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MLF Experimental Report	提出日 Date of Report 2011/07/01
課題番号 Project No. 2010A0068 実験課題名 Title of experiment Ordering and Stabilization of Pb- and Bi- Doped La2Mo2O9 実験責任者名 Name of principal investigator Shigeomi Takai 所属 Affiliation Tottori University	装置責任者 Name of responsible person Takashi Kamiyama 装置名 Name of Instrument/(BL No.) SHRPD / BL-08 実施日 Date of Experiment 2010/06/14 - 2010/06/16

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。(適宜、図表添付のこと)
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

$La_2Mo_2O_9$

$La_{2-x}Pb_xMo_2O_{9-x/2}$ (x = 0.01, 0.02, 0.03, 0.04, 0.05, 0.06)

$La_{2-x}Bi_xMo_2O_9$ (x = 0.02, 0.04, 0.06)

All samples were powder form.

2. 実験方法及び結果 (実験がうまくいかなかった場合、その理由を記述してください。)
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

Sample Preparation:

Pure- and substituted-$La_2Mo_2O_9$s were prepared by conventional solid state reaction method started from La_2O_3, MoO_3, PbO and Bi_2O_3 reagents. The mixtures of starting materials were calcined at 500°C, pressed into pellets under 200 MPa and then sintered at 1000°C. Crystalline phases of the obtained samples were checked by laboratory-scale X-ray diffraction and α-β phase transitions were confirmed by DSC.

Characterization:

XRD revealed that all samples represented α- or β- $La_2Mo_2O_9$ phases although the diffraction patterns of these two phases resemble each other. Thermal analyses indicated clearly the phase transition as shown in Fig. 1. While pristine $La_2Mo_2O_9$ represents sharp endothermic peak around 580°C.measured in the heating direction, the endothermic peak due to the phase transition depresses with Pb-substitution and completely disappeared around x = 0.05 or 0.06.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

Powder Neutron Diffraction:

Neutron diffraction patterns were collected at room temperature on the TOF neutron diffractometer "SHRPD" at J-PARC (BL-08). Typically 3 – 4 hours of data collection was performed for each sample with the amount of 12 – 13 g. Rietveld refinements were carried out using Z-code.

Fig. 2 shows the TOF-neutron diffraction pattern of $La_{2-x}Pb_xMo_2O_{9-x/2}$ (x = 0.06), which can be fitted by that calculated assuming cubic β-phase ($P2_13$) as illustrated in Fig. 3. Although, in the case x = 0.05, no apparent superstructural peak was detected in the diffraction pattern, Rietveld refinement cannot be made within the allowed range of profile parameters. Therefore, the cubic β-phase was found to be stabilized for x ≥ 0.06 down to room temperature as estimated by the conductivity measurements. The refined structure parameters were listed in Table 1. Oxide ion vacancies are mostly formed at O3 site as well as partially at O2, the tendency of which is the similar to other cubic $La_2Mo_2O_9$s substituted by various ions.

For Bi-doped $La_2Mo_2O_9$ system with cubic symmetry, similar results were obtained as tabulated in Table 2. Comparing the Pb- and Bi-doped samples, the occupation factor of O2 was slightly smaller in Pb-substituted sample with higher occupancy at O3. Higher vacancy concentration of O2 site in $La_{2-x}Pb_xMo_2O_{9-x/2}$ is supposed to account for the higher oxide ion conduction at relatively lower temperatures.

Structure analysis for monoclinic α-phase is now investigated.

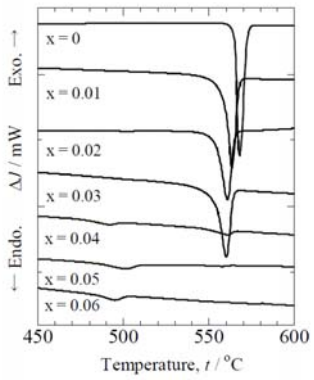

Fig. 1 DSC traces of $La_{2-x}Pb_xMo_2O_{9-x/2}$ measured in the heating direction.

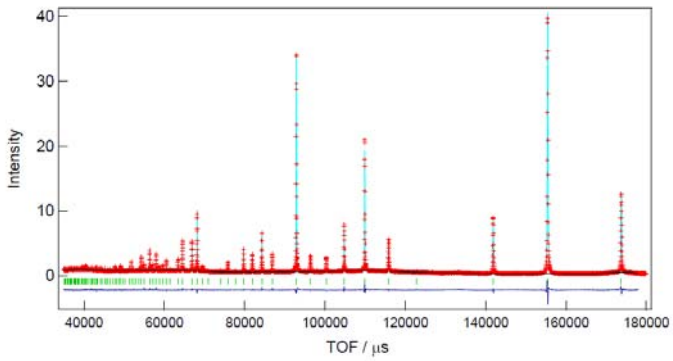

Fig. 2 Neutron diffraction pattern of $La_{2-x}Pb_xMo_2O_{9-x/2}$ (x = 0.06).

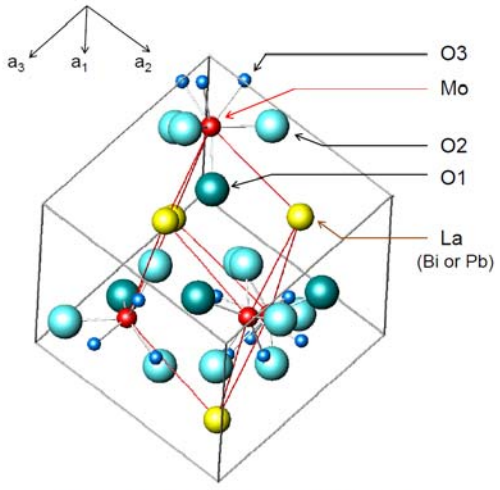

Fig. 3 Schematic view of cubic-$La_2Mo_2O_9$ (β-phase).

Table 1 Results of the Rietveld refinement of $La_{2-x}Pb_xMo_2O_{9-x/2}$ (x = 0.06).

Atom	Site	*g*	*x*	*y*	*z*
La / Pb	4*a*	0.97 / 0.03	0.8522(1)	0.8522	0.8522
Mo	4*a*	1	0.1669(1)	0.1669	0.1669
O1	4*a*	0.923	0.3135(2)	0.3135	0.3135
O2	12*b*	0.754	0.9899(2)	0.1794(4)	0.3446(3)
O3	12*b*	0.433	0.8889(7)	0.6707(1)	0.5585(3)

Note. a = 7.16376(5), R_{wp} = 5.0 %, S = 1.58

Table 2 Results of the Rietveld refinement of $La_{2-x}Bi_xMo_2O_9$ (x = 0.06).

Atom	Site	*g*	*x*	*y*	*z*
La / Bi	4*a*	0.97 / 0.03	0.8534(1)	0.8534	0.8534
Mo	4*a*	1	0.1671(1)	0.1671	0.1671
O1	4*a*	0.933	0.3137(2)	0.3137	0.3137
O2	12*b*	0.833	0.9883(2)	0.1767(3)	0.3421(3)
O3	12*b*	0.356	0.8982(2)	0.6518(2)	0.5587(2)

Note. a = 7.15926(4), R_{wp} = 5.5 %, S = 1.61