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SYNTHESIS AND SUPERSTRUCTURE OF $La_{2/3}(Mg_{1/2}W_{1/2})O_3$

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A new perovskite $La_{2/3}(Mg_{1/2}W_{1/2})O_3$ having an orthorhombic multiple-cell was synthesized. The lattice constants were a=7.8157(5) Å, b=7.8344(6) Å and c=2 × 7.9067(6) Å. The superstructure was found to be due to a NaCl-type ordering of B ions as well as an ordering of A-site vacancies.

An ordering of A-site vacancies in the perovskite structure has been found in $La_{1/3}NbO_3$ 1) and $La_{2/3}TiO_3$ 2). These two compounds have a unit of structure involving two perovskite subcells. In the previous work 3), a series of A-deficient solid solutions between $La_{1/3}NbO_3$ and WO_3 were found to exist over a wide range, having the ordered arrangement of A-site vacancies along the c-axis. Recently a phase for which the starting composition was $La_{2/3}(Mg_{1/2}W_{1/2})O_3$ was prepared. The X-ray analysis showed that this new compound was a perovskite phase with a complex superstructure. Attempts to synthesize the analogous Ni and Zn compounds were unsuccessful. $La_{2/3}(Mg_{1/2}W_{1/2})O_3$ is of interest for the structural investigation. The purpose of the present study was to examine the ordered distribution of cations and vacancies in this compound and to interpret the superstructure.

The title compound was prepared from reagents of La_2O_3, MgO and WO_3. The components were mixed in the stoichiometric molar ratio and then fired for 6 h each at 1200 and 1250 (twice) °C in air. The X-ray pattern was taken with a Philips diffractometer, using CuKα radiation and a proportional counter. No second phase was observed in the complex X-ray pattern. The reflections were measured at a scanning speed of (1/8)°/min and the Bragg angles were corrected with a silicon standard. The lattice constants were refined by the least-squares method 4). The observed intensities were measured by cutting out and weighing tracings of the peaks. The intensity computation was carried out according to a method previously reported. 5)

The X-ray diffraction data for $La_{2/3}(Mg_{1/2}W_{1/2})O_3$ are given in Tables 1 and 2.

The X-ray pattern is basically characteristic of the perovskite structure, and the line-splittings indicate an appreciable distortion from ideal cubic symmetry. The reflection intensities in Table 2 is considerably weak. Assuming that these reflections in Table 2 are ignored, all the reflections in Table 1 could be indexed on the basis of an orthorhombic cell with the dimensions a=7.8157(5) Å, b=7.8344(6) Å and

Table 1. X-ray data of major refections for $La_{2/3}(Mg_{1/2}W_{1/2})O_3$

hkl§	d_{obs}	d_{cal}	I_{obs}	I_{cal}	hkl§	d_{obs}	d_{cal}	I_{obs}	I_{cal}
001**	7.89	7.91	11.2	11.6	024	1.764	1.765	1.3	0.6
111*	4.52	4.53	46.7	37.7	204		1.764		
002	3.95	3.95	3.8	1.2	042	1.756	1.755		
020	3.91	3.92			402		1.752		
200		3.91			240	1.750	1.751		
021**	3.50	3.51	12.2	7.4	420		1.749		
201**		3.50			241**	1.707	1.710	3.7	1.9
022	2.778	2.783	100.0	100.0	421**		1.709		
202		2.780			224	1.608	1.608	39.8	40.7
220	2.764	2.767			242	1.599	1.601		
003**	2.633	2.636	2.2	0.9	422		1.599		
221**	2.609	2.611	2.4	3.4	043**	1.570	1.572	1.9	0.7
113*	2.377	2.379	24.2	24.0	403**		1.570		
131*	2.362	2.364			134**	1.544	1.545	0.5	0.5
311*	2.359	2.360			314**		1.544		
222	2.266	2.267	2.1	1.2	115*	1.521	1.521	9.2	8.7
023**	2.184	2.187	0.6	2.1	333*	1.511	1.511		
203**		2.185			151*	1.508	1.508		
004	1.976	1.977	34.0	32.5	511*	1.505	1.505		
040	1.957	1.959			025**	1.466	1.466	3.2	1.7
400	1.953	1.954			205**		1.466		
223**	1.908	1.908	6.5	2.7	243**	1.457	1.459		
041**	1.896	1.901			423**		1.457		
401**		1.900			044	1.390	1.391	16.5	20.0
133*	1.803	1.805	10.1	11.2	404		1.390		
313*		1.803			440	1.383	1.383		
331*	1.796	1.796							

§ Index hkl based on an orthorhombic doubled cell (a=7.8157 Å, b=7.8344 Å, c=7.9067 Å).

* Superstructure line due to a NaCl-type ordering.

** Superstructure line due to an ordering of A-site vacancies.

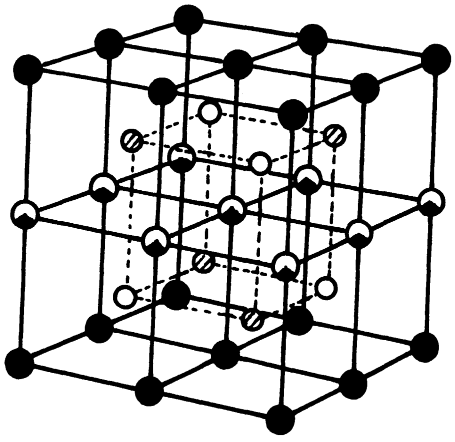
c=7.9067(6) Å. The cell dimensions suggest that a NaCl-type ordering of Mg^{2+} and W^{6+} ions occurs at the B-sites. In this case possible reflections have either all odd or all even indices. In fact, many of the observed reflections were consistent with the face-centered absence rule. As shown in Table 1, however, many reflections marked by double asterisks occur with only h+k=2n for (hkl) planes. This indicates that $\mathrm{La}_{2/3}(\mathrm{Mg}_{1/2}\mathrm{W}_{1/2})\mathrm{O}_3$ has a (001) face-centered lattice. Especially, the appearance of 001 reflection at about d=7.89 Å points to a doubling of the c-axis in the perovskite subcell, as found in $\mathrm{La}_{2/3}\mathrm{TiO}_3$2). Consequently the cation vacancies in $\mathrm{La}_{2/3}(\mathrm{Mg}_{1/2}\mathrm{W}_{1/2})\mathrm{O}_3$ are considered to occur only at two-thirds of the A-sites in alternate c-planes. Thus a superstructural model is proposed as shown in Fig. 1.

Next a doubling of the c-axis in the doubled-cell was found to be necessary to index the additional reflection in Table 2. $\mathrm{La}_{2/3}(\mathrm{Mg}_{1/2}\mathrm{W}_{1/2})\mathrm{O}_3$ comes to have a large multiple-cell of the size 2a' × 2b' × 4c', where a', b', c' refer to the perovskite subcell. In this case, all the reflections in Tables 1 and 2 obey a body-centered absence rule, h+k+l=2n. In addition, the conditions limiting possible reflections were h+l=2n for (h0l) planes and k+l=2n for (0kl) planes, respectively. So the probable space group is one of I222, $I2_12_12_1$, Imm2, Immm or Imma. The space group I222 is chosen from three-dimensional symmetry of B ions in the NaCl-type ordering. It is difficult, however, to visualize an ordered arrangement which requires a quadrupling of the c-axis in the perovskite subcell. As the additional

Table 2. X-ray data of additional reflections

hkl§	d_{obs}	d_{cal}	I_{obs}	hkl§	d_{obs}	d_{cal}	I_{obs}
011	7.01	7.03	4.0	031	2.570	2.577	0.6
101		7.01		301		2.571	
013	4.37	4.38	1.5	233	2.005	2.008	0.4
103		4.37		323		2.006	
121	3.42	3.42	2.4	235	1.787	1.790	0.5
211		3.42		325		1.789	
015	2.932	2.933	1.5	143	1.784	1.787	
105		2.932		413		1.784	
123	2.921	2.917		251	1.446	1.448	0.4
213		2.916		521		1.446	

§ Index hkl based on a further large multiple-cell (a=7.8157 Å, b=7.8344 Å, c=2 × 7.9067 Å) reflections in Table 2 were considerably weak, they probably arise from atomic displacement in the neighboring perovskite subcells. Thus the basic superstructure of $La_{2/3}(Mg_{1/2}W_{1/2})O_3$ is concluded to consist of the ordered arrangement as shown in Fig. 1. In order to confirm the proposed superstructure, the reflection intensities for $La_{2/3}(Mg_{1/2}W_{1/2})O_3$ were calculated on the basis of ideally close-packed positions and were compared with those observed. The effect of atomic displacements on intensity was ignored. However, a good agreement between observed and calculated intensities was obtained as shown on the right side of each reflection in Table 1. The reliability factor observed intensities of the 37 peaks was 0.13. Consequently the proposed superstructure seems reasonable in the rough approximation. The pycnometrically measured density of 6.67 g/cm^3 was in good agreement with the calculated value of 6.71 g/cm^3. This supports that this new compound has the chemical formula of $La_{2/3}(Mg_{1/2}W_{1/2})O_3$.



● : La^{3+} ion ○ : Mg^{2+} ion

◒ : vacancy or La^{3+} ion ⊘ : W^{6+} ion

Fig. 1. Superstructure of $La_{2/3}(Mg_{1/2}W_{1/2})O_3$. Oxygen ions are not shown.

In conclusion, $La_{2/3}(Mg_{1/2}W_{1/2})O_3$ is an ordered perovskite with the dimensions a=7.8157(5) Å, b=7.8344(6) Å and c=2 × 7.9067(6) Å. The multiple-cell consists of 16 perovskite subcells and the origin of basic superstructure is due to the NaCl-type ordering of Mg^{2+} and W^{6+} ions as well as the ordering of A-site vacancies along alternate c-planes. The space group probably is I222. This compound is the first representative of a new perovskite variant.

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