Neutron diffraction study on $PbMoO_4$-based oxide ion conductors

Shigeomi Takai, Takashi Furusho, *Kenich Oikawa,
**Takashi Kamiyama and Takao Esaka

Tottori University, *JAERI, **KENS

Koyama-cho Minami, Tottori, Tottori, 680-8552 Japan
*Tokai-mura, Naka-gun, Ibaraki, 319-1195, Japan
**High Energy Accelerator Research Organization, Oho, Tsukuba, Ibaraki 305-0801 Japan

Scheelite-type structured $PbMoO_4$ represents high oxide ion conduction at elevated temperatures when lead ions were partly substituted by lanthanum ions as $Pb_{1-x}La_xMoO_{4+x/2}$ or $Pb_{1-x}La_{2x/3}MoO_4$. Powder density measurements indicated that the both systems compensated the charge by forming oxide ion interstitials and cation vacancies, respectively. While the general features of the above systems resembled with those of $PbWO_4$-based oxide ion conductors, $Pb_{0.9}La_{0.1}MoO_{4.05}$ (x = 0.1 of the former system) exhibited particularly high oxide ion conductivity below 700°C. In the present study, TOF neutron diffraction experiments were carried out on $PbMoO_4$-based oxide ion conductors ($Pb_{1-x}La_xMoO_{4+x/2}$ and $Pb_{1-x}La_{2x/3}MoO_4$) and the refined structures were discussed comparing with the conduction properties.

Samples of $PbMoO_4$, $Pb_{1-x}La_xMoO_{4+x/2}$ (x = 0.1) and $Pb_{1-x}La_{2x/3}MoO_4$ (x = 0.1 – 0.3) were prepared by conventional solid sate reaction method. Samples were crushed, charged in a cylindrical vanadium holder and powder neutron diffraction experiments were carried out by using the TOF neutron diffractometer Vega at the pulsed spallation neutron facility KENS. The diffraction data were analyzed by Rietveld method using programs RIETAN (2001T and /or TN)1) assuming $I4_1/a$ symmetry.

The representative diffraction pattern for $PbMoO_4$ was shown in Fig. 1, from which the structure can be refined assuming scheelite-type. The results were tabulated in Table 1, which agreed well with the previous report2) including regular oxide ion position. With the lanthanum substitution, any drastic change in atomic position was not observed, while the lattice parameters, *a* and *c*, decreased for both substituted systems ($Pb_{1-x}La_xMoO_{4+x/2}$ and $Pb_{1-x}La_{2x/3}MoO_4$).

In $Pb_{1-x}La_xMoO_{4+x/2}$ (x = 0.1), occupation factor of regular oxide ion was slightly larger than unity when the refinement was performed allowing only oxide ion occupancy to vary and ignoring interstitials. This indicated that additional oxide ions were expected to be introduced. Since oxide ion interstitials were thought to occupy the 8*e* position of $I4_1/a$ (0 0 *z*) for the tungstate system ($Pb_{1-x}La_xWO_{4+x/2}$)3), the occupation factors of interstitials were calculated for various *z* to estimate the most probable localized position of interstitials in the present system ($Pb_{1-x}La_xMoO_{4+x/2}$). Fig. 2 shows the positional dependence of the occupation factors of oxide ion interstitials assuming that of regular oxide ion to be unity. Whereas the occupancy maxima were observed around *z* = 0.2 and 0.3, the tendency of which resembled with that of tungstate ($Pb_{1-x}La_xWO_{4+x/2}$), the calculated occupancy at the intermediate position between these two maxima remained positive value in contrast to the tungstate. Accordingly, the enhanced possibility for the interstitials to occupy at the interemediate position between the two peaks was estimated in $Pb_{1-x}La_xMoO_{4+x/2}$ comparing with $Pb_{1-x}La_xWO_{4+x/2}$. This indicated the much more frequent ionic jump between these maxima for molybdate, resulting in the enhancement in ionic conductivity.

For $Pb_{1-x}La_{2x/3}MoO_4$ system, the refined occupation factor of lead-site was reduced from unity, i.e. cation vacancy formation due to the lanthanum substitution was confirmed. The structural parameters gradually varied with the lanthanum concentration without any drastic change.

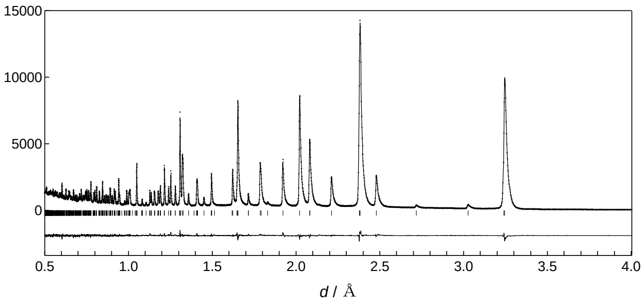

Fig. 1 Neutron diffraction pattern of $PbMoO_4$. (+): measured, solid line: calculated. Difference intensities are given at the bottom.

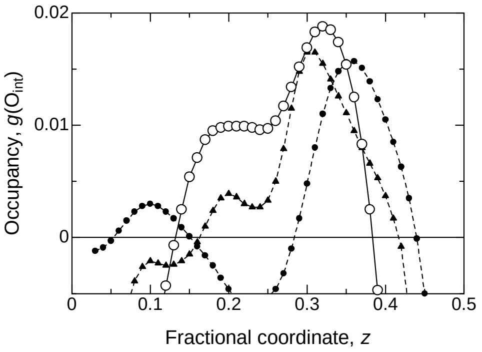

Fig. 2 Calculated occupation factors of oxide ion interstitials assuming 8*e* site of $I4_1/a$. ○: $Pb_{1-x}La_xMoO_{4+x/2}$ (x = 0.1), ● and ▲: $Pb_{1-x}La_xWO_{4+x/2}$ (x = 0.1 and 0.2).

Table 1 Refined structural parameters of $PbMoO_4$s.

	$PbMoO_4$	$Pb_{1-x}La_xMoO_{4+x/2}$	$Pb_{1-x}La_{2x/3}MoO_4$	
		x = 0.1	x = 0.1	x = 0.3
a / Å	5.43489(7)	5.42955(12)	5.43065(4)	5.41974(6)
c / Å	12.1053(2)	12.0973(3)	12.0887(1)	12.0630(2)
g_{Pb}	1	1	0.935(3)	0.891(4)
x_O	0.7644(1)	0.7639(2)	0.7638(1)	0.7622(2)
y_O	0.1365(1)	0.1354(1)	0.1360(1)	0.1365(2)
z_O	0.0809(1)	0.0811(1)	0.0808(1)	0.0813(9)
R_{wp}	3.40	4.52	4.16	5.02
S	1.41	1.89	1.79	1.51

References
1. T. Ohta, F. Izumi, K. Oikawa, T. Kamiyama, Physica B 234-236 (1997) 1093.
2. J. Leciejewicz, Z Kristallogr. 121 (1965) S. 158.
3. S. Takai, S. Touda, K. Oikawa, K. Mori, S. Torii, T. Kamiyama, T. Esaka, Solid State Ionics 148 (2002) 123.