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Dependency of Long-range Order Parameter on the Ordered Structure of $Pb(Mg_{1/3}Nb_{2/3})O_3$ Solid Solutions

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$Pb(Mg_{1/3}Nb_{2/3})O_3$ 고용체의 규칙격자 구조에 있어서 장거리 규칙도의 의존성

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요 약

$Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) 고용체의 고분해능 격자 이미지에 있어서 장거리 규칙도의 의존성을 컴퓨터 이미지 시뮬레이션을 이용하여 연구하였다. 컴퓨터 이미지 시뮬레이션은 multislice 방법으로 시편두께, 초점 거리, 장거리 규칙도를 변화시켜 실시하였다. PMN에 있어서, 규칙격자 구조를 가지는 격자 이미지는 장거리 규칙도에 주로 의존하는 것을 발견하였다. 완전한 규칙격자 구조를 가지는 이미지는 유사 육방정 형태를 보였다. 장거리 규칙도가 감소함에 따라, 유사 육방정 형태로부터 직사각형 형태로 변화되었고, 완전한 불규칙격자 구조를 가지는 이미지는 직사각형 형태를 보였다. 또한, 한 주어진 장거리 규칙도에서 시뮬레이션으로 얻은 이미지는 B-위치 양이온의 함량에 관계없이 거의 동일하였다.

Key words : $Pb(Mg_{1/3}Nb_{2/3})O_3$, Long-range Order Parameter, Computer Image Simulation, Ordered Structure

INTRODUCTION

Relaxor ferroelectrics and other structurally related compounds, $Pb(B(I)_xB(II)_{1-x})O_3$, are emerging as a technologically important class of materials for use in a wide variety of applications such as piezoelectric and electrostrictive actuators (Cross LE *et al.*, 1980; Uchino K, 1986), thermal detectors (Whatmore RW *et al.*, 1987), electro-optic modulators (Bonner WA *et al.*, 1967), and multilayer ceramic capacitors (Shrout TR, 1987). The ferroelectric-paraelectric phase transition of the ferroelectric compounds is mainly influenced by the degree in which the B-site cations are ordered on the B-site sublattice.

The ordered structures of $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST) have previously been investigated using X-ray diffraction (Bonneau P *et al.*, 1988; Lin LJ *et al.*, 1990) and high-resolution transmission electron microscopy (HRTEM) (Krause HB *et al.*, 1979; Husson E *et al.*, 1988; Kang ZC, 1990; Park K, 1997(a), 1997 (b)). In the previous study (Park K, 1997(a), 1997(b)), the nonstoichiometric ordering of Mg and Nb cations in ordered regions of PMN was observed along the ⟨111⟩directions. The long-range order parameter approximately ranged from 0.2 to 0.7. Although HRTEM is a useful tool for an investigation of the ordered structures on an atomic scale, the lattice images of the ordered regions can not explain how the long-range order parameter affects the lattice images. In this study, the dependency of long-range order parameter on the ordered structures of PMN was studied by computer simulations of high-resolution lattice images.

EXPERIMENTAL

$Pb(Mg_{1/3}Nb_{2/3})O_3$ samples were prepared by the precalcination method (Swartz SL *et al.*, 1982). Computer image simulations were carried out using the multislice program (Cowley JM *et al.*, 1957, 1959(a), 1959(b)) for various sample thicknesses, t, and defocusing values of the objective lens, Δf, at given long-range order parameters, S. The principle of the multislice method is to divide the crystal into a number of thin slices perpendicular to the incident beam direction (Cowley JM, 1984). The multislice program was written by O'Keefe and Skarnulis during the period 1970~1980 (Skarnulis AJ, 1975).

In this simulation work, the sample thicknesses were chosen from 2.2 to 20.0 nm with a step of 1.1 nm, the long-range order parameters from the maximum long-range order parameter, S_{max}, to 0.0 with a step of 0.2, and the defocusing values from −52 to −100 nm with a step of 12 nm. The input microscope parameters used in the computer simulation of the images are given in Table 1.

Table 1. Input microscope parameters used in the computer simulation of lattice images.

Operating voltage (V)	200 kV
Radius of objective aperture (rs)	3.37 nm^{-1}
Spherical aberration coefficient (Cs)	2.3 mm
Semi-angle of illumination	1.0 mrad
Half-width of Gaussian spread of vibration	0.0 nm
Half-width of Gaussian spread of defocus	5 nm

RESULTS AND DISCUSSION

Figs. 1(a) and (b) show the high-resolution lattice images from the ordered and disordered regions of $Pb(Mg_{1/3}Nb_{2/3})O_3$, respectively. Disordered region shows a rectangular pattern, while ordered region shows a contrast modulation along the ⟨111⟩directions, indicating a chemical ordering along the ⟨111⟩directions. It has been reported that the long-range order parameter for the ordered region approximately ranged from 0.2 to 0.7 (Park K, 1997(a), 1997 (b)). However, the lattice image of the ordered region can not tell the degree of long-range ordering. Therefore, in order to understand the dependency of long-range order parameter on the ordered structures, it is necessary to simulate the lattice images under various sample thicknesses, t, and defocusing values of the objective lens, Δf, at given long-range order parameters, S.

Proposed models of ordered and disordered structures (Galasso FS, 1969) in PMN for computer image simulations are shown in Figures 2(a) and (b), respectively. Fig. 2(a) shows that the 1 : 1 ordering of Mg and Nb cations on B-site planes occurs along the <111>directions. For various occupancies and fractions of the Mg and Nb cations on the distinct B-site sublattices and the fraction of Mg or Nb sites, the long-range orderparameter, S, and structure factor were calculated. Complete long-range ordering ($S=1.0$) corresponds to all B(I)- and B(II)-sites being occupied by Mg and Nb, respectively, which can only be obtained for a local Mg : Nb ratio of 1 : 1. For deviation from 1 : 1 stoichiometric composition, the order parameter is smaller than 1.0. The maximum order parameter, S_{max}, for Pb $(Mg_x Nb_{1-x})O_3$ with local Mg:Nb ratios of 2:3 and 3:2 is 0.8, and the S_{max} for Pb $(Mg_x Nb_{1-x})O_3$ with a local Mg:Nb ratio of 1 : 2 is 0.67. The values of S_{max} and long-range order parameter were calculated by the relation proposed by Smirnov (Smirnov A, 1966).

Figs. 3(a)-(c) show the simulated lattice images of $Pb(Mg_xNb_{1-x})O_3$ with local Mg:Nb ratios of 1 : 1, 2 : 3 and 1 : 2, respectively, which were obtained under various defocusing values (−64 to −100 nm), sample thicknesses (4.5 to 14.7 nm), and long-range order parameters. These simulated images show how the long-range order parameter affects the lattice images. The lattice images with a complete ordered structure ($S=1.0$) show a pseudo-hexagonal pattern. With decreasing the order parameter, the calculated images change slowly from a pseudo-hexa-gonal pattern to a rectangular pattern. Finally, the lattice images with a complete disordered structure ($S=0.0$) show a rectangular pattern.

It is also important to note that the simulated images of the Pb $(Mg_xNb_{1-x})O_3$ with local Mg : Nb ratios of 1 : 1, 2 : 3, 3 : 2, and 1 : 2 obtained at a given long-range order parameter are basically the same pattern, irrespective of B-site cation composition. As an example, for Pb $(Mg_x Nb_{1-x})$ O_3 with local Mg : Nb ratios of 1 : 1, 2 : 3, 3 : 2, and 1 : 2, the simulated images for sample thicknesses of 5.7 and 11.4 nm at an order parameter of 0.6 are shown in Figures 4(a) and (b), respectively. These figures clearly reveal that at an order parameter of 0.6, the simulated lattice images of the Pb $(Mg_xNb_{1-x})O_3$ with a local Mg; Nb ratio of 1 : 1 are basically equal to those of the Pb $(Mg_xNb_{1-x})O_3$ with local Mg : Nb ratios of 2 : 3, 3 : 2, and 1 : 2.

CONCLUSIONS

Simulated high-resolution lattice images of the ordered structures were predominantly dependent on the long-range order parameter. The lattice images of complete ordered structure were a pseudo-hexagonal pattern. With decreasing the order parameter, the simulated images changed gradually from a pseudo-hexagonal pattern to a rectangular pattern. The lattice images of complete disordered structure were a rectangular pattern. In addition, the simulated images obtained from the Pb $(Mg_xNb_{1-x})O_3$ with different Mg:Nb ratios at a given long-range order parameter were basically the same patterns, irrespective of Mg and Nb ratios.

ABSTRACT

The dependency of long-range order parameter on the ordered structure of Pb $(Mg_{1/3}Nb_{2/3})O_3$

solid solutions has been investigated by means of computer simulations of high-resolution lattice images. The computer image simulations were performed by the multislice method in a wide range of sample thicknesses, defocusing values, and long-range order parameters. It was found that the lattice images of the ordered structures were predominantly dependent on the long-range order parameter. The lattice images in a complete ordered structure showed a pseudo-hexagonal pattern. As the order parameter decreases, the simulated images changed slowly from a pseudo-hexagonal pattern to a rectangular pattern. The lattice images in a complete disordered structure showed a rectangular pattern. Also, the simulated images of the Pb $(Mg_xNb_{1-x})O_3$ with different Mg:Nb ratios obtained at a given long-range order parameter were basically the same patterns, irrespective of Mg and Nb compositions.

ACKNOWLEDGEMENT

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REFERENCES

Bonneau P, Garnier P, Husson E, Morell A, 1988. Structural study of PMN ceramics by X-ray diffraction between 297 and 1023 K, Mater. Res. Bull. 24, 201-206

Bonner WA, Dearborn EF, Geusic JE, Marcos HM, Van Uitert LG, 1967. Dielectric and electro-optic properties of lead magnesium niobate, Appl. Phys. Lett. 10, 163-165

Cowley JM, Moodie AF, 1957. The scattering of electrons by atoms and crystals. I. A new theoretical approach, Acta Crystallogr. 10, 609-619

Cowley JM, Moodie AF, 1959(a). The scattering of electrons by atoms and crystals. II. The effects of finite source size, Acta Crystallogr. 12, 353-359

Cowley JM, Moodie AF, 1959(b). The scattering of electrons by atoms and crystals. III. Single-crystal diffraction patterns, Acta Crystallogr. 12, 360-367

Cowley JM, 1984. Diffraction physics, North-Holland, Amsterdam, p. 64

Cross LE, Jang SJ, Newnham RE, Nomura S, Uchino K, 1980. Large electrostrictive effects in relaxor ferroelectrics, Ferroelectrics 23, 187-192

Galasso FS, 1969. Structure, Properties and Preparation of Perovskite-Type Compounds, ed. R. Sinoluchowski and N. Kurti, Pergamon Press, New York, p. 12

Husson E, Chubb M, Morell A, 1988. Superstructure in Pb $(Mg_{1/3}Nb_{2/3})O_3$ ceramics revealed by high resolution electron microscopy, Mater. Res. Bull. 23, 357-361

Kang ZC, Caranoni C, Siny I, Nihoul G, Boulesteix C, 1990. Study of the ordering of Sc and Ta atoms in Pb_2ScTaO_6 by X-ray diffraction and high resolution electron microscopy, J. Solid State Chem. 87, 308-320

Krause HB, Cowley JM, Wheatley J, 1979. Short-range ordering in $Pb(Mg_{1/3}Nb_{2/3})O_3$, Acta Crystallogr. A35, 1015-1017

Lin LJ, Wu TB, 1990. Ordering behavior of lead magnesium niobate ceramics with a-site substitution, J. Amer. Ceram. Soc. 73, 1253-1256

Park K, 1997(a). High-resolution Transmission Electron Microscopy of Ordered Structure for Lead Magnesium Niobate Solid Solutions, Korean J. Electron Microscopy 27, 101-109

Park K, 1997(b). Microstructural Studies of Pb $(Mg_{1/2}Nb_{2/3})O_3$ Solid Solutions by High-resolution Transmission Electron Microscopy, Korean Journal of Materials Research 7, 517-521

Shrout TR, Halliyal A, 1987. Preparation of lead-based ferroelectric relaxors for capacitors, Amer. Ceram. Soc. Bull. 66, 704-711

Skarnulis AJ, 1975. Ph. D. Dissertation, Arizona State University.

Smirnov A, 1966. Molecular Kinetic Theory of Metals, Nauka Press, Moscow, p. 185

Swartz SL, Shrout TR, 1982. Fabrication of perovskite lead magnesium niobate, Mater. Res. Bull. 17, 1245-1250

Uchino K, 1986. Electrostrictive actuators: materials and applications, Amer. Ceram. Soc. Bull. 65, 647-652

Whatmore RW, Osbond PC, Shorrocks NM, 1987. Ferroelectric materials for thermal IR detectors, Ferroelectrics 76, 351-367

FIGURE LEGENDS

Fig. 1. Experimental high-resolution lattice images from the (a) ordered and (b) disordered regions of Pb ($Mg_{1/3}Nb_{2/3}$)O_3.

Fig. 2. Proposed models of (a) ordered and (b) disordered structures for PMN.

Fig. 3. Simulated lattice images obtained under four different defocusing values and sample thicknesses at given long-range order parameters for Pb (Mg_xNb_{1-x})O_3 with local Mg : Nb ratios of (a) 1 : 1, (b) 2 : 3, and (c) 1 : 2.

Fig. 4. Simulated lattice images obtained at sample thicknesses of (a) 5.7 and (b) 11.4 nm under an order parameter of 0.6 for the Pb (Mg_xNb_{1-x})O_3 with various local Mg : Nb ratios.

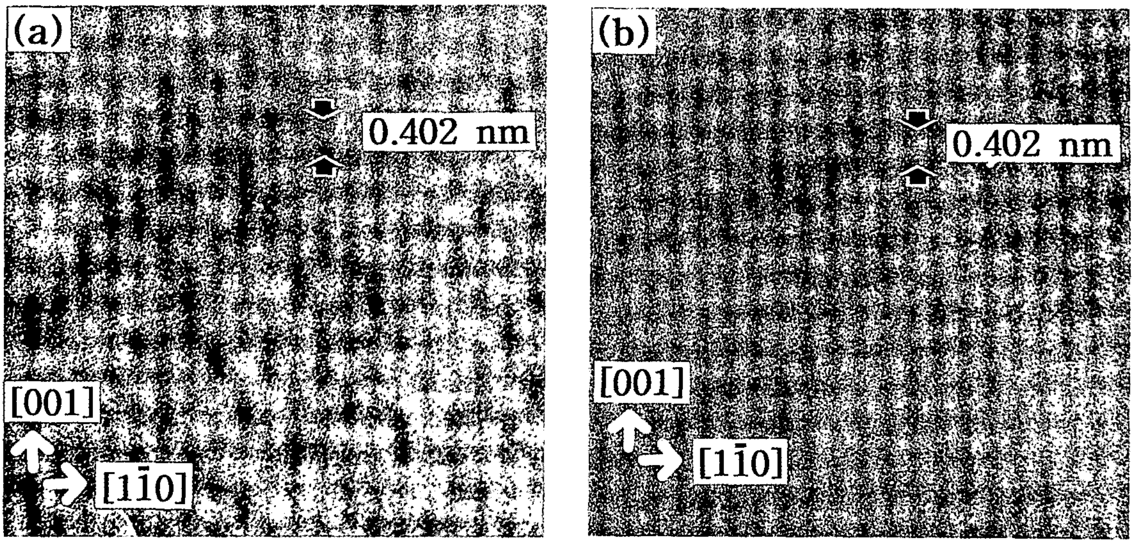

Fig. 1.

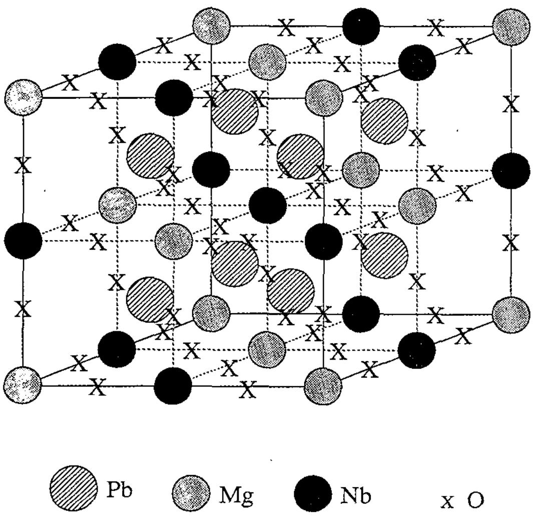

Fig. 2a.

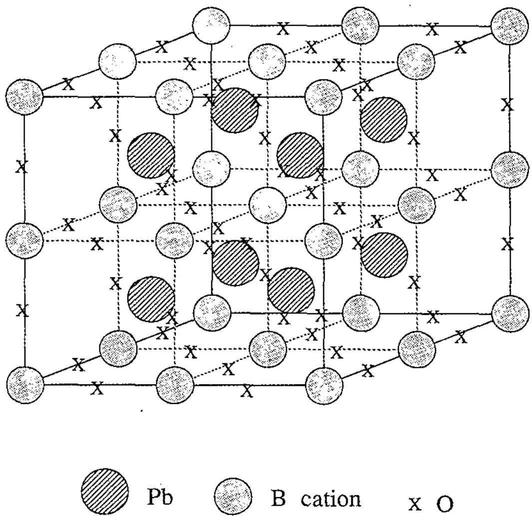

Fig. 2b.

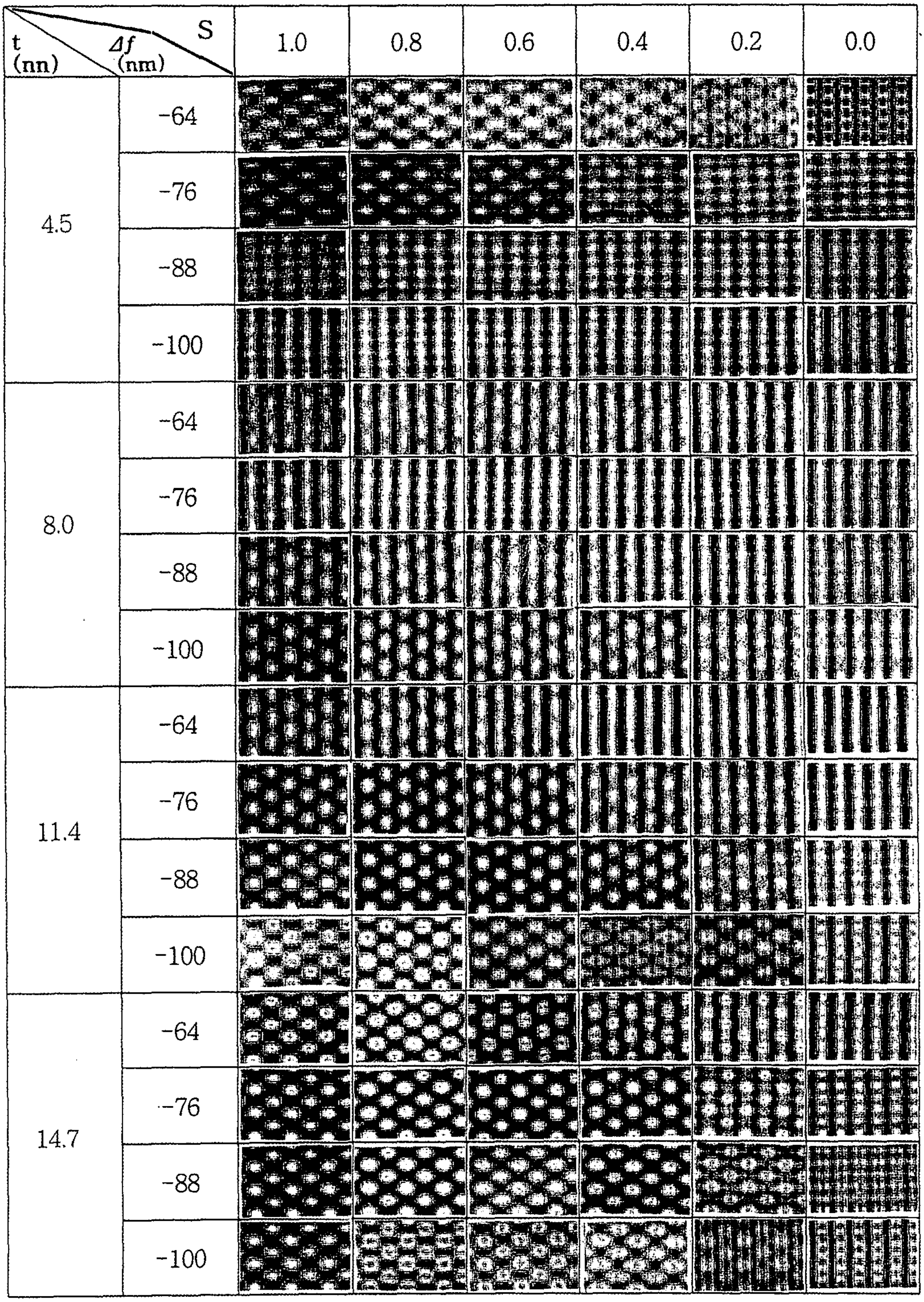

Fig. 3a.

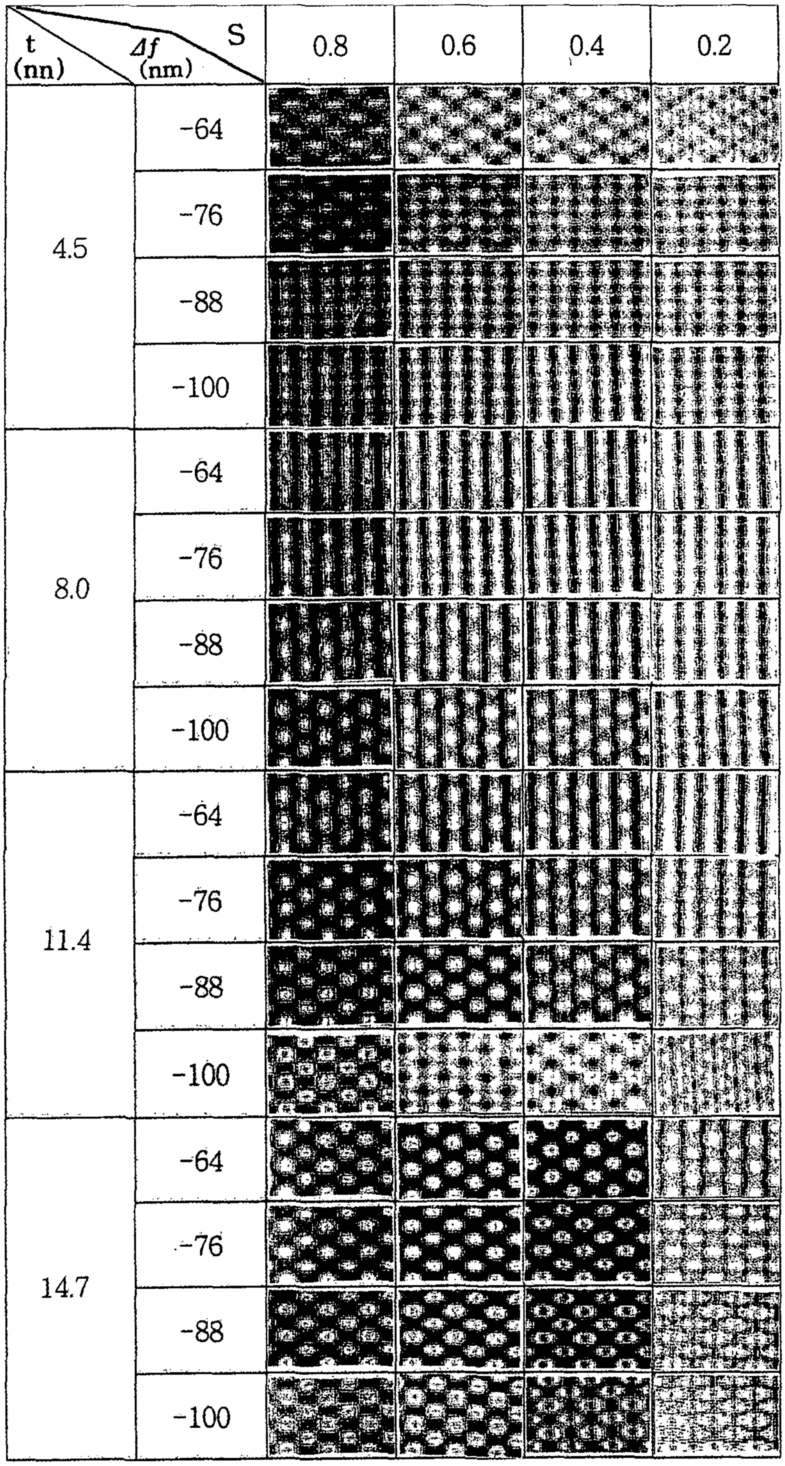

Fig. 3b.

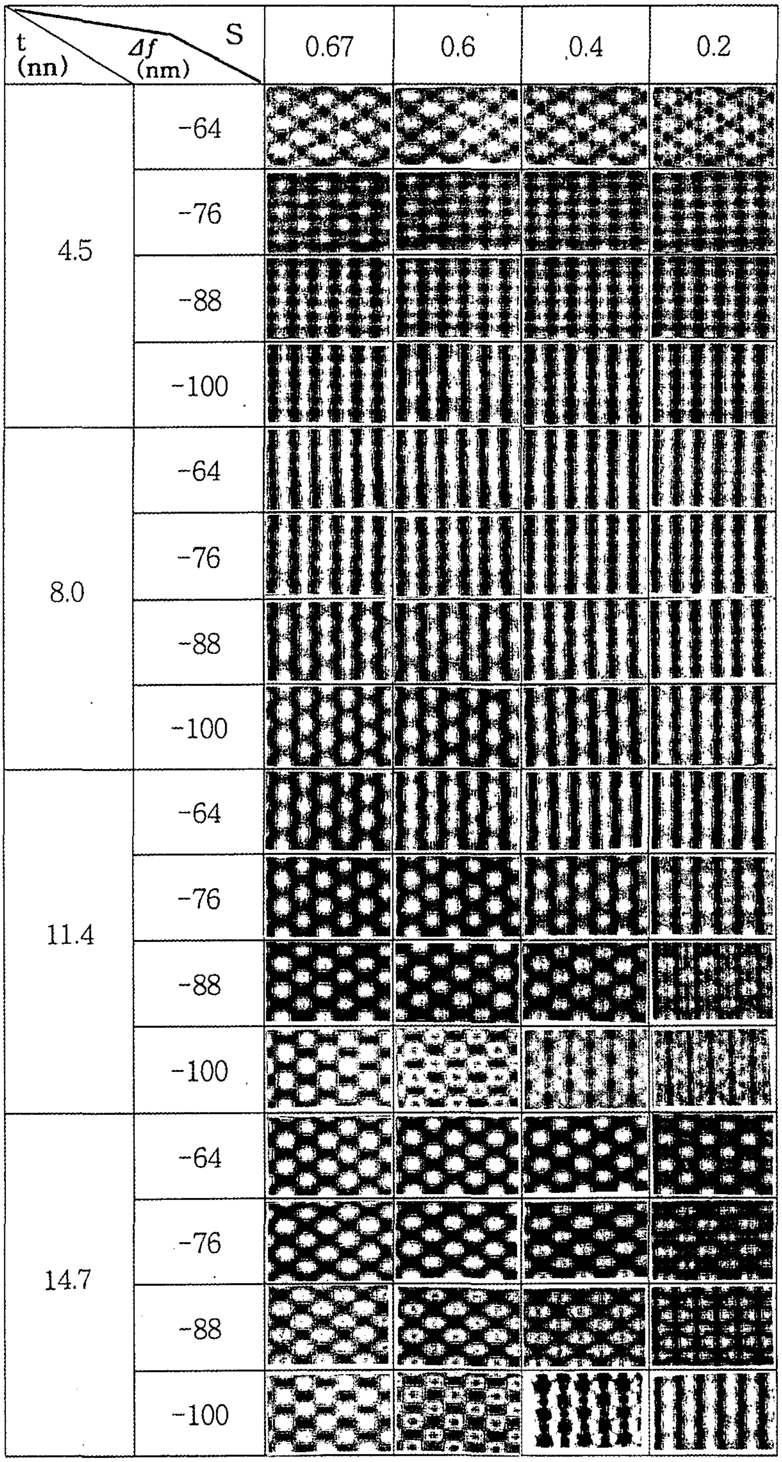

Fig. 3c.

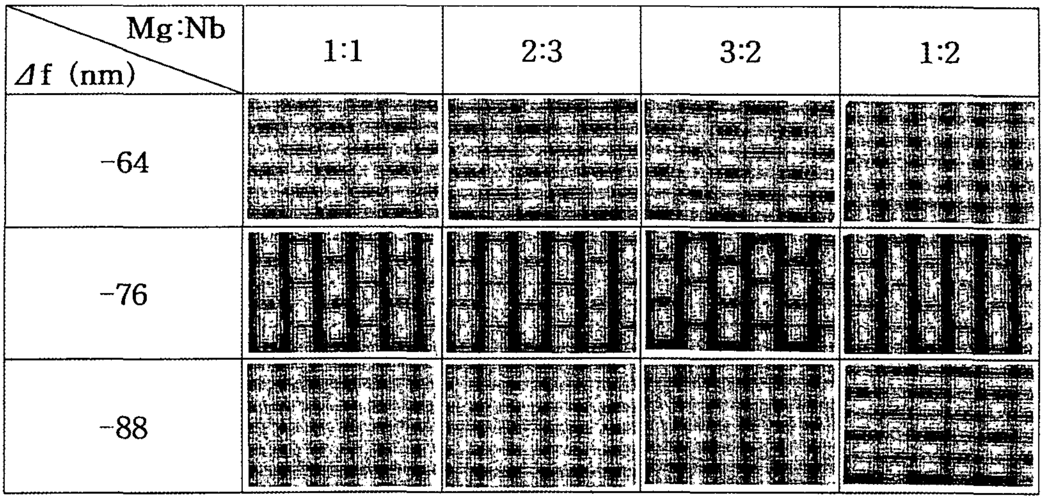

Fig. 4a.

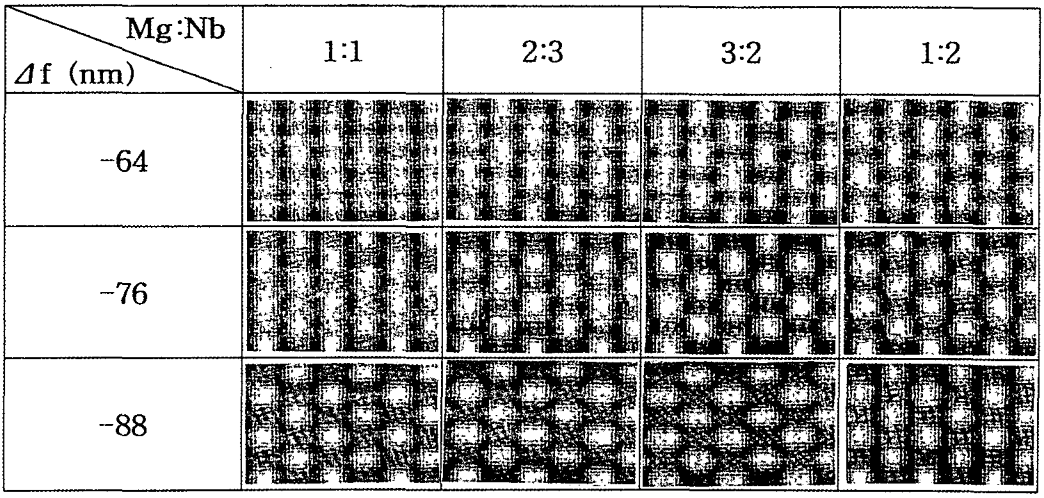

Fig. 4b.