Cation Ordering in (NaLa)(MgW)O_6 with the Perovskite Structure

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The title compound with an ordered monoclinic (pseudotetragonal) perovskite structure has been prepared. The lattice constants are a=5.5239(5), b=5.5253(4), c=7.8936(6) Å, β=90.16(1)°, and Z=2. The superstructure was found to be due to a layer-like ordering of Na^+ and La^{3+} ions along alternate c-planes as well as a NaCl-type ordering of Mg^{2+} and W^{6+} ions in the octahedral sites. This new compound is the first example for the occurence of cation ordering in the A site. The origin of the superstructure was discussed.

There are many examples of ABO_3-type perovskites where cation ordering occurs in the B site when ions of different size and charge substitute for a single B atom. Generally, cation ordering is unlikely to occur in the A site. An ordering of A-site vacancies, however, has been found only in some compounds such as $La_{0.33}NbO_3$[1,2] and $La_{0.67}TiO_3$[3]. Recently we have reported that $La_{1.33}$(MgW)O_6 crystallized in an orthorhombically distorted perovskite structure, showing a NaCl-type ordering of B ions as well as an ordering of A-site vacancies along alternate c-planes.[4] Our attempt to prepare a new perovskite of (NaLa)(MgW)O_6 composition was successful. The X-ray diffraction pattern was highly similar to that of $La_{1.33}$(MgW)O_6 in general features. This new compound is therefore considered having a layer-like ordering of Na^+ and La^{3+} ions in the A site. This remarkable ordering phenomenon at the larger cation sublattice has been observed in the perovskite-related compounds (NaLn)TiO_4(Ln=lanthanoids.[5] The superstructure of Na^+ and La^{3+} ions may result in a poor charge compensation in the octahedral surroundings. The new compound (NaLa)(MgW)O_6 is challenging for a crystal chemical investigation. The purpose of the present work is to examine the cation distribution in this compound and to interpret the origin of the superstructure.

Experimental

The title compound was prepared from Na_2CO_3, La_2O_3, MgO and WO_3 of high purity. 2.5 Mol% of excess Na_2CO_3 was added to a stoichiometric composition for vaporization of Na_2O at elevated temperatures. The weighed batch was heated at 950 °C for 4 h in air. The reacted mixture was further ground, pressed into disks and reheated twice at 1100 °C for 6 hrs on a Pt foil in a closed alumina crucible. As shown in Fig. 1(a), the X-ray diffraction analysis of the product showed that the phase crystallized well and that it did not contain any additional compound. The reflections were measured at a scanning speed of (1/8)° 2θ/min and the Bragg angles were corrected with a silicon standard. The lattice constants were refined by the least-squares method.[6] The observed intensities were measured by cutting out and weighing tracings of the peaks. Infrared absorption measurements between 1200—250 cm^{-1} were made for powder specimens dispersed in a pressed KBr disk, using a Perkin-Elmer infrared spectrophotometer model 180.

Results and Discussion

The title compound (NaLa)(MgW)O_6 shows an X-ray powder pattern characteristic of the perovskite structure, as can be seen by comparison with that of a simple perovskite (NaLa)Ti_2O_6[7] in Fig. 1(b). The X-ray diffraction data for (NaLa)(MgW)O_6 are given in Table 1. The superstructural reflections marked by an asterisk arise from a NaCl-type ordering of Mg^{2+} and W^{6+} ions in the oxygen-octahedral sites. In addition to their reflections, extra reflections marked by double asterisks are observed in the X-ray powder pattern of (NaLa)(MgW)O_6. Various kinds of line-splitting phenomena indicate appreciable distortion from ideally cubic symmetry. All the reflections in Table 1 could be satisfactorily indexed on the basis of a monoclinic unit cell with β close to 90°. Its lattice constants were refined for selected 41 observed reflections by the least-squares method. This gave a=5.5239(5), b=5.5253(4), c=7.8936(6) Å, and β=90.16(1)°. The cell-edges are approximately $\sqrt{2}a'$ for the a- and b-axis and $2a'$ for the c-axis, where a' is the length of the perovskite-like subcell edge. Since the a and b dimensions are very nearly equal, the monoclinic unit cell is considered to be pseudotetragonal. The pycnometrically measured density of 6.46 g/cm^3 was in good agreement with the calculated value of 6.42 g/cm^3 for two formula units of (NaLa)(MgW)O_6 per cell. This result supports that the new compound has the chemical formula of (NaLa)(MgW)O_6.

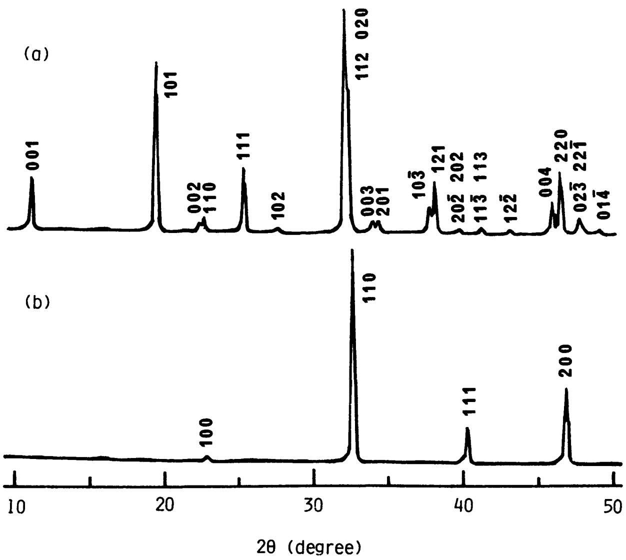

Fig. 1. X-Ray powder patterns of perovskites (NaLa)(MgW)O_6 (a) and (NaLa)Ti_2O_6 (b).

The reflections given in Table 1 show no systematic

Table 1. X-Ray diffraction data for $(NaLa)(MgW)O_6$

h k l	d_{obsd}	d_{cal}	I_{obsd}	I_{cal}
0 0 1**	7.88	7.89	17	25
1 0 1*	4.52	4.52	50	54
0 0 2	3.95	3.95	7	3
1 1 0	3.90	3.91		
1 1 1**	3.50	3.50	20	16
1 0 2**	3.21	3.21	1	6
1 1 $\bar{2}$		2.779	100	100
1 1 2	2.775	2.774		
0 2 0	2.762	2.763		
0 0 3**	2.631	2.631	4	2
2 0 1**	2.606	2.605	4	7
1 0 $\bar{3}$*	2.376	2.378	26	35
1 0 3*	2.374	2.376		
1 2 1*	2.357	2.357		
2 0 $\bar{2}$	2.264	2.266	1	3
2 0 2	2.261	2.263		
1 1 $\bar{3}$**	2.184	2.184	2	4
1 1 3**	2.179	2.180		
1 2 $\bar{2}$**	2.095	2.096	1	3
2 1 2**	2.090	2.092		
0 0 4	1.9738	1.9734	11	15
2 2 0	1.9530	1.9532	23	28
0 2 $\bar{3}$**	1.9058	1.9053	8	6
2 0 3**	1.9039	1.9024		
2 2 $\bar{1}$**	1.8970	1.8969		
0 1 $\bar{4}$**	1.8591	1.8584	1	1
1 2 $\bar{3}$*	1.8023	1.8023	10	16
1 2 3*		1.8001		
2 1 3*	1.7990	1.7988		
3 0 $\bar{1}$*	1.7944	1.7943		
0 3 $\bar{1}$*	1.7932	1.7936		
1 1 $\bar{4}$	1.7633	1.7628	3	2
2 2 $\bar{2}$	1.7515	1.7520		
2 2 2		1.7492		
1 3 0	1.7476	1.7472		
1 3 $\bar{1}$**	1.7060	1.7062	5	4
3 1 1**	1.7046	1.7046		
0 2 4	1.6051	1.6058	38	53
3 1 $\bar{2}$	1.5986	1.5990		
1 3 $\bar{2}$	1.5981	1.5982		
2 2 $\bar{3}$**	1.5696	1.5698	2	2
2 2 3**	1.5672	1.5669		
2 1 $\bar{4}$**	1.5436	1.5438	1	1
2 1 4**	1.5398	1.5400		
1 0 $\bar{5}$*	1.5188	1.5191	8	13
2 3 $\bar{1}$*	1.5049	1.5047		
2 3 1*	1.5041	1.5038		
1 1 $\bar{5}$**	1.4651	1.4649	4	1
2 2 $\bar{4}$	1.3894	1.3896	15	26
2 2 4	1.3868	1.3868		
0 4 0	1.3818	1.3813		
1 2 $\bar{5}$*	1.3296	1.3296	7	13
3 2 $\bar{3}$*	1.3255	1.3254		
3 2 3*	1.3223	1.3227		
4 0 $\bar{2}$	1.3045	1.3046	1	1
3 3 $\bar{1}$**	1.2850	1.2852	1	1
3 3 $\bar{1}$**	1.2839	1.2844		
1 0 $\bar{6}$**	1.2809	1.2806		
1 1 $\bar{6}$	1.2479	1.2475	14	11
3 3 $\bar{2}$	1.2369	1.2373		
2 4 0	1.2356	1.2354		
4 0 3**	1.2217	1.2214	1	1
4 1 $\bar{3}$*	1.1953	1.1952	2	5
3 1 $\bar{5}$**	1.1729	1.1728	4	1
1 3 5**	1.1711	1.1709		
4 0 $\bar{4}$	1.1329	1.1329	5	9
0 4 4	1.1314	1.1316		
4 2 $\bar{3}$**	1.1190	1.1192	2	1
2 4 3**	1.1180	1.1178		
4 2 3**	1.1169	1.1171		

* Superstructural reflection due to a NaCl-type ordering of B-site ions. ** Superstructural reflection due to a layer-like ordering of A-site ions.

absences for general reflections of *hkl* type, and the monoclinic cell is therefore primitive. This X-ray pattern, except the additional reflections marked by double asterisks, obeys a body-centered absence rule. On the other hand, the additional reflections marked by double asterisks occur with only $h+k=2n$ for (*hkl*) planes, if a few reflections of very weak intensity are ignored. This indicates that $(NaLa)(MgW)O_6$ has a *C*-face-centered lattice for special atoms. Especially, the appearance of relatively strong *001* reflection at about 7.88 Å, which can not be assigned to the NaCl-type ordering of the B ions, points to a doubling of the c′-axis in the small perovskite subcell, as found in $La_{0.33}NbO_3$[2] and $La_{0.67}TiO_3$.[3] In the compound $(NaLa)(MgW)O_6$, a cation ordering of Na^+ and La^{3+} ions is therefore considered to occur along alternate c-planes. Thus a superstructure model based on cation ordering is proposed as shown in Fig. 2. The perovskite subcell is designated by dotted outlines.

The extinction rule deduced from the observed reflections in Table 1 is as follows; *0k0*: ($k=2n$). So two space groups, $P2_1$ (No. 4) and $P2_1/m$ (No. 11), satisfy the extinction rule and simultaneously give the monoclinic crystal system[8]. The space group of monoclinic $(NaLa)(MgW)O_6$ probably belongs to $P2_1$, judging from the three-dimensional symmetry of the B ions in the NaCl-type ordering. The c-axis in $(NaLa)(MgW)O_6$ is regarded as a characteristic axis of the pseudotetragonal (actually monoclinic) cell.

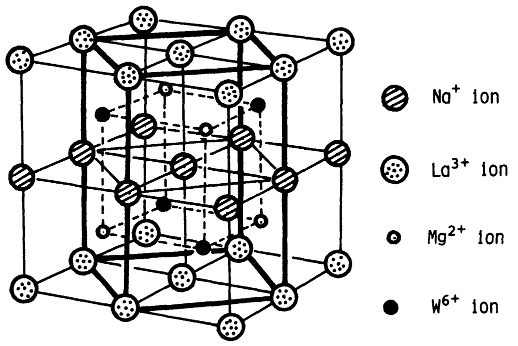

Fig. 2. Superstructure of $(NaLa)(MgW)O_6$, where oxygen ions are not shown.
Monoclinic unit cell: heavy solid line. Perovskite-like subcell: dotted line,

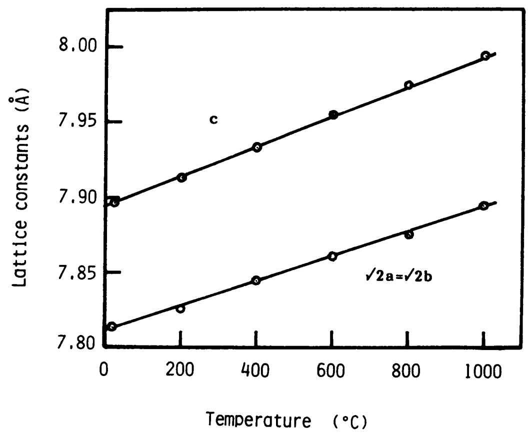

Fig. 3. Temperature dependence of lattice constants for $(NaLa)(MgW)O_6$.

Figure 3 shows the variation of the lattice constants of monoclinic $(NaLa)(MgW)O_6$ with temperature. The unit cell was tetragonal at 200 °C, and phase transitions were absent up to 1000 °C. The marked change in the cell dimensions with temperature is not accompanied by any appreciable change in the degree of tetragonality, and the superstructural reflections marked by double asterisks did not disappear even at 1000 °C. This result shows a crystallographic tendency similar to $La_{0.33}NbO_3$,[9] $La_{0.67}TiO_3$,[3] and $La_{1.33}(MgW)O_6$,[10] in which the A-site vacancies are ordered along alternate c-planes. Generally, the low symmetry of ordinary perovskites is expected to improve at high temperatures. The title compound $(NaLa)(MgW)O_6$ also differs from ordinary perovskites in the nature of tetragonal distortion. Hence the basic cell distortion in this compound is concluded to be tetragonal. The monoclinic distortion deviated from the tetragonal symmetry probably arises from atomic displacements in the neighboring perovskite subcells.

In order to confirm the proposed superstructure (Fig. 2), the theoretical intensities for $(NaLa)(MgW)O_6$ were calculated using ideal position parameters on the assumption of a tetragonal cell and were compared with the observed intensities in Table 1. In intensity calculations, the effects of atomic displacements and crystal distortion (actually monoclinic) on reflection intensity were neglected to avoid troublesome position parameters. In such a rough test, however, a qualitatively good agreement between the observed and calculated intensities was obtained as shown on the right side of each reflection in Table 1. The reliability factor R for the intensities of 36 peaks was 28%. This result gives good evidence for the general correctness of the proposed structure. Consequently the basic superstructure of $(NaLa)(MgW)O_6$ is concluded to arise from the NaCl-type ordering of the B ions as well as the layer-like ordering of the A ions, although cation ordering is unlikely to occur among the A-site ions in the perovskite structure. In this respect, the new compound $(NaLa)(MgW)O_6$ is an exceptional case.

Figure 4 gives the infrared absorption spectra of perovskites $(NaLa)(MgW)O_6$ and $(NaLa)Ti_2O_6$. In the case of cubic $(NaLa)Ti_2O_6$, two strong absorption band peaks were observed at 600 and about 340 cm^{-1}. On the basis of Last's mode assignment[11] on the perovskites, the high frequency band corresponds to the Ti–O stretching mode, while the lower frequency band does to the Ti–O bending mode. On the other hand, the spectrum of monoclinic $(NaLa)(MgW)O_6$ is more complicated. Two strong absorption bands at 685 and about 400 cm^{-1} are assigned to the internal modes of oxygen octahedra. The extra bands probably arises from the monoclinic distortion from ideal cubic symmetry, which would split degenerate modes to give additional frequencies as mentioned by some investigators.[12–14] However, it should be noted that two strong bands (marked a black circle) were found at 870 and 820 cm^{-1}. In view of the spectral positions, the two bands must be due to the B–O vibrational mode. The strong bands at very high wavenumbers, which are not expected for a regular octahedron, indicate a strong deviation from cubic symmetry. Such a remarkable spectrum[15] has been found in perovskite-related compounds $(NaLn)TiO_4$, where the Na^+ and Ln^{3+} ions are ordered on the larger cation sublattice. In the case of $(NaLn)TiO_4$, a strong band is located around 900 cm^{-1} in addition to the normal vibrations. This striking band is absent in Sr_2TiO_4. This fact that this mode was observed at very high wavenumbers has been concluded to be due to the superstructure of Na^+ and Ln^{3+} ions which results in a poor charge compensation in the octahedral surroundings. Consequently the infrared spectrum of $(NaLa)(MgW)O_6$ supports that a layer-like ordering of Na^+ and La^{3+} ions occurs on the A site.

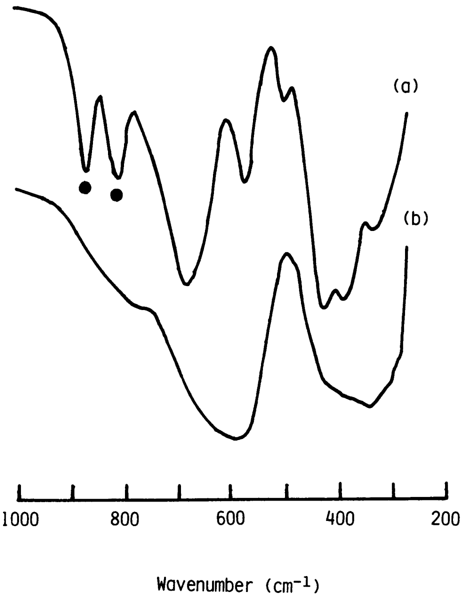

Fig. 4. Infrared absorption spectra of perovskites $(NaLa)(MgW)O_6$ (a) and $(NaLa)Ti_2O_6$ (b).

Our attempt to prepare the corresponding Ni and Zn compounds to $(NaLa)(MgW)O_6$ was unsuccessful. A similar result[4] has been obtained for the replacements of Ni^{2+} and Zn^{2+} ions for Mg^{2+} ion in cation-deficient perovskite $La_{1.33}(MgW)O_6$. Since these three cations are roughly equal in size, the failure of the preparation is not thought to be mainly due to the ionic size effect.

Thus the Mg/W combination not only contributes to the framework as constituent ions, but also plays an important role in the stabilization of the perculiarly ordered perovskite structure.

According to the X-ray structure analysis[2] of orthorhombic (pseudotetragonal) $La_{0.33}NbO_3$, the Nb^{5+} ions are displaced from the centers of the oxygen octahedra which themselves suffer distortion so as to retain only one of their four-fold axes. The particular displacement of the Nb^{5+} ions must be connected with the ordering of A-site vacancies along alternate c-planes. Recently we have reported that A-site vacancies are randomly distributed in the cubic $La_{0.33}NbO_3$ phase crystallized by rapid quenching of its melt.[16] Further, the pseudotetragonal perovskites $La_{0.33}NbO_3$ and $(NaLa)(MgW)O_6$ show the temperature-independent tetragonality, in addition to the layer-like ordering of A-site ions. Consequently, $(NaLa)(MgW)O_6$ is also considered to have similar off-centered octahedra to $La_{0.33}NbO_3$. This conclusion is supported by the infrared data of $(NaLa)(MgW)O_6$. Such a severly distorted octahedral-site seems to be unfavorable surroundings for Ni^{2+} and Zn^{2+} ions owing to strong crystal field effect of Ni^{2+} ($3d^8$) ion and tetrahedral site-preference of Zn^{2+} ($3d^{10}$) ion. This situation is reflected in the nonexistence of $NiSiO_3$ and $ZnSiO_3$ pyroxenes (the existence of $MgSiO_3$ pyroxene), since the pyroxene structure[17] consists of severely distorted octahedra and single chains of SiO_4 tetrahedra. Thus the Mg^{2+} ion makes no small contribution to the stabilization of this type of superstructure. The origin of the superstructure is represented as follows: The difference in charge between the Na^+ and La^{3+} ions is enough to cause cation ordering to occur among the A-site ions. The electrostatic imbalance due to the layer-like ordering of Na^+ and La^{3+} ions is compensated by the particular displacement of the Mg^{2+} and W^{6+} ions for the c direction, and such an electrostatic interaction gives rise to the pseudotetragonal distortion. In consequence, two strong absorption bands at very high wavenumbers were observed in the infrared spectrum of $(NaLa)(MgW)O_6$. The temperature-independent tetragonality shown in Fig. 3 is closely related with the layer-like ordering of A-site ions along alternate c-planes.

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