

## Thermoelectric Properties of $Y_2Mo_2O_7$ -based Pyrochlore Solid Solutions

Hidero Unuma, Satoshi Kawasumi, Norio Kawamura,  
Kunio Watanabe and Michio Sugawara

Department of Chemistry and Chemical Engineering,  
Faculty of Engineering, Yamagata University  
4-3-16 Jonan, Yonezawa, Yamagata 992-8510, JAPAN  
Fax 81-238-26-3413, e-mail: unuma@yz.yamagata-u.ac.jp

As an attempt to search new *n*-type thermoelectric oxides, the Seebeck coefficient and the electrical conductivity of  $Y_2Mo_2O_7$ -based solid solutions were measured in a temperature range from 300 to 1100K.  $Y^{3+}$  was partly substituted with  $Ca^{2+}$  and  $La^{3+}$ , and  $Mo^{4+}$  was partly substituted with  $Ti^{4+}$ . All the samples showed *n*-type semiconductivity. Substitution of a part of  $Y^{3+}$  with  $Ca^{2+}$  increased both the Seebeck coefficient and the electrical conductivity. The highest power factor obtained was  $23 \times 10^{-6} \text{ W/mK}^2$ .

Key words: pyrochlore, oxide, *n*-type semiconductor, thermoelectricity

### 1. INTRODUCTION

Oxides of pyrochlore-type structure, expressed as  $A_2B_2O_7$ , are attracting attention as promising thermoelectric materials. One of the reasons is that the arrangements of A and B ions are those of "Kagome" structure which may cause spin frustration of electron leading to an enhancement of the Seebeck coefficient.

Although magnetic properties of pyrochlore-type oxides have been studied extensively, studies of thermoelectric properties have been scarce [1-3]. Subramanian et al. [1] measured the Seebeck coefficient and the electrical conductivity of a series of  $Ln_2Mo_2O_7$  ( $Ln = Sm-Yb, Y$ ) compounds and showed that some of those have the Seebeck coefficients ranging from about -2 to -35  $\mu\text{V/K}$  in a temperature range from 77 to 800 K with the electrical resistivity of several  $\text{m}\Omega\text{cm}$ . Iikubo et al. [2] reported that the Seebeck coefficient of  $Y_{2-x}Nd_xMo_2O_7$  pyrochlores lies in a range from 0 to -25  $\mu\text{V/K}$  below 300 K. Zhou et al. [3] reported that  $Ln_{2-x}Bi_xRu_2O_7$  ( $Ln = Nd$  and  $Yb$ ) solid solutions showed the Seebeck coefficients ranging from 20 to 40  $\mu\text{V/K}$ , the electrical resistivity ranging from 1 to 3  $\text{m}\Omega\text{cm}$ , and the highest power factor was  $0.8 \times 10^{-4} \text{ W/mK}^2$  at 1000K.

The thermoelectric properties cited above seem to be insufficient for practical use; the Seebeck coefficient has to be increased and the electrical conductivity has to be enhanced. In order to increase the Seebeck coefficient, a dilution of carrier concentration should be the first measure. For the enhancement of the electrical conductivity of pyrochlore compounds, an incorporation of large A cation is effective [1, 2, 4] probably because the expansion of the unit cell straighten the B-O-B bonding angle, by which the mobility of the carrier may increase.

Compared with the higher performance of *p*-type thermoelectric oxides, better *n*-type thermoelectric oxides have to be searched.

In the present work, starting from an *n*-type thermoelectric oxide,  $Y_2Mo_2O_7$ , we attempted to improve its performance through ionic substitution to enhance both the Seebeck coefficient and the electrical

conductivity. In  $Y_2Mo_2O_7$ , the electronic carrier originates from 4d electrons in  $Mo^{4+}$  [1].

### 2. EXPERIMENTAL

#### 2.1 Sample preparation

The compositions investigated in this work were  $Y_{2-x}La_xMo_2O_7$  ( $x = 0.1$  and  $0.2$ ),  $Y_{2-x}Ca_xMo_2O_7$  ( $x = 0.1$  and  $0.2$ ), and  $Y_2Mo_{2-x}Ti_xO_7$  ( $x = 0.1$  and  $0.2$ ).

The sintered samples were prepared according to Sato and Greedan [4]. Pertinent amounts of  $Y_2O_3$ ,  $La_2O_3$ ,  $CaCO_3$ ,  $MoO_3$ , and  $TiO_2$  (all analytical grade purity) were mixed, pressed into pellets at a pressure of 200MPa. The pellets were reaction-sintered at 1723 K for 6 hours in a flow of  $CO_2/CO$  (1:1) mixed gas.

#### 2.2 Characterization

X-ray diffraction analysis was conducted using  $CuK\alpha$  radiation. Seebeck coefficient and the electrical conductivity were measured in a temperature range from 350 to 1100 K in an Argon atmosphere.

### 3. RESULTS AND DISCUSSION

All the samples were single-phased solid solutions without any trace of impurity phases as examined by the X-ray diffraction, indicating that the ionic substitution was completed in the present composition range. Since the bulk density of the samples was around 60 - 65 %, independent on the composition, the effect of the bulk density on the electrical conductivity may be neglected.

Fig. 1 shows the temperature dependence of the Seebeck coefficient, the electrical conductivity and the power factor of  $Y_{2-x}La_xMo_2O_7$  solid solutions. The Seebeck coefficient was not affected by the incorporation of  $La^{3+}$ , while the electrical conductivity increased with increasing  $La^{3+}$  content. Since the ionic radius of  $La^{3+}$  in 8-fold coordinated site (130 pm) is larger than that of  $Y^{3+}$  (116 pm), the incorporation of  $La^{3+}$  resulted in an increase in the electrical conductivity. It has been demonstrated that an increase in  $La^{3+}$  content in  $Y_{2-x}La_xMo_2O_7$  solid solutions expands the unit cell [5].

Fig. 2 shows the temperature dependence of the Seebeck coefficient, the electrical conductivity and the

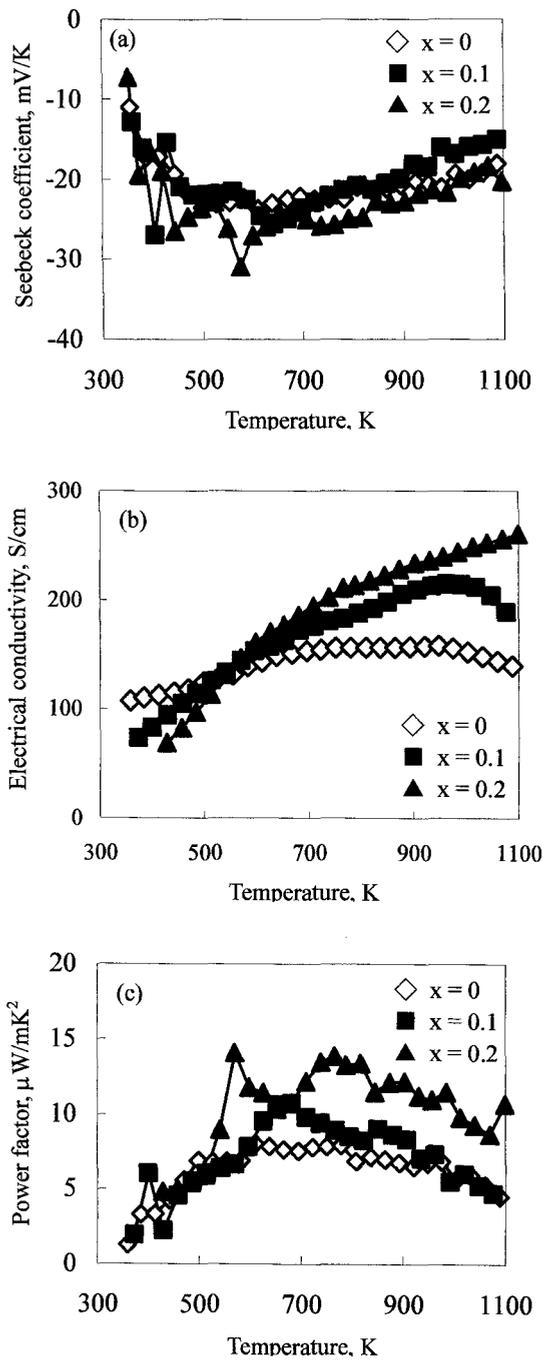


Fig. 1 Temperature dependence of (a) the Seebeck coefficient, (b) the electrical conductivity and (c) the power factor of  $Y_{2-x}La_xMo_2O_7$  solid solutions.

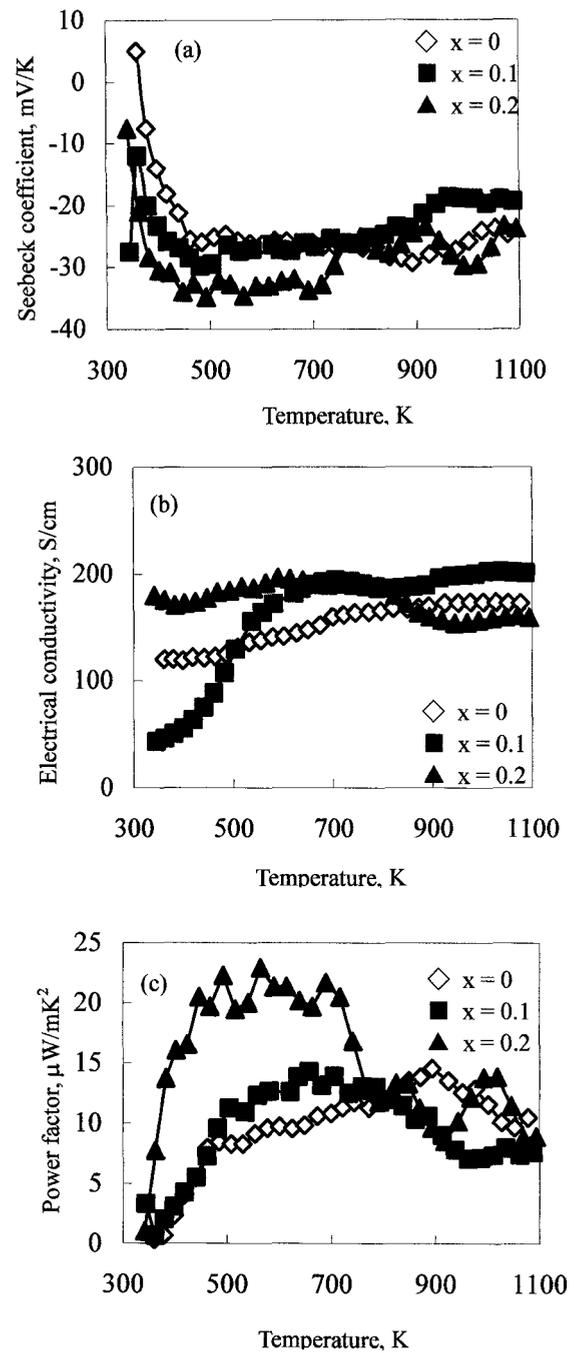


Fig. 2 Temperature dependence of (a) the Seebeck coefficient, (b) the electrical conductivity and (c) the power factor of  $Y_{2-x}Ca_xMo_2O_7$  solid solutions.

power factor of  $Y_{2-x}Ca_xMo_2O_7$  solid solutions. In the temperature range from 500 to 800 K, both the thermopower (the absolute value of the Seebeck coefficient) and the electrical conductivity increased.

The increase in the thermopower may be attributed to the decrease in the carrier concentration as follows; an incorporation of  $Ca^{2+}$  at an expense of  $Y^{3+}$  may require the creation of  $Mo^{5+}$  at an expense of  $Mo^{4+}$  to maintain the charge neutrality, and the an increase in the number of  $Mo^{5+}$  concentration means a decrease in the number of the available  $4d$  electrons as charge carriers.

In spite of the consideration of a decrease in the carrier concentration, the electrical conductivity was not deteriorated. That would be attributed to the expansion of the unit cell as large  $Ca^{2+}$  ion (126 pm) substitutes for  $Y^{3+}$  ion.

As a result of the increases in both the thermopower and the electrical conductivity, the power factor increased largely as shown in the figure (c). The highest power factor was  $23 \times 10^{-6} \text{ W/mK}^2$  between 500 and 700 K.

Fig. 3 shows the temperature dependence of the Seebeck coefficient, the electrical conductivity and the power factor of  $Y_2Mo_{2-x}Ti_xO_7$  solid solutions. By substituting  $Ti^{4+}$  with no  $d$  electron for  $Mo^{4+}$ , we aimed the decrease in the carrier concentration. As we expected, the thermopower increased with increasing  $Ti^{4+}$  content. However, the electrical conductivity was accordingly deteriorated. As the result, the power factor did not increase very much because of a drastic decrease in the electrical conductivity.

Consequently, in  $Y_2Mo_2O_7$ -based pyrochlore solid solutions, it was found to be possible to increase both the absolute value of the Seebeck coefficient thermopower and the electrical conductivity at the same time by substituting a part of  $Y^{3+}$  with an ion having a larger size and a lower valence. As an example, a partial substitution of  $Y^{3+}$  with  $Ca^{2+}$  was an effective measure.

The highest power factor obtained in this work, however, was still smaller than that reported by Zhou et al. for  $Ln_{2-x}Bi_xRu_2O_7$  pyrochlores, mainly because of the low electrical conductivity. The optimization of the composition and the increase in the bulk density should lead to better  $n$ -type thermoelectric pyrochlore-type oxides.

#### 4. SUMMARY

- (1)  $Y_2Mo_2O_7$ -based pyrochlore-type solid solutions were  $n$ -type semiconductors.
- (2) The incorporation of larger A site ions than  $Y^{3+}$  ( $Ca^{2+}$  and  $La^{3+}$ ) increased the electrical conductivity.
- (3) The incorporation of ions that may decrease the carrier concentration ( $Ca^{2+}$  for  $Y^{3+}$  and  $Ti^{4+}$  for  $Mo^{4+}$ ) increased the thermopower.
- (4) The incorporation of  $Ca^{2+}$  for a part of  $Y^{3+}$  improved both the thermopower and the electrical conductivity. As the result, the highest power factor was obtained for  $Y_{1.8}Ca_{0.2}Mo_2O_7$ , being  $23 \times 10^{-6} \text{ W/mK}^2$  between 500 and 700K.

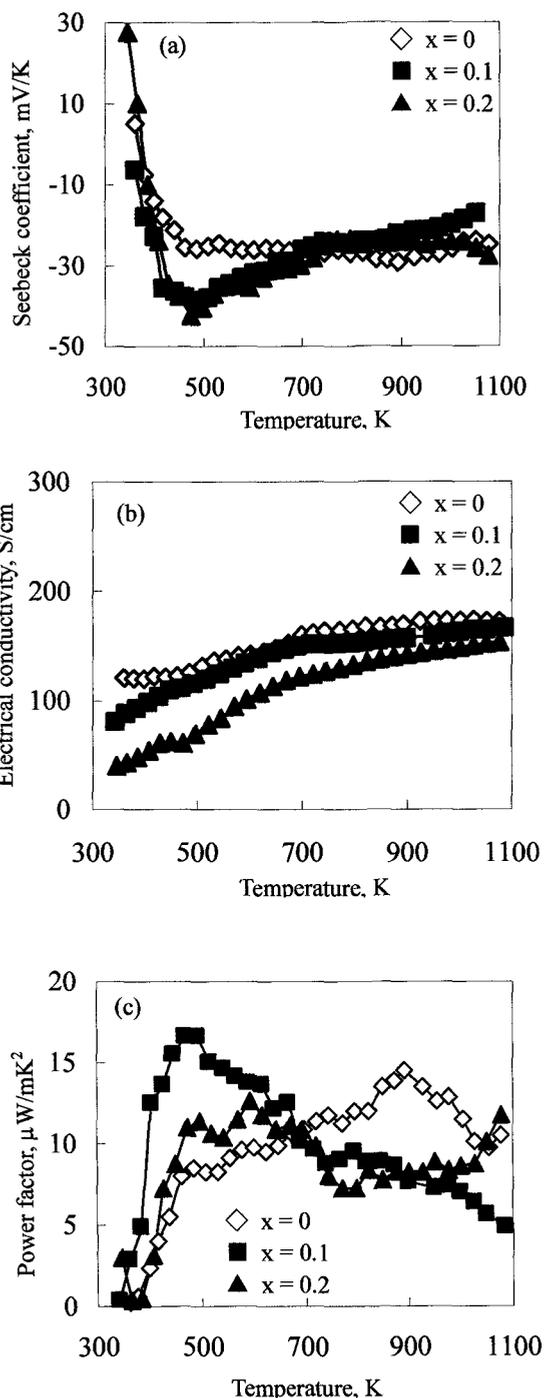


Fig. 3 Temperature dependence of (a) the Seebeck coefficient, (b) the electrical conductivity and (c) the power factor of  $Y_2Mo_{2-x}Ti_xO_7$  solid solutions.

#### REFERENCES

- [1] M. A. Subramanian, G. Aravamudan and G. V. Subba Rao, *Mater. Res. Bull.*, **15**, 1401-08 (1980).

- [2] S. Iikubo, S. Yoshii, T. Kageyama, K. Oda, Y. Kondo, K. Murata and S. Sato, *J. Phys. Soc. Japan*, **70**, 212-18 (2001).
- [3] Y. Zhou, I. Matsubara, R. Funahashi and S. Sodeoka, *Mater. Lett.*, **51**, 347-50 (2001).
- [4] J. E. Greedan, M. Sato, N. Ali and W. R. Datars, *J. Solid State Chem.*, **68**, 300-06 (1987).
- [5] M. Sato and J. E. Greedan, *ibid.*, **67**, 248-53 (1987).

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