O_3-Ta_2O_5-MgO in water vapour. © *2000 Kluwer Academic Publishers*

1. Introduction

The oxides of defect fluorite structure are generally solid oxide ionic conductors and are of interest for their applications to electrolytes of solid oxide fuel cells, electrolysers and gas sensors [1, 2]. In this fluorite structure, cations are in eightfold coordination with their nearest neighbors, and each anion is surrounded tetrahedrally by four cations [3]. There are also many oxides such as CeO_2, ThO_2 and UO_2 which have the fluorite structure. HfO_2 and ZrO_2 also retain the fluorite structure down to room temperature by formation of solid solutions with divalent cationic oxides such as MgO and CaO or trivalent cationic oxides such as Y_2O_3 [4, 5]. By doping the fluorite-type oxide with oxides whose cationic valences are less than those of the host cations, oxygen ion vacancies are produced, thereby achieving electrical neutrality in the substituted fluorite lattice [6]. The formation of the fluorite and other related structures in the system Y_2O_3-Ta_2O_5-MO (M = Mg, Ca, Sr or Ba) was reported by authors [7].

Iwahara *et al.* observed high protonic conductivity in $SrCeO_3$ at high temperatures by doping trivalent cations like Y, Yb, Sc etc. [8], and also reported that $CaZrO_3$ had gas stability and higher mechanical strength but its protonic conductivity was lower than $SrCeO_3$ [9]. Iwahara *et al.* also reported that $SrZrO_3$ had gas stability and almost unit proton transport number and therefore it became possible to be applied to practical usage [10]. Norby *et al.* observed protonic conductivity at high P_{H_2O} in C-type (cubic) rare earth metal oxides containing oxygen vacancies by doping divalent metallic oxides [11–13].

The protonic conductivity has been studied worldwidely in 1990s, however, protonic conductors so far reported are confined only to perovskite and C-type rare earth oxides [14–17]. The protonic conduction has not been observed yet in fluorite structure oxides.

Therefore, this study is concerned with the fluorite phases in Y_2O_3-Ta_2O_5-MgO system to investigate whether the protonic conduction contributes to the electrical conductivity of this system in water vapour, probably for the first time in fluorite structure. The research for the water vapour pressure effect on the electrical conductivity in the system Y_2O_3-Ta_2O_5-MgO may be helpful to explain the mechanism of contribution of the protonic conduction in this system.

2. Experiment

Y_2O_3 (Kojundo Co., purity $> 99.99\%$), Ta_2O_5 (Aldrich Co., purity $> 99.0\%$), and MgO (Kojundo Co., purity $> 99.9\%$) were used as the starting materials. To produce the fluorite phase $Y_{0.8}Ta_{0.2}O_{1.7}$ and other related fluorite phases in Y_2O_3-Ta_2O_5-MgO system, Y_2O_3, Ta_2O_5 and MgO powders were mixed according to exact molar ratios corresponding to the compositions of all required specimens and milled in an alumina mortar. The mixed powder was pressed into discs before heated at 1350°C for 24 h in air. The heat-treated discs were pulverized into powder and pressed into discs again. This process of heat treatment and pulverizing was repeated twice for homogenization of the compositions of the specimens. The pulverized powder was pressed into both bar-type and disc-type specimens and pressed isostatically under 20000 lb_f in^{-2}. The specimens were fired at 1650°C for 5 h and cooled down to room temperature at rate of 10°C min^{-1}. The specimens had the relative density of 91%. The prepared specimens were analysed by the X-ray powder diffraction method to confirm the formation of the fluorite phase. Electrical conductivity of the specimens of the fluorite phases was measured by the 4 probe method. To observe the effect of temperature and water vapour pressure on the electrical conductivity of $Y_{0.8}Ta_{0.2}O_{1.7}$ fluorite phase, both the temperature and the water vapour pressure P_{H_2O} were varied in a reducing atmosphere (Ar + 7% H_2 gas mixture) during the measurement of the electrical conductivity to exclude the interference of hole conduction.

3. Results and discussion

Fig. 1 shows the results of the electrical conductivity measurement for 8 mol% MgO doped and undoped $Y_{0.8}Ta_{0.2}O_{1.7}$ specimens, which were all identified as the fluorite single phases, in dry and wet air atmospheres. 8 mol% MgO-doped $Y_{0.8}Ta_{0.2}O_{1.7}$ specimen (17.8 mol% oxygen ion vacancy) showed lower electrical conductivity than the undoped one in both dry and wet air. It was reported that the solid solution of the fluorite single phase could be obtained by doping MgO to tetravalent metal oxides such as ZrO_2 [4] and HfO_2 [5]. In this case, oxygen ion vacancies are produced to meet the electroneutrality with the sites of divalent cations (Mg^{2+}) substituted for tetravalent cations [6], and the oxygen ionic conduction occurs through these vacancies at high temperatures. The fluorite phase was reported to be produced in $Y_{0.8}Ta_{0.2}O_{1.7}$-MgO system up to 12 mol% MgO addition [7].

As can be seen in Fig. 1, 8 mol% MgO-doped $Y_{0.8}Ta_{0.2}O_{1.7}$ fluorite specimen shows the lower electrical conductivity than the undoped one. There may be many factors which cause the electrical conductivity of 8 mol% MgO-doped $Y_{0.8}Ta_{0.2}O_{1.7}$ fluorite specimen to decrease. The excessive oxygen ion vacancies formed in oxygen ionic conductors by doping lower valent metallic ions was reported to be the main factor which decreased the electrical conductivity in ZrO_2-R_2O_3 system (R means the rare earth oxides) [18]. That is, the ionic conductivity increased as R_2O_3 was increasingly added up to a critical value because of the increase in oxygen ion vacancy. However, the ionic conductivity decreased when the addition of R_2O_3 exceeded the critical value [18]. Therefore, it is assumed that 8 mol% MgO may be an excessive doping to $Y_{0.8}Ta_{0.2}O_{1.7}$ fluorite phase because 8 mol% MgO-doped $Y_{0.8}Ta_{0.2}O_{1.7}$ fluorite phase specimen showed lower electrical conductivity than the undoped one as shown in Fig. 1.

For further understanding of the effect of concentration of the oxygen ion vacancy on the electrical conductivity of the fluorite phases in the system Y_2O_3-Ta_2O_5-MgO, the concentration of the oxygen ion vacancy was varied by preparing the specimens A, B, C, D, E and F of the various compositions of the fluorite phases in the Y_2O_3-Ta_2O_5-MgO system as shown in Fig. 2, which were all confirmed to be the fluorite phases in a previous study [7]. The effect of the concentration of oxygen ion vacancy on the electrical conductivity of the fluorite phases is represented in Fig. 3. As can be seen in Fig. 3, the specimen C ($Y_{0.8}Ta_{0.2}O_{1.7}$ phase), which has 15 mol% oxygen ion vacancies, shows the maximum conductivity. Other fluorite phase specimens, which have lower or higher concentrations of oxygen

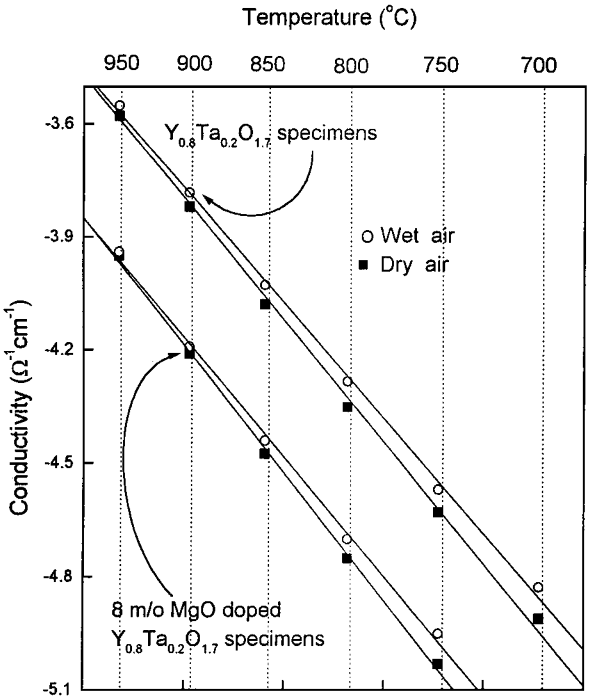

Figure 1 Electrical conductivity of $Y_{0.8}Ta_{0.2}O_{1.7}$ and 8 mol% MgO doped $Y_{0.8}Ta_{0.2}O_{1.7}$ fluorite phases in dry air and wet air saturated with water vapour at 25°C(P_{H_2O} = 0.031 atm).

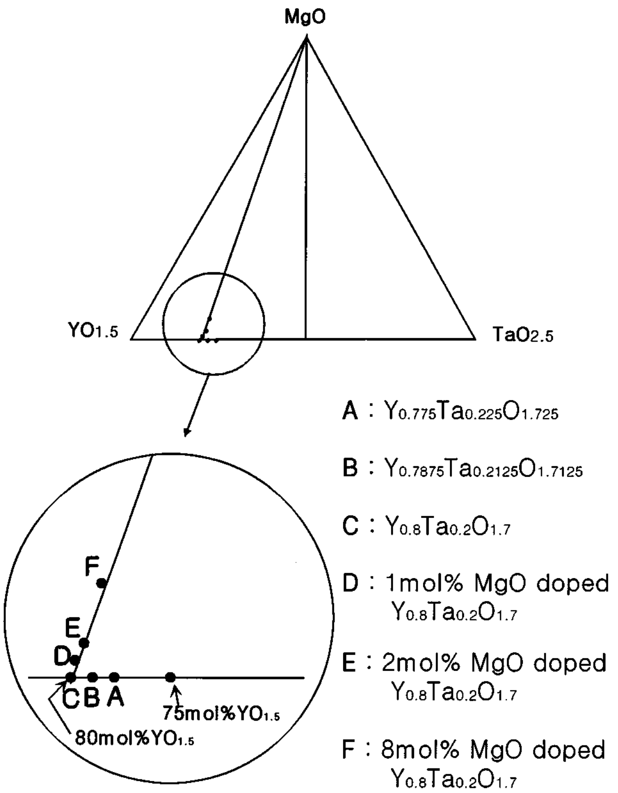

Figure 2 Fluorite phases A, B, C, D, E and F in Y_2O_3-Ta_2O_5-MgO ternary system.

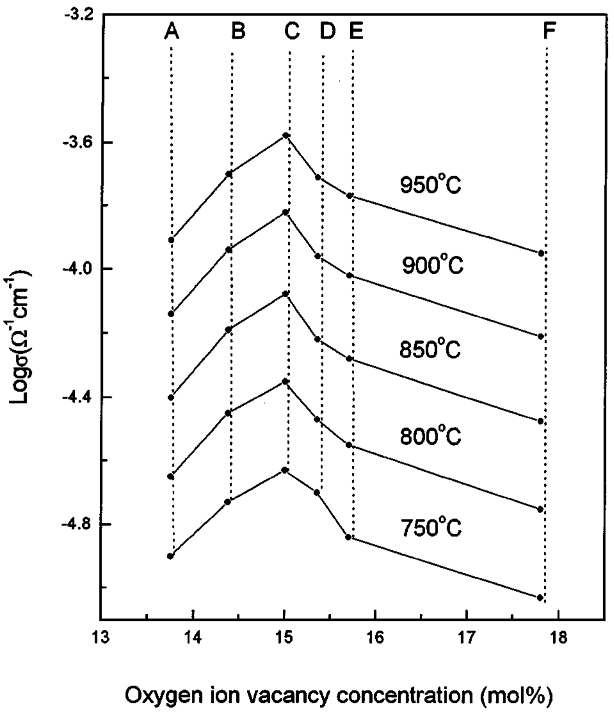

Figure 3 Electrical conductivity of fluorite phases A, B, C, D, E and F as a function of concentration of oxygen ion vacancy.

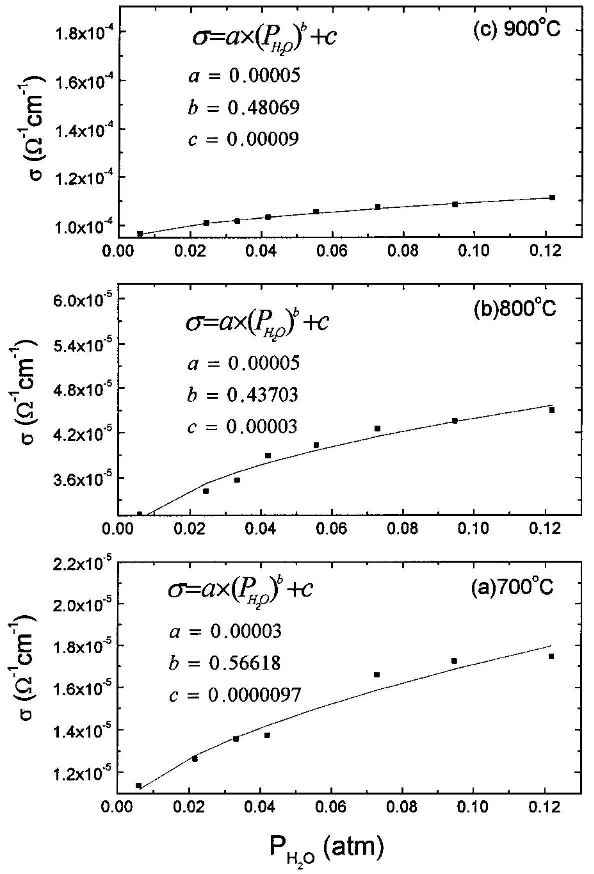

Figure 4 Effect of water vapour on electrical conductivity of $Y_{0.8}Ta_{0.2}O_{1.7}$ fluorite phases at various temperatures; (a) 700°C (b) 800°C and (c) 900°C.

ion vacancy than 15 mol%, show the lower conductivity than the specimen C. This means that 15 mol% is the optimum concentration of the oxygen ion vacancy in the fluorite phases in the system Y_2O_3-Ta_2O_5-MgO because the maximum electrical conductivity was observed at 15 mol% of the oxygen ion vacancy. The specimens A and B, the concentration of the oxygen ion vacancy of which is lower than 15 mol%, show the increase in the electrical conductivity with increase in the concentration of the oxygen ion vacancy. However, the electrical conductivity of the speciemns A and B is lower than that of the specimen C, $Y_{0.8}Ta_{0.2}O_{1.7}$ phase, due to the increase of the oxygen ion vacancies. On the other hand, the specimens D, E and F, the concentration of the oxygen ion vacancy of which is higher than 15 mol%, show the decrease in the electrical conductivity with increase in the concentration of the oxygen ion vacancy. The electrical conductivity of the specimens D, E and F is lower than that of the specimen C, probably due to the excessive oxygen ion vacancies. Thus, 15 mol% of the oxygen ion vacancy is assumed to be the critical value, showing the maximum electrical conductivity in the system Y_2O_3-Ta_2O_5-MgO.

Fig. 4 shows the electrical conductivity of $Y_{0.8}Ta_{0.2}O_{1.7}$ fluorite phase in the reducing atmosphere (Ar + 7% H_2 gas mixture) as the functions of water vapour pressure and temperature. Since $Y_{0.8}Ta_{0.2}O_{1.7}$ fluorite phase was reported to represent the hole conduction at high oxygen partial pressure [19], the electrical conductivity was measured in the reducing atmosphere (Ar + 7% H_2 gas mixture) to exclude the possible interference of the hole conduction. The electrical conductivity increased as the water vapour pressure increased, as shown in Fig. 4. This result may be due to the contribution of protonic conduction in $Y_{0.8}Ta_{0.2}O_{1.7}$ fluorite phase in the water vapour atmosphere. In addition, the curve-fitting of the relation between electrical conductivity and water vapour pressure shows that the electrical conductivity of $Y_{0.8}Ta_{0.2}O_{1.7}$ fluorite phase increases linearly with the root of the water vapour pressure, $P_{H_2O}^{1/2}$ as shown in Fig. 4. In water vapour atmosphere, however, protons may be produced by the reaction between water vapour and the defect fluorite structure of $Y_{0.8}Ta_{0.2}O_{1.7}$ by Equation 1.

$$H_2O + V_O^{\bullet\bullet} = O_O^{\times} + 2H_i^{\bullet} \qquad (1)$$

In $Y_{0.8}Ta_{0.2}O_{1.7}$ fluorite phase, negative defects formed by doping the lower valent cations to tetravalent cationic sites, Y_{M+4}^{+3} in this study, are compensated by positive defects like oxygen ion vacancies $[V_O^{\bullet\bullet}]$, electron holes $[h^{\bullet}]$ and protons $[H_i^{\bullet}]$ [20], resulting in Equation 2 to meet the electrical neutrality,

$$2[V_O^{\bullet\bullet}] + [h^{\bullet}] + [H_i^{\bullet}] = [Y'_M] = \text{constant} \qquad (2)$$

where $[Y'_M]$ is the concentration of Y^{+3} ions substituted for tetravalent cationic sites. In the region where both the oxygen and the water vapour pressures are very low as the case in this study, the oxygen ion vacancies are the dominant positive defects, and Equation 2 can be simplified to Equation 3,

$$2[V_O^{\bullet\bullet}] = [Y'_M] = \text{constant} \qquad (3)$$

In this case, it is quite possible that protons are easily produced by the reaction between water vapour and the oxygen ion vacancies $[V_O^{\bullet\bullet}]$ according to Equation 1.

If protons are produced by the reaction of Equation 1, the total electrical conductivity may increase because the mobility of the smaller protons are faster than that of the larger oxygen ions. In addition, the equilibrium constant of Equation 1 can be written as Equation 4,

$$\mathrm{K}_1 = \frac{[\mathrm{H}_\mathrm{i}^{\bullet}]^2[\mathrm{O}_\mathrm{O}^{\times}]}{P_{\mathrm{H_2O}}[\mathrm{V}_\mathrm{O}^{\bullet\bullet}]} \tag{4}$$

The protonic concentration can be written as Equation 5 by rearranging Equation 4,

$$[\mathrm{H}_\mathrm{i}^{\bullet}] = \mathrm{K}_1^{\frac{1}{2}} P_{\mathrm{H_2O}}^{\frac{1}{2}} [\mathrm{V}_\mathrm{O}^{\bullet\bullet}]^{\frac{1}{2}} [\mathrm{O}_\mathrm{O}^{\times}]^{-\frac{1}{2}} \tag{5}$$

Hence, it can be expected from Equation 5 that the proton concentration increases linearly with $P_{\mathrm{H_2O}}^{1/2}$. Actually, the measured electrical conductivity linearly increases in proportion to $P_{\mathrm{H_2O}}^{1/2}$, as shown in Fig. 4, implying that the increase in electrical conductivity with $P_{\mathrm{H_2O}}^{1/2}$ is due to the contribution of the protonic conduction. As can be seen in Fig. 4, the extrapolation of the curve fitting of σ against $P_{\mathrm{H_2O}}^{1/2}$ to zero water vapour pressure gives $\sigma = 8.91 \times 10^{-5}\ \Omega^{-1}\,\mathrm{cm}^{-1}$ ($\log \sigma = -4.05$) at the point of $P_{\mathrm{H_2O}} = 0$ and 900°C, which is very close to the electrical conductivity value $7.94 \times 10^{-5}\ \Omega^{-1}\,\mathrm{cm}^{-1}$ ($\log \sigma = -4.1$) which was measured in the pure oxygen atmosphere at 900°C by Kim [19], one of the authors. The increase in electrical conductivity with increasing the water vapour pressure is more remarkable at the lower temperature, 700°C, than at the higher temperatures, 800°C and 900°C, as can be seen in Fig. 4. This means that the reaction of Equation 1 is more active at the lower temperatures than at the higher temperatures. This is in good agreement with the fact that the equilibrium constant of Equation 4 increases with decreasing temperature [21]. Therefore, it can be said that the electrical conductivity of $\mathrm{Y_{0.8}Ta_{0.2}O_{1.7}}$ fluorite phase is greatly contributed by the protonic conduction in water vapour. $\mathrm{BaCeO_3}$ perovskite phases and rare earth oxides were also reported to represent the electrical conductivity contributed by protonic conduction [16, 20].

The electrical conductivity of 8 mol% MgO-doped and undoped $\mathrm{Y_{0.8}Ta_{0.2}O_{1.7}}$ fluorite phases measured in wet air saturated with water vapour at 25°C($P_{\mathrm{H_2O}} = 0.031$ atm) are exhibited in Fig. 1 together with the electrical conductivity measured in dry air. The electrical conductivity of both 8 mol% MgO-doped and undoped $\mathrm{Y_{0.8}Ta_{0.2}O_{1.7}}$ fluorite phases in air saturated with water vapour at 25°C($P_{\mathrm{H_2O}} = 0.031$ atm) was higher than that in dry air. The difference of the electrical conductivity between in wet air and in dry air becomes larger with decreasing temperature, as can be seen in Fig. 1. This implies that the protons are produced by the reaction of Equation 1 between the water vapour and the oxygen vacancies ($\mathrm{V}_\mathrm{O}^{\bullet\bullet}$), and these produced protons are considered to contribute greatly to the electrical conductivity. The proton moves more easily and faster than the oxygen ion because the proton is smaller than the oxygen ion. Hence, the activation energy for the protonic conduction is assumed to be smaller than that of the oxygen ion conduction. The activation energy values were measured from the Arrhenius plot of the electrical conductivity as shown in Fig. 1 and are given in Table I together with other reported values of the perovskite oxides [16] and the rare earth sesquioxides [22]. As given in Table I, the activation energy values of 8 mol% MgO doped and undoped $\mathrm{Y_{0.8}Ta_{0.2}O_{1.7}}$ fluorite phases in the wet air were 1.26 and 1.22 eV, respectively. Thus, the activation energy in dry air is consistently about 0.08 eV greater than that in wet air for all measurements, implying that the activation energy for protonic conduction is about 0.08 eV lower than that for oxygen ionic conduction in this system. Other reported values also show that the activation energy for protonic conduction is lower than that for oxygen ionic conduction.

TABLE I Activation energy values for 8 mol% MgO doped and undoped $\mathrm{Y_{0.8}Ta_{0.2}O_{1.7}}$ fluorite phases in wet and dry air are compared with other reported value for perovskites and rare earth sesquioxides

Composition	Wet air (protons) (eV)	Dry air (oxygen vacancies) (eV)	References
8 mol% MgO doped	1.26	1.34	This work
$\mathrm{Y_{0.8}Ta_{0.2}O_{1.7}}$	1.22	1.29	This work
5 mol% $\mathrm{NdO_{1.5}}$ doped $\mathrm{BaCeO_3}$	0.57	0.61	[16]
10 mol% $\mathrm{YbO_{1.5}}$ doped $\mathrm{BaCeO_3}$	0.54	0.58	[16]
20 mol% $\mathrm{GdO_{1.5}}$ doped $\mathrm{BaCeO_3}$	0.58	0.62	[16]
2 mol% CaO doped $\mathrm{Dy_2O_3}$	0.98	1.9	[22]
2 mol% CaO doped $\mathrm{GdErO_3}$	1.03	1.3	[22]
2 mol% CaO doped $\mathrm{Er_2O_3}$	1.04	2.5	[22]

Consequently, it can be said that the electrical conductivity of 8 mol% MgO-doped and undoped $\mathrm{Y_{0.8}Ta_{0.2}O_{1.7}}$ fluorite phases is greatly contributed by the protonic conduction in water vapour atmosphere.

4. Conclusions

Electrical conductivity of the fluorite phases in the system $\mathrm{Y_2O_3}$-$\mathrm{Ta_2O_5}$-MgO was studied and the results are summarized as follows:

1. $\mathrm{Y_{0.8}Ta_{0.2}O_{1.7}}$ fluorite phase, having 15 mol% oxygen ion vacancy concentration, showed the maximum electrical conductivity. The electrical conductivity of the other fluorite phases, having higher or lower oxygen ion vacancy concentrations than 15 mol%, showed lower values than that of the $\mathrm{Y_{0.8}Ta_{0.2}O_{1.7}}$ fluorite phase due to the excessive or deficient oxygen ion vacancy concentrations, respectively.
2. The electrical conductivity of $\mathrm{Y_{0.8}Ta_{0.2}O_{1.7}}$ increased linearly with the root of water vapour pressure, $P_{\mathrm{H_2O}}^{1/2}$. The increase in the electrical conductivity was larger at lower temperature, 700°C, than at higher temperatures, 800°C and 900°C. This implies that the protonic conduction contributes to the electrical conductivity of the fluorite phase $\mathrm{Y_{0.8}Ta_{0.2}O_{1.7}}$ in the existence of water vapour due to the formation of protons by the reaction of water vapour with oxygen ion vacancies in the fluorite phase.

3. The activation energy values of 8 mol% MgO doped and undoped $Y_{0.8}Ta_{0.2}O_{1.7}$ fluorite phases in the wet air were 1.26 and 1.22 eV, respectively, and these values were about 0.08 eV lower than those in the dry air for both phases.

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