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# Crystal Distortion and Cation Distribution in the System $La_{1/3}NbO_3$-$WO_3$

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**Synopsis.** It has been found that $WO_3$ is soluble in $La_{1/3}NbO_3$ up to *ca.* 35 mol %. The solid solutions showed an ordered perovskite structure. The orthorhombic distortion changes into a tetragonal one at 20 mol %. The temperature dependence of the tetragonality of typical samples has been examined and the nature of the tetragonal distortion discussed.

$La_{1/3}NbO_3$ is an orthorhombically distorted structure containing two perovskite subcells.$^{1)}$ Iyer *et al.* reported that the perovskite-type unit cell contains a preferential distribution of $La^{3+}$ ions on alternate c-planes, as shown in Fig. 1.$^{2)}$ $WO_3$, on the other hand, is well-known to have a perovskite structure without A-site ions. A-site deficient perovskites with a wide range of non-stoichiometry, such as $La_{1-x}TiO_3$$^{3)}$ ($x$=0.03—0.33) and $Sr_{1-x}NbO_3$$^{4)}$ ($x$=0.05—0.30), have been reported to be of simple perovskite structure type. $La_{2/3}TiO_3$ is an exception and has the same ordered structure as $La_{1/3}NbO_3$.$^{5)}$ It is of interest crystallographically to understand how solid solutions between $La_{1/3}NbO_3$ and $WO_3$ can be formed and whether such ordered arrangement is maintained. The present paper describes the structural properties of this system.

## Experimental

The samples were prepared by conventional ceramic techniques, using $La_2O_3$, $Nb_2O_5$, and $WO_3$ as starting materials. Two-cycle firing was carried out in air at 1050—1270 °C for several hours, the samples being left to cool in the furnace. The products were analyzed by X-ray diffraction method, using Cu $K\alpha$ radiation. The lattice constants were determined from the best resolved lines of (004), (020), and (200), which appeared at $2\theta$=46—47°. Observed intensities were obtained from the diffractometer tracing by weighing the relative areas under the peaks. The theoretical intensities of the reflection lines were calculated according to a method previously reported.$^{6)}$

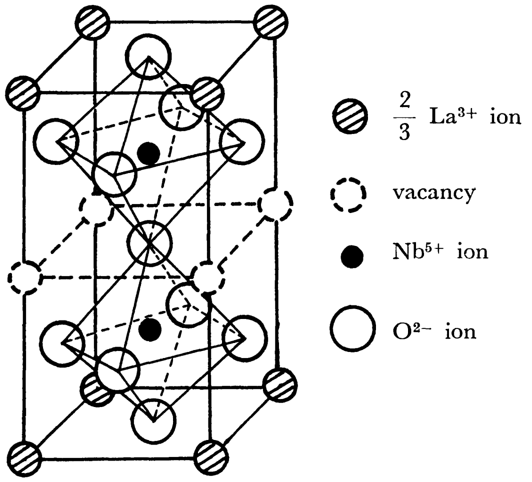

Fig. 1. Crystal structure of $La_{1/3}NbO_3$.

## Results and Discussion

The $La_{1/3}NbO_3$–$WO_3$ system showed single-phase patterns similar to that for $La_{1/3}NbO_3$ up to a composition containing 35 mol % $WO_3$. In a 40 mol % $WO_3$ sample, a further phase appeared in small amounts besides the perovskite-like compound. The room temperature lattice constants are shown in Fig. 2. The crystal lattice became contracted by the partial substitution of $W^{6+}$ ions for $Nb^{5+}$ ions. The $c/2a$ ratio decreased with increasing amounts of $WO_3$. The orthorhombic distortion changed into a tetragonal one at 20 mol % $WO_3$ and the tetragonality decreased with further increase of $WO_3$, but the perovskite subcell did not become cubic. The decrease in crystal distortion is probably attributable to the size effect of B-site ions. The intensities of superstructure lines were also observed to decrease with increasing amounts of $WO_3$. The relative intensities of the typical lines of (001), (011), and (111) are shown by the solid lines in Fig. 3, the intensities of which depend on the $La^{3+}$ ion concentration in this type of perovskite structure. It is impossible, however, to neglect the effect of high scattering power of the $W^{6+}$ ion on intensity. In this respect the partial substitution of $Mo^{6+}$ ions is more favored since the two scattering powers of the $Nb^{5+}$ and $Mo^{6+}$ ions are nearly equal. Unfortunately attempts to prepare solid solutions in the $La_{1/3}NbO_3$–$MoO_3$ system failed. In order to examine the cation distribution, the theoretical intensities of superstructure lines were calculated using Iyer's crystal data,$^{2)}$ the results of which are shown by the broken lines in Fig. 3 in comparison with the observed values. Good agreement between the calculated and the observed intensities was obtained. Therefore, the ordered ar-

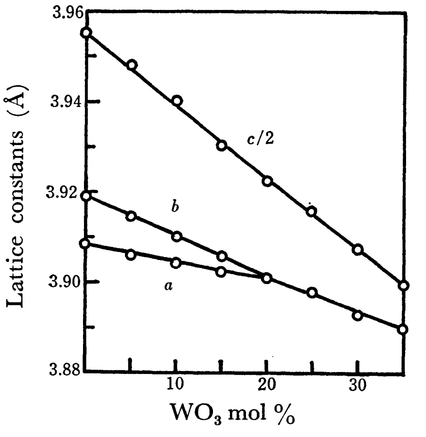

Fig. 2. Lattice constants in the $La_{1/3}NbO_3$-$WO_3$ system.

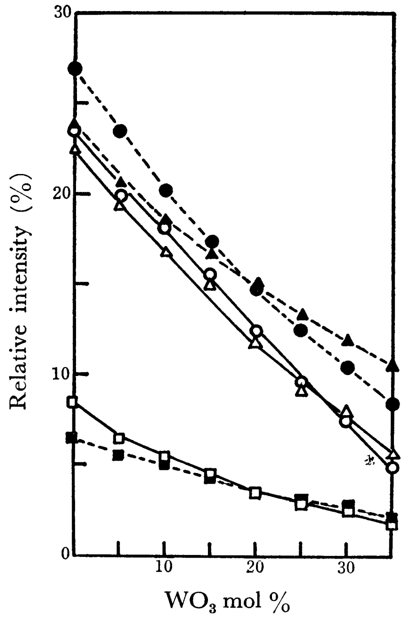

Fig. 3. Observed intensities *vs.* those caluculated for typical superstructure lines in this system.
○: $I_{\text{obsd}}(001)$, ●: $I_{\text{calcd}}(001)$,
△: $I_{\text{obsd}}(011)$, ▲: $I_{\text{calcd}}(011)$,
□: $I_{\text{obsd}}(111)$, ■: $I_{\text{calcd}}(111)$.
$I_{\text{obsd}}(001)$ represents observed intensity of (001) line, and $I_{\text{calcd}}(111)$ represents the sum of the calculated intensities of (111) and (003) lines which appeared at the nearly same value of $2\theta$.

rangement of $La^{3+}$ ions as shown in Fig. 1 is completely maintained in the solid solution in the $La_{1/3}NbO_3$–$WO_3$ system. This is quite different from the situations showing simple perovskite phases of composition $La_{1-x}TiO_3$ ($x$=0.03—0.30), except $La_{2/3}TiO_3$ ($x$=0.33) with the ordered structure.

Figure 4 shows the variation of lattice constants of $La_{1/3}NbO_3$ with temperature. The orthorhombic subcell changes into a tetragonal one above *ca.* 190 °C. The $c/2a$ ratio is almost independent of temperature. For the 20 mol % $WO_3$ sample, the crystal lattice gradually expands with temperature, and the tetragonality remains almost unchanged. The superstructure lines for both samples did not disappear even at 1000 °C. Generally, the low symmetry of ordinary perovskites is expected to improve at high temperatures. It is likely that $La_{1/3}NbO_3$ and its solid solutions differ from ordinary perovskites in the nature of tetragonal distortion. In $La_{1/3}NbO_3$ two $Nb^{5+}$ ions are located at ±(1/2, 1/2, $z$), $z$=0.262. The intensities of the superstructure lines are relatively sensitive to the atomic $z$ parameter from the structure factor. With increase in the $z$ value, the (001) line tends to become weaker while the (011) line becomes stronger. For example, the calculated values of (001) and (011) lines for the 20 mol % $WO_3$ sample were 16.0 and 9.9 at $z$=0.25, and 14.7 and 14.9 at $z$=0.262, respectively. The corresponding observed values were 12.4 and 11.8, respectively. It becomes apparent that the differences between the calculated and observed intensities decrease by the deviation of $Nb^{5+}$ and $W^{6+}$ ions from the B positions of ±(1/2, 1/2, 1/4). In terms of charge balance, this antiparallel displacement of $Nb^{5+}$ and $W^{6+}$ ions with high valency is considered an important role for the formation of this type of superstructure, where the corner sites are occupied by corresponding amounts of $La^{3+}$ ion and the vertical edge centre sites are vacant. It might be related to the origin of superstructure that the tetragonality in $La_{1/3}NbO_3$ and its solid solution remains nearly unchanged with temperature.

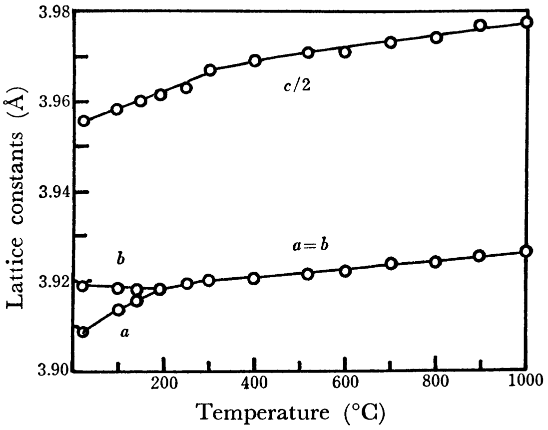

Fig. 4. Temperature dependence of lattice constants for $La_{1/3}NbO_3$.

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