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Rapidly quenched sodium tungsten bronzes

MASAHIRO TATSUMISAGO, TSUTOMU MINAMI, MASAMI TANAKA
*Department of Applied Chemistry, University of Osaka Prefecture, Sakai,
Osaka 591, Japan*

Rapid quenching was applied to the sodium tungsten bronzes, Na_xWO_3, of different x values. The crystallization processes of the coloured flakes obtained were analysed by differential thermal analysis and X-ray powder diffraction. It was found that an "amorphous bronze" phase is present in the quenched $Na_{0.71}WO_3$, whereas quenched $Na_{0.84}WO_3$ was composed of tungsten crystal and Na_2O–WO_3 glass. This difference is explained by the following equilibrium present in the melt of Na_xWO_3:

$$3x\mathrm{Na_2WO_4} + (6-4x)\mathrm{WO_3} + x\mathrm{W} \rightleftarrows 6\mathrm{Na}_x\mathrm{WO_3}$$

This equilibrium is shifted to the right when x is small ($x < 0.7$), while it is shifted to the left when x is large ($x > 0.8$).

1. Introduction

Recent development of several rapid quenching techniques (e.g. [1]) has made it easy to make specific compounds amorphous. For example, $LiNbO_3$ and $PbTiO_3$, known as the ferroelectrics, were prepared in the amorphous state by rapid quenching [2, 3].

The sodium tungsten bronzes, Na_xWO_3, are non-stoichiometric compounds with x ranging from 0 to 1 [4]. These bronzes are metallic in nature [5] in spite of being oxides, and they have been widely investigated for their electrical properties. If these bronze compounds could be prepared in the amorphous state, they would attract much interest from the standpoint of developing new, conductive materials.

We tried to prepare some sodium tungsten bronzes in the amorphous state by using a rapid quenching apparatus combining a thermal-image furnace and a twin roller. This paper reports the characterization of the quenched Na_xWO_3 and their crystallization processes by differential thermal analysis and X-ray powder diffraction.

2. Experimental procedure

Sodium tungsten bronze crystals (raw materials for quenching) were prepared from reagent-grade chemicals $Na_2WO_4 \cdot 2H_2O$, WO_3 and W, according to the method given in the literature [4]. The x values of Na_xWO_3 prepared were determined from the lattice constant, a, obtained by X-ray diffraction measurements, assuming that the following equation holds [4]:

$$a = 0.0819x + 3.7846$$

The crystalline Na_xWO_3 powders were pressed into rods and then sintered under reduced pressure at about 980 K.

Melting and quenching of the sintered rods were carried out under an argon atmosphere using the apparatus combining a thermal-image furnace and a twin roller reported elsewhere [6]. Differential thermal analysis (DTA) was carried out also in an argon atmosphere at a heating rate of $10\,\mathrm{K\,min^{-1}}$ in the temperature range 300 to 973 K.

X-ray diffraction measurements were carried out under reduced pressure in a temperature-regulated cell at temperatures ranging from 287 to 1023 K with a Rigaku Denki "Roter-frex" diffractometer.

3. Results and discussion

3.1. Properties of quenched Na_xWO_3

Rapid quenching was tried for the sintered rods of Na_xWO_3 of four compositions. Table I lists the compositions, colour, glass transition temperatures (T_g) and crystallization temperatures (T_c) of the quenched Na_xWO_3. Also given are the data of $Na_2W_2O_7$ glass for reference. Each quenched Na_xWO_3 consisted of transparent or semi-

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TABLE I Composition, colour, glass transition temperature (T_g) and crystallization temperature (T_c) of quenched Na_xWO_3 and glassy $Na_2W_2O_7$

Composition	Colour	T_g (K)	T_c (K)
$Na_{0.84}WO_3$	dark brown	620	637
$Na_{0.79}WO_3$	dark brown	631	656, 705
$Na_{0.71}WO_3$	dark blue	638	671, 697
$Na_{0.60}WO_3$	dark blue	647	673, 697
$Na_2W_2O_7$	colourless	611	653

transparent flakes (about 5 mm x 10 mm x 10 μm) and the colour changed with value of x; the flakes with relatively large x values ($x = 0.84$, 0.79) appeared dark brown and those with relatively small x ($x = 0.71$, 0.60) appeared dark blue.

Both T_g and T_c were observed in all the quenched Na_xWO_3, indicating that any quenched Na_xWO_3 contains glassy parts. It is worth noting that T_g and T_c values of the quenched Na_xWO_3, both of which tend to increase with a decrease in x, are close to those of the $Na_2W_2O_7$ glass. Thus, the glassy parts in the quenched Na_xWO_3 are considered to be closely related in composition with the Na_2O–WO_3 glasses, such as $Na_2W_2O_7$ glass. It should also be noted that two T_c's were observed except for $x = 0.84$, although any Na_2O–WO_3 glass has only one T_c [7].

3.2. X-ray diffraction of quenched Na_xWO_3

Fig. 1 shows the X-ray powder diffraction patterns of the four quenched Na_xWO_3 at ambient temperature. In the compositions with relatively large x, $x = 0.84$ and 0.79, a sharp peak attributable to tungsten crystal was observed. On the other hand, in the compositions with relatively small x, $x = 0.71$ and 0.60, the only crystalline phase observed was Na_xWO_3 [4]. Since the halo pattern, typical of the amorphous state, was also observed in each sample, the greater part of each quenched Na_xWO_3 must be amorphous.

3.3. Variation of X-ray diffraction with temperature

Fig. 2 shows the variation with temperature of the X-ray powder diffraction patterns of the quenched $Na_{0.84}WO_3$. At ambient temperature a peak due to the tungsten crystal was observed, as shown in Fig. 1. As the temperature increases up to 653 K which was just above T_c, however, many new peaks appear; these peaks are attributed to the $Na_2W_2O_7$ crystal. Further heating to 823 K not only strengthens the peaks due to the $Na_2W_2O_7$ crystal but also brings about other new peaks, attributable to Na_xWO_3 crystal. On further heating to 923 K the peaks due to the Na_xWO_3 crystal are strengthened and the peaks due to the $Na_2W_2O_7$ and tungsten crystals are weakened. Finally, at 973 K the peaks due to the $Na_2W_2O_7$ crystal almost disappear and only the peaks due to the Na_xWO_3 crystal remain.

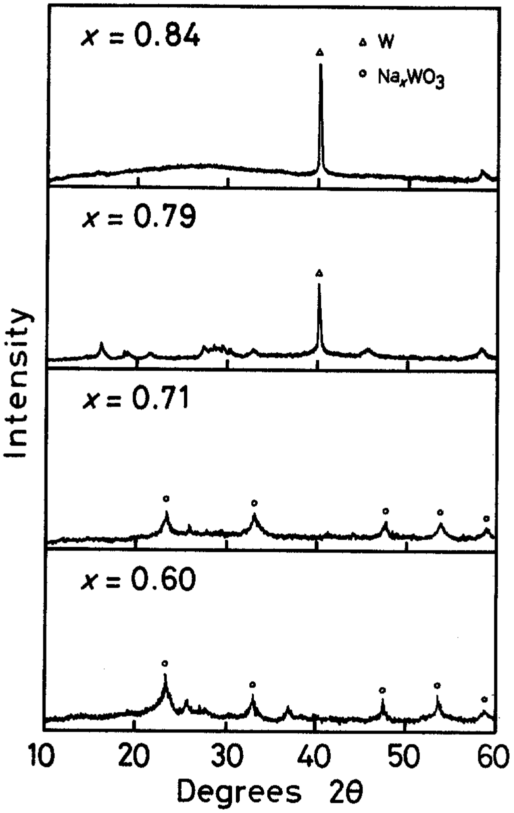

Figure 1 X-ray powder diffraction patterns of the quenched Na_xWO_3 at ambient temperature.

On the basis of these experimental results, it is concluded that the quenched $Na_{0.84}WO_3$ is composed of tungsten crystal and Na_2O–WO_3 glass of composition near $Na_2W_2O_7$. Thus, on heating, the glassy parts were completely crystallized to yield mainly the $Na_2W_2O_7$ crystal by about 800 K, and then the $Na_2W_2O_7$ crystal reacted with the tungsten crystal to form the Na_xWO_3 crystal finally at about 970 K.

Fig. 3 shows the variation with temperature of the X-ray powder diffraction patterns of the quenched $Na_{0.71}WO_3$. In this case, only broad peaks due to Na_xWO_3 crystal are observed at ambient temperature and these peaks are

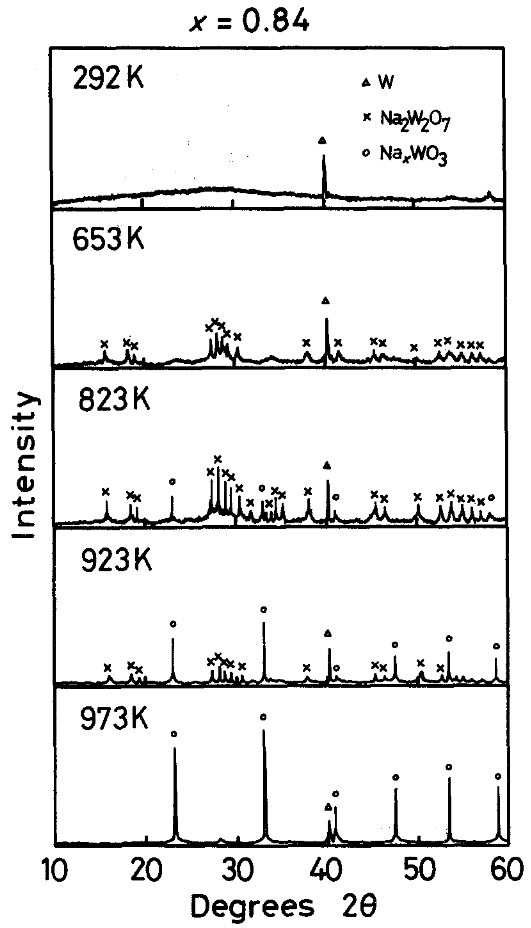

Figure 2 X-ray powder diffraction patterns of quenched $Na_{0.84}WO_3$ measured at several temperatures.

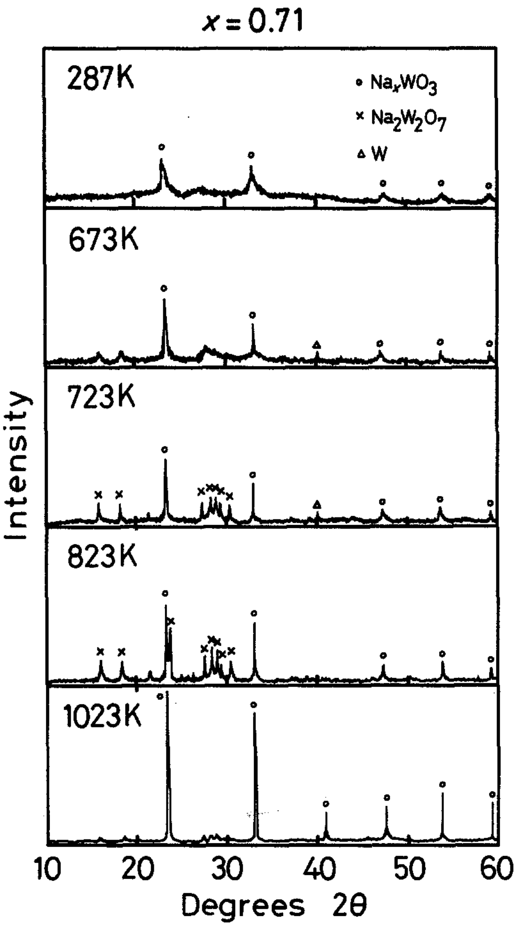

Figure 3 X-ray powder diffraction patterns of quenched $Na_{0.71}WO_3$ measured at several temperatures.

strengthened when the temperature was raised to 673 K ($\approx T_c$). Although weak peaks due to the $Na_2W_2O_7$ crystal arise on further heating, those peaks finally disappear and only the sharp peaks due to the Na_xWO_3 crystal remain at 1023 K, as in the case of $x = 0.84$. This result shows that the quenched $Na_{0.71}WO_3$ also contains a Na_2O–WO_3 glass with a composition near $Na_2W_2O_7$ because the $Na_2W_2O_7$ crystal was formed in the course of heating. However, the "amorphous Na_xWO_3" phase is considered to be present because the heating up to 637 K strengthened the peaks caused by the Na_xWO_3 crystal; the strengthening of the peaks due to the Na_xWO_3 crystal must have been brought by crystallization of the amorphous Na_xWO_3 phase. Furthermore, observation of two T_c's may be associated with the presence of amorphous Na_xWO_3 phase. In other words, the second T_c could correspond to the crystallization of the amorphous Na_xWO_3 phase; in Na_2O–WO_3 glasses two T_c's were not observed [7], as stated in Section 3.1.

3.4. Melting and quenching process

The reaction for the preparation of sodium tungsten bronzes from a melt is based on the equation [4]:

$$3x\mathrm{Na_2WO_4} + (6-4x)\mathrm{WO_3} + x\mathrm{W} \rightleftarrows 6x\mathrm{Na}_x\mathrm{WO_3}$$

However it was reported that the value of x in the reaction product Na_xWO_3 obtained deviated from the expected value because of the molar ratio of the reactants: the components on the left-hand side remained unreacted when the x value was large (≈ 1.0), and that the deviation was not observed when the x value was smaller than 0.6 [8, 9].

The variation of the X-ray diffraction patterns with a change in x (Fig. 1) is explained by assuming that the equilibrium represented by the equation above is present in the melting process of sintered rods of Na_xWO_3. When x is relatively large ($x > 0.8$), this equilibrium is shifted to the left. The components Na_2WO_4 and WO_3 in the mixtures of the left-hand side of the equation were rapidly quenched to form the Na_2O–WO_3 glass, and thus the flakes with $x = 0.79$ and 0.84 were mainly composed of Na_2O–WO_3 glass and tungsten crystal. On the other hand, when x is relatively small ($x < 0.7$), the equilibrium is shifted to the right. The flakes with $x = 0.71$ and 0.60 thus contained larger amounts of Na_xWO_3 rather than Na_2O–WO_3 glass or tungsten crystal, and part of the Na_xWO_3 was present in the amorphous state.

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