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A Study on the Ordering of Na Ions in Na_xWO_3 ($0.5 \leq x \leq 1.0$)

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Crystal structures of Na_xWO_3 ($0.5 \leq x \leq 1.0$) were investigated Transmission electron microscopy (TEM) studies indicate that there is an ordering of sodium ions when x=0.75 The direction of ordering is [110] and the wavelength of ordering is twice of the interplanar distance of (110) plane. It has been confirmed that a superlattice containing eight $Na_{0.75}WO_3$ is the unit cell of ordered structure. In this unit cell, Na sites at (000) and (½½½) are vacant The ordered phase was preserved after the annealing at 600°C in the air. In reduced Na_xWO_3 with x=0.5 and 1.0, extra phases were found with the partially ordered perovskite phase. After annealing at 600°C, theses phases transformed to the phases found in calcined specimens.

Key words : Sodium tungsten bronze, Ordering, TEM, Stability

I. Introduction

The nonstoichiometric Na_xWO_3 known as sodium tungsten bronze has a wide composition ranges. It is a cubic in the range of $0.3<x<1$[1,2] and its electrical conductivity exhibits metallic behavior in $0.48<x<1$.[3,4] In cubic bronze Na_xWO_3, the lattice parameter, a, varies linearly with sodium concentration, x and following equation relates the lattice constant and sodium concentration:[3,5]

$$a = (0.0820x + 3.7845)$$

However, it has been suggested that lattice parameter does not follow the above equation for large x (x>0.85) due to the presence of metallic tungsten.[6] Ordering of Na ions has been investigated using neutron scattering. The unit cell of ordered structure was suggested as the superlattice containing eight $Na_{0.75}WO_3$.[7,8] The ordering of Na ions was used to explain the resistivity minimum observed at x=0.75.[9] A number of works have been done on the electrical properties of the Na_xWO_3 system. However, a limited works have been carried out on its crystal structure. Therefore, the unit cell of ordered structure and the range of its existence were not fully confirmed.

In this work, the phases and the ordering of Na ions in Na_xWO_3 ($0.5 \leq x \leq 1.0$) were studied by XRD and TEM. The experimental results showed that the unit cell of ordered structure is the superlattice containing eight $Na_{0.75}WO_3$. Computer simulation was carried out using the ordered unit cell.

II. Experimental Details

Reagent-grade powders of 99% Na_2CO_3 and 99.9% WO_3 were mixed in the appropriate ratio. ball milled and calcined in an alumina crucible at 600°C for 4 hrs. The powders were pressed and annealed in alumina tube at 670°C for 24 hrs under N_2:H_2=100:2. Na_xWO_3 powder was dissolved in CCl_4 and mounted on meshed Cu grid for TEM observation. Rigaku D/Max-Rc X-ray was used for X-ray measurement and Hitachi H-9000 NAR TEM was used to observe specimens. MacTempas was used to simulate the diffraction patterns.

III. Results and Discussion

Figure 1(a) is X-ray diffraction spectrum of Na_xWO_3 with x=0.75 calcined at 600°C for 4 hrs. An attempt was made to identify the phases in the specimen. But the phases could not be identified with powder diffraction file. Figure 1(b) shows X-ray spectrum of the specimen with same composition reduced at 670°C for 24 hrs. The diffraction spectrum was indexed as cubic perovskite structure with lattice parameter of 0.384 nm. It is smaller than calculated lattice parameter of $Na_{0.75}WO_3$ (0.3846 nm). Since the difference is small, the cubic perovskite phase in our specimen is considered to have a composition very close to $Na_{0.75}WO_3$. The stability of perovskite phase was examined by annealing the reduced specimen at 600°C for 2 hrs in the air. The perovskite phase was well preserved even after the annealing as can be seen in Fig. 1(c).

Figure 2 is high resolution lattice image of reduced $Na_{0.75}WO_3$ specimen with [001] beam direction. The inset is the diffraction pattern taken from the same area. In high resolution image, it can be seen that new mo-

dulation has been developed along [110] direction besides the regular lattice fringes. Moreover, the diffraction pattern shows extra spots at ½(110) position. These results clearly indicate that there is an ordering along [110] direction. The wavelength of modulation was 0.54 nm which is twice of the interplanar distance of (110) plane. Previously, ordering of Na ions in Na_xWO_3 in the composition range of $0.56<x<0.86$ has been investigated using the neutron diffraction and the ordering was found at $x=0.75$.[7] The unit cell of ordered structure was suggested as a superlattice containing eight Na_xWO_3 with (000) and (½½½) sites vacant.[7,8] Figure 3(a) shows the unit cell of ordered structure where Na sites at (000) and (½½½) are vacant. For $0.75<x<1.0$, some of vacant sites were expected to be filled by Na ions developing partially ordered structure.[7] In addition, the maximum electrical conductivity of Na_xWO_3 near $x=0.75$ was explained using the lattice parameter of ordered unit cell.[10] Computer simulation of diffraction pattern was carried out using the ordered unit cell. Figure 3(b) shows simulated [001] diffraction pattern. The extra spots appeared at ½(110) position matches the experimental results. Furthermore, according to the computer simulation, in order for Na_xWO_3 phase to develope the ordering along [110] direction, its composition should be $Na_{0.75}WO_3$. Thus, ordering developed in our $Na_{0.75}WO_3$ specimen is considered to be nearly perfect. The resistivity of the polycrystalline $Na_{0.75}WO_3$ specimen was measured to be 10^{-4} Ωcm. This is comparable with values measured in single crystals.

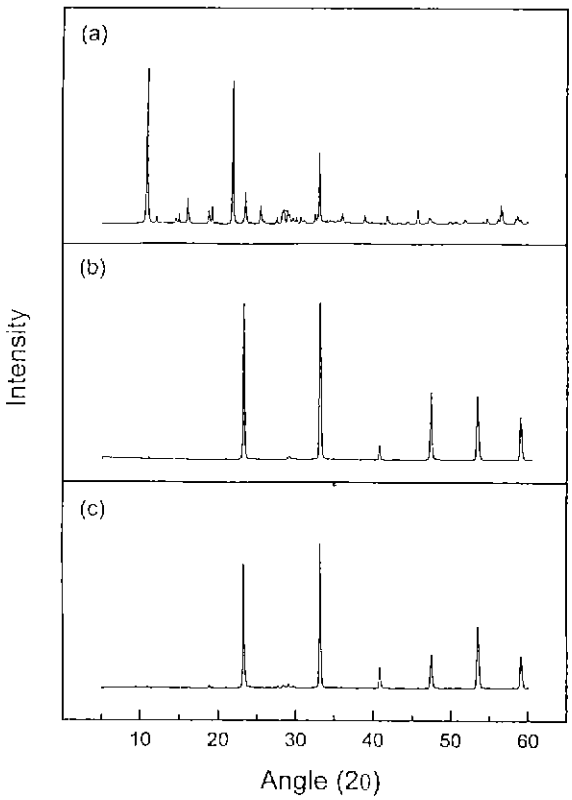


Fig. 1. X-ray diffraction spectra of Na_xWO_3 with $x=0.75$ (a) calcined at 600°C for 4 hrs, (b) reduced at 670°C for 24 hrs and (c) annealed at 600°C for 2 hrs.

Figure 4(a) shows X-ray diffraction spectrum of Na_xWO_3 with $x=0.5$ calcined at 600°C for 4 hrs. The crystal structure of the specimen was triclinic ($Na_2W_4O_{13}$)

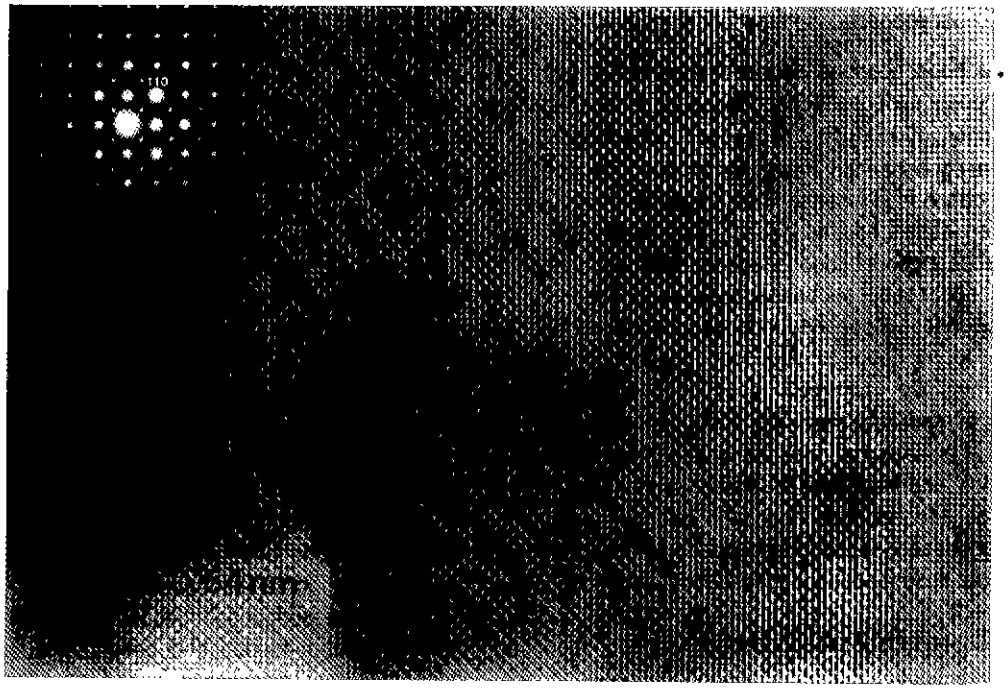


Fig. 2. High resolution lattice image with [001] beam direction taken from the reduced Na_xWO_3 with $x=0.75$. The inset is the diffraction pattern taken from the same area

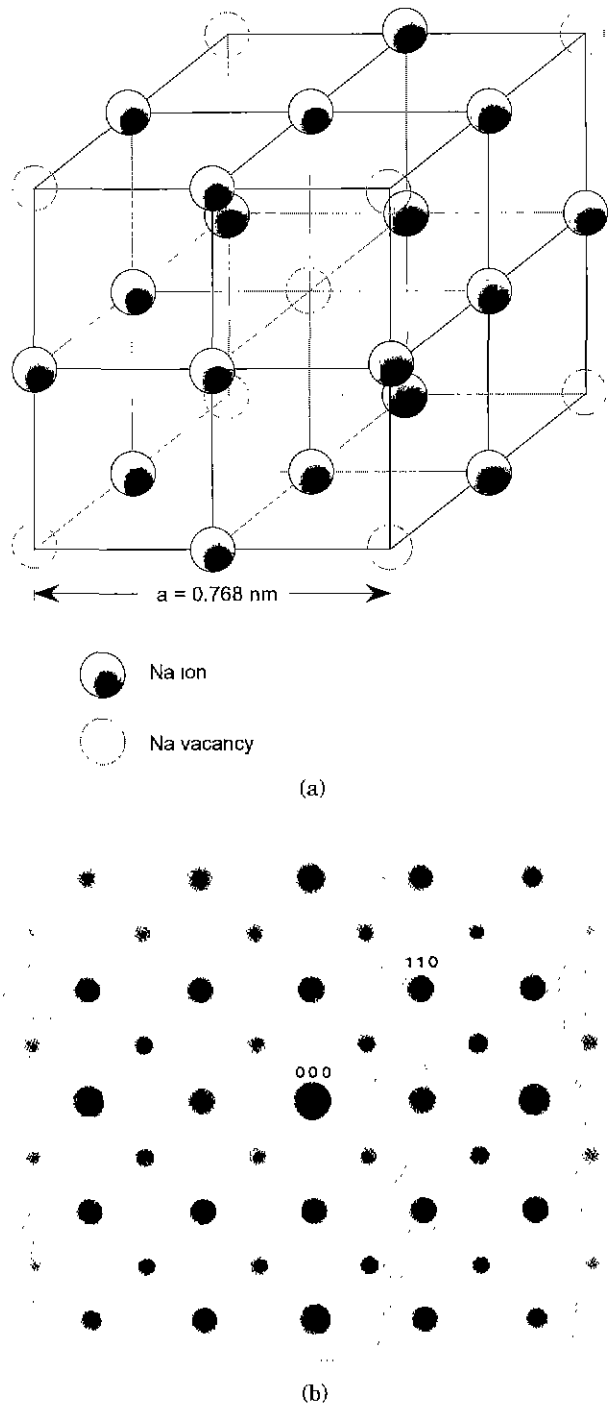


Fig. 3. (a) The unit cell of ordered Na_xWO_3 with x=0.75 (Na ion sites only shown) and (b) computer simulated diffraction pattern with [001] beam direction using the unit cell shown in Fig. 3(a).

with a=0.826 nm, b=0.843 nm, c=0.389 nm. Figure 4(b) is X-ray diffraction spectrum of the specimen with same composition reduced at 670°C for 24 hrs. Analysis of the peak position and intensity indicates that tetragonal and cubic perovskite phases coexist in this specimen The tetragonal phase was identified as $Na_{0.28}WO_3$ with a=b= 1.209 nm and c=0.375 nm. The lattice parameter of the

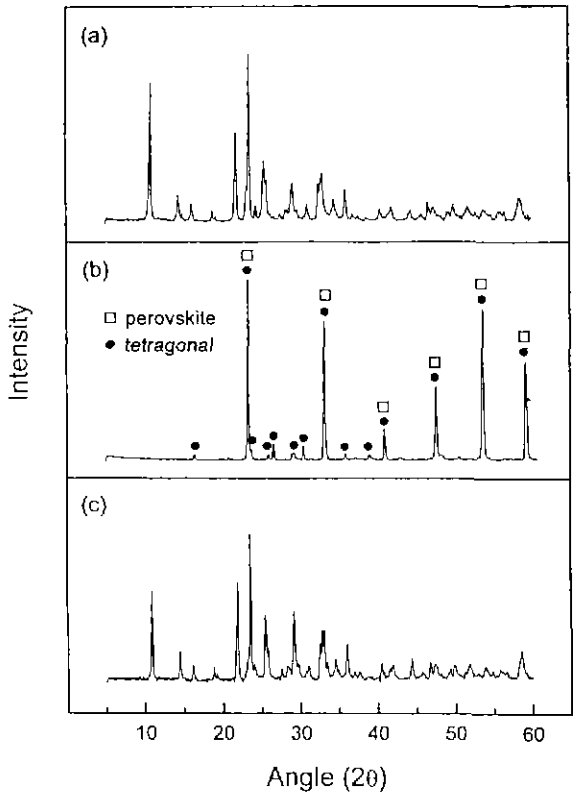
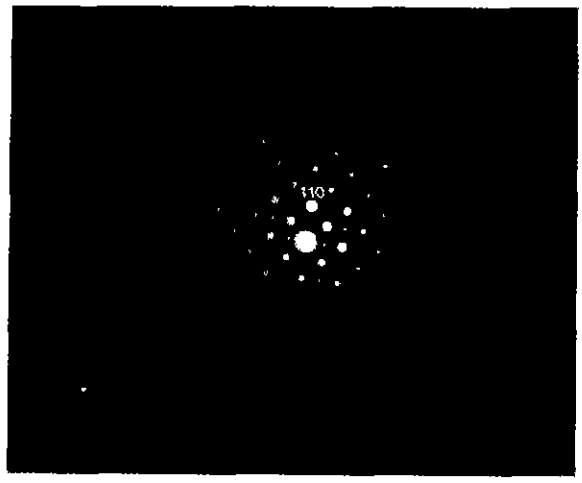


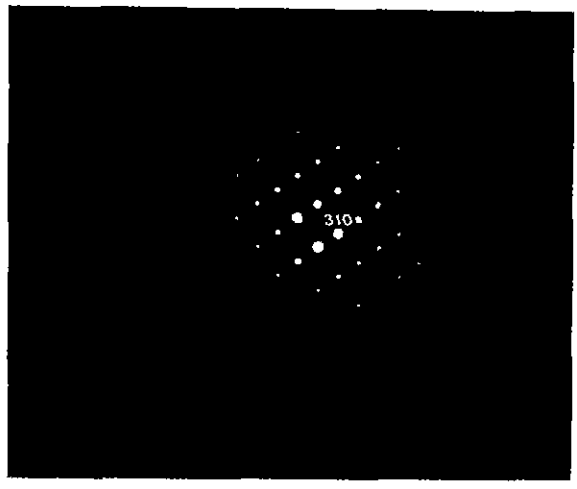
Fig. 4. X-ray diffraction spectra of Na_xWO_3 with x=0.5 (a) calcined at 600°C for 4 hrs, (b) reduced at 670°C for 24 hrs and (c) annealed at 600°C for 2 hrs.

perovskite phase was measured to be 0.382 nm. Since this parameter is smaller than that of $Na_{0.75}WO_3$ (a=0.384 nm), the perovskite phase was considered to be $Na_{0.75-y}WO_3$ where y is less than 0.25. The reduced specimen was annealed at 600°C for 2 hrs in the air. The X-ray diffraction spectrum of annealed specimen was the same as that of calcined specimen (see Fig. 4(c)). Thus, it is concluded that tetragonal and cubic perovskite phases in reduced specimen were unstable and they transformed to the triclinic phase during the annealing.

TEM study on the reduced specimen was carried out. The results are shown in Fig. 5(a) and 5(b). Figure 5(a) is [001] diffraction pattern of perovskite phase Na_xWO_3 with x =0.5 and it is indeed the diffraction pattern of $Na_{0.75-y}WO_3$ phase. In this diffraction pattern, extra spots were found at ½(110) position indicating the presence of ordering of Na ions in $Na_{0.75-y}WO_3$ phase. According to the computer simulation, in order for Na_xWO_3 to have perfect ordering along [110] direction, x in Na_xWO_3 should be 0.75. Thus, the ordered structure developed in $Na_{0.75-y}WO_3$ ($y < 0.25$) phase is considered as a Na-deficient partially ordered structure. In this structure, Na vacancies are created besides vacancies at (000) and (½½½) sites. Figure 5(b) shows electron diffraction pattern taken from different area of the same specimen. It could be either a diffraction pattern of $Na_{0.75-y}WO_3$ phase with [110] zone axis or a diffraction pattern of $Na_{0.28}WO_3$ tetragonal phase with [1 $\bar{3}$ $\bar{10}$] zone axis. If it



(a)



(b)

Fig. 5. Electron diffraction patterns of (a) perovskite phase with [001] zone axis and (b) tetragonal phase with [1 3 $\bar{1}$0] zone axis taken from Na_xWO_3 with x=0.5.

is the diffraction pattern of partially ordered $Na_{0.75-y}WO_3$, extra spots should be observed at ½(110) position. However since these extra spots were not found in diffraction pattern, the observed pattern is considered as the diffraction pattern of tetragonal phase with [1 $\bar{3}$ $\bar{1}$0] zone axis. Thus, TEM analysis confirms the X-ray result showing coexistence of two phases in reduced Na_xWO_3 with x=0.5.

For Na_xWO_3 with x=1.0, $Na_{1-z}WO_3$ cubic perovskite and Na_2WO_4 cubic phases were obtained after the reduction as shown in Figs. 6(a) and 6(b). The lattice parameter of $Na_{1-z}WO_3$ phase was 0.385 nm which is slightly larger than that of $Na_{0.75}WO_3$. Thus, z should be smaller than 0.25. However, these phases transformed to the calcined phase after the annealing (see Fig 6(c)). Diffraction pattern of reduced specimen of same composition is shown in Fig. 7. It is [001] zone axis perovskite diffraction pattern of $Na_{1-z}WO_3$ phase. Appearance of extra spots at ½(110) positions in this pattern indicates that ordering of Na ions was also considered to have developed in this

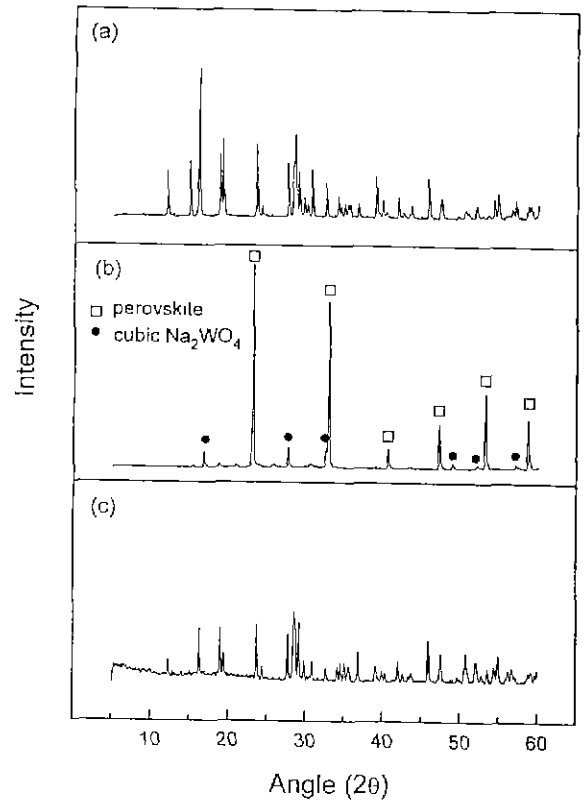


Fig. 6. X-ray diffraction spectra of Na_xWO_3 with x=1.0 (a) calcined at 600°C for 4 hrs, (b) reduced at 670°C for 24 hrs and (c) annealed at 600°C for 2 hrs.

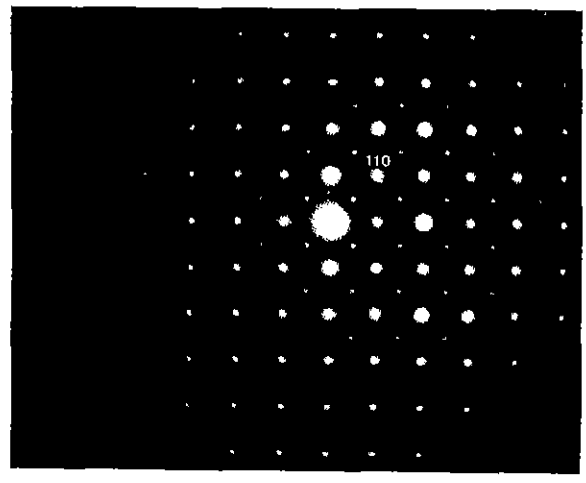


Fig. 7. Electron diffraction pattern of $Na_{1-z}WO_3$ phase with [001] zone axis taken from Na_xWO_3 with x=1.0.

phase. Moreover, this ordered phase is considered to be partially ordered because some of Na vacancies in perfectly ordered structure are expected to be occupied by Na ions.

IV. Conclusions

The crystal structures in Na_xWO_3 ($0.5 \leq x \leq 1.0$) were

studied using XRD and TEM. For Na_xWO_3 with x=0.75, perfect ordering of Na ions was developed along the [110] direction and the wavelength of ordering is twice of the interplanar distance of (110) plane. The unit cell of ordered structure is a superlattice containing eight $Na_{0.75}WO_3$ as suggested by previous investigation. In this unit cell, Na sites at (000) and (½½½) are vacant. The computer simulated diffraction pattern using the unit cell matches the experimental results. The completely ordered phase formed in Na_xWO_3 with x=0.75 was preserved even after the annealing at 600°C. Partially ordered perovskite phase with other phases were observed in Na_xWO_3 with x=0.5 and 1.0. However, after the annealing at 600°C for 2 hrs, these phases transformed to the phases found in calcined specimens.

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