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Lattice Constants of Tetragonal Sodium Potassium Tungsten Bronzes

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Sodium potassium tungsten bronzes, $Na_xK_yWO_3$, having various values of x and y were prepared by electrolytically treating a fused mixture of carbonates of the two alkali metals and tungsten(VI) oxide. Lattice constants, a and c, of the tetragonal crystals were estimated by the X-ray powder method. Similarity of the crystal lattice of these bronzes to that of potassium tungsten bronzes, instead of to that of sodium tungsten bronzes, suggests that the lattice constants of the sodium potassium bronzes are by far more influenced by the potassium content than by the sodium content.

Tungsten bronzes are nonstoichiometric crystalline compounds represented by a general formula, Na_xWO_3, in which M is a metal ion and x has a value less than unity. Among them, sodium tungsten bronzes[*2] Na_xWO_3 and potassium tungsten bronzes K_yWO_3, especially the former, are the most popular.

Sodium bronzes have been prepared with relative ease over a wide range of x value. Their color and crystal system vary with values of x, and the crystal surfaces exhibit a characteristic metallic luster. On the other hand, the crystals of the potassium bronzes show neither variety in color nor metallic luster as in of sodium bronzes.

The marked difference in appearance between the two series of bronzes might be clarified by investigating the crystals of sodium potassium bronzes, intermediate or mixed bronzes having a general formula $Na_xK_yWO_3$ where the sum of x and y is less than unity. Also the role of metal ions could be revealed by determining the color and structure of the crystals.

Several kinds of sodium potassium bronzes have been prepared and their crystals investigated,[1–3] but with little information. We prepared sodium potassium bronzes with a wider range of composition and higher purity. Tetragonal crystals were

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[*2] Hereinafter, the tungsten bronze is designated as bronze.

1) G. von Knorre, *J. Prakt. Chem.*, [2]**27**, 49 (1883).

2) W. Feit, *Ber.*, **21**, 134 (1888).

3) E. O. Brimm, J. C. Brantley, J. H. Lorenz and M. H. Jellinek, *J. Amer. Chem. Soc.*, **73**, 5427 (1951).

subjected to X-ray diffraction in order to obtain their lattice constants.

Experimental

Materials. All chemicals used were of reagent grade. Tungsten rods supplied by Tokyo Tungsten Co., Ltd. were 2 mm in diameter and specified to be 99.98% pure.

Preparation. A powdered mixture consisting of anhydrous sodium, potassium carbonates and tungsten(VI) oxide $WO_3 \cdot H_2O$ (Table 1), was thoroughly melted in a porcelain crucible by heating at 800±15°C in an electric furnace. Two tungsten rods were placed in the crucible as electrodes with one end of each rod immersed in the melted mixture. An electric voltage was applied between the two electrodes so that the voltage drop across the electrodes was 1.0—1.2 V. A direct current, 2—5 A, was supplied. Crystals were soon formed at the cathode. After carrying out electrolysis for several hours, the current was switched off and the electrodes were removed. The melted mixture, along with the crystals, was allowed to cool to room temperature, and the remaining mass was treated first with boiling water, then with a hot nitric acid solution and finally with a hot sodium hydroxide solution. Thus the remaining crystals could be obtained.

Analytical Procedure. A powdered and weighed sample was fused in a nickel crucible together with a mixture of sodium carbonate and sodium nitrate in the ratio of 1 to 3 by weight,[4] and the fused product was dissolved in water. In the first place, potassium was determined gravimetrically as potassium tetraphenylborate precipitate $KB(C_6H_5)_4$. Subsequently tungsten was oxidized completely to sexivalent state with nitric acid, precipitated with hydrochloric acid and cinchonine, and the precipitate was ignited and weighed as WO_3. If the two procedures of precipitation were carried out in reverse order, an erroneous value for the potassium content would result from to the presence of excessive cinchonine in the solution which is used for the determination of potassium. Values of x and y for sodium potassium bronzes were estimated assuming that the ratio of tungsten to oxygen was 1 : 3[5] in bronzes, and also that the remainder which was obtained by subtracting the contents of potassium, tungsten and oxygen from the initial weight of the sample was estimated as sodium content.

Lattice Constants. The diffraction pattern of the powder was obtained with an X-ray diffractometer, compact type from Rigaku Denki Co., Ltd., Tokyo, using Cu-Kα radiation, $\lambda = 1.5418$ Å. Values of lattice distance, d, calculated from the pattern of each sample were then used to determine the appropriate lattice constants a and c by the usual procedure. The values of a and c were accurate within the error ±0.01 Å.

Density. The density of crystals was measured with a pycnometer using water as the immersion liquid. The values of density were reproducible within ±0.03 g/cm³. The accuracy of the data was proved by the density of metallic cadmium which was observed by the same procedure, the value 8.61 g/cm³ being sufficiently close to the value 8.642 g/cm³.[6]

Results and Discussion

Brimm *et al.*[3] prepared sodium potassium bronzes by merely fusing a mixture of Na_2WO_4, K_2WO_4, WO_3 and metallic tungsten. In the present work, however, carbonates were preferred to tungstates as starting materials on account of lower melting point and easier access. The bronzes produced by the process of Brimm *et al.* were by no means free from contamination, presumably of fine particles of metallic tungsten and some compounds of tungsten of lower oxidation states, as demonstrated by X-ray powder photography.[3,7] Thus we employed the electrolytic process of Knorre.[1] Sienko and Mazumder[8,9] prepared tungsten bronzes in an atmosphere of argon. In the present work materials were kept open to atmosphere without any difficulties. Crystals having uniform color and metallic luster were obtained.

The tetragonal crystals in square prisms of the sodium potassium bronzes are listed in Table 1. They are not exhaustive, but only those whose values of x and y and lattice constants were determined are shown. In Table 1 are shown, in successive columns, compositions of the starting materials, colors, compositions and the lattice constants a and c. Twenty one species of bronzes are arranged in the table in decreasing order of the alkali metal contents of the starting materials.

Crystals of tetragonal sodium bronzes were more or less bluish purple, probably because the tetragonal structure was limited to a narrow region of x. In the case of potassium bronzes, however, blue and reddish purple crystals were formed independent of the composition of the starting materials. In contrast, a variety of colors ranging from reddish purple to blue is covered by the group of tetragonal sodium potassium bronzes, as seen in the table. The crystal shown as No. 12 in Table 1 was the most reddish.

The ratios of Na to K in the bronzes were very nearly equal to the ratios of sodium carbonate to potassium carbonate in the composition of starting materials. But there were some exceptions. For instance, when the starting materials contained approximately ten times as much Na as K (Nos. 7, 8 and 9, Table 1), the product was a mixture of a small amount of needle-shaped blue crystals of

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[4] L. E. Conroy and M. J. Sienko, *J. Amer. Chem. Soc.*, **74**, 3520 (1952).

[5] B. A. Raby and C. V. Banks, *Anal. Chem.*, **36**, 1106 (1964).

[6] "CRC Handbook of Chemistry and Physics," 47th Ed., Chemical Rubber Co. (1966), B-161.

[7] W. R. Gardner and G. C. Danielson, *Phys. Rev.*, **93**, 46 (1954).

[8] M. J. Sienko, *J. Amer. Chem. Soc.*, **81**, 5556 (1959).

[9] M. J. Sienko and B. R. Mazumder, *ibid.*, **82**, 3508 (1960).

TABLE 1. COMPOSITION AND LATTICE CONSTANTS OF TETRAGONAL SODIUM POTASSIUM BRONZES

No.	Composition* of materials for preparation	Color** of product	Composition					
			Content (% wt)		$Na_xK_yWO_3$		Lattice constant	
	$Na_2CO_3 : K_2CO_3 : WO_3$		K	WO_3	x	y	a (Å)	c (Å)
1	2 : 1 : 4.5	p	4.640	90.38	0.56	0.30	12.28	3.83
2	1 : 2 : 4.5	rp	5.901	90.73	0.37	0.39	12.29	3.84
3	3 : 1 : 7	p	3.772	93.55	0.29	0.24	12.26	3.83
4	2 : 1 : 5.25	rp	4.515	93.59	0.20	0.29	12.30	3.83
5	1 : 1 : 3.5	rp	6.117	91.15	0.30	0.40	12.30	3.83
6	1 : 2 : 5.25	rp	5.395	93.63	0.10	0.34	12.30	3.84
7	15 : 1 : 32	b	1.094	94.89	0.43	0.07	12.17	3.78
8	10 : 1 : 22	b	1.639	92.97	0.58	0.10	12.18	3.79
9	6 : 1 : 14	bp	2.027	94.05	0.42	0.13	12.21	3.80
10	3 : 1 : 8	p	3.621	93.88	0.27	0.23	12.27	3.82
11	2 : 1 : 6	p	4.497	93.37	0.23	0.29	12.28	3.83
12	1 : 1 : 4	rp	4.858	92.37	0.30	0.31	12.29	3.83
13	1 : 2 : 6	p	5.465	91.61	0.32	0.35	12.28	3.83
14	1 : 5 : 12	p	5.934	92.08	0.22	0.38	12.28	3.83
15	1 : 20 : 42	p	6.763	92.18	0.12	0.43	12.28	3.83
16	2 : 1 : 6.75	p	3.350	92.69	0.43	0.21	12.24	3.82
17	1 : 1 : 4.5	p	4.676	93.50	0.20	0.30	12.28	3.83
18	1 : 2 : 6.75	p	5.120	93.58	0.14	0.32	12.26	3.83
19	1 : 5 : 13.5	p	6.215	91.83	0.21	0.40	12.27	3.83
20	2 : 1 : 7.5	bp	3.215	92.92	0.42	0.21	12.22	3.81
21	1 : 1 : 5	bp	4.500	94.32	0.13	0.28	12.26	3.82

* expressed in molar ratio ** rp: reddish purple, p: purple, bp: bluish purple, b: blue

sodium potassium bronze and a large amount of cubic sodium bronze.

It is noteworthy that the color of crystals varies from blue to reddish purple in accordance with the increase of the y values instead of the sum of x and y. In other words, the color of the crystal with a small y value was blue and that with a large y value was reddish.

Magnéli[10] stated that the tungsten-oxygen octahedra in tetragonal tungsten bronzes join each other by sharing oxygen atoms at the corners so as to form a framework with the formula WO_3, where the lattice contains empty tunnels which run right through the structure whose projections on the 001 plane consist of triangle, square and pentagon. Alkali metal atoms in bronzes are considered to be accomodated in either of the square and pentagonal empty tunnels. Particularly, in the crystal structure of the bronzes $Na_xK_yWO_3$, the potassium ions which are larger than the sodium ions would be accomodated more easily in the pentagonal interstices. On the other hand, dimensional consideration concerning the W–O bond length in comparison with the ionic size of K suggests that the square tunnels, as well as the triangular ones, would be too small to accomodate potassium ions. Thus it seems that the potassium ions should exist only in pentagonal spaces. Referring to the structure of sodium potassium bronzes, Wadsley[11] proposed that the interstitial ions are assorted according to their size. The present interpretation is consistent with the opinion of Magnéli and Wadsley, and is further supported by the following experimental facts.

Current efficiency in the electrolytic preparation was much lower for preparing potassium bronzes than for sodium bronzes. The process in which potassium bronzes were formed from a starting material consisting of potassium carbonate and tungsten(VI) oxide hardly proceeded, but the presence of only a twentieth part of sodium carbonate in one part of potassium carbonate remarkably facilitated the preparation of bronze, a sodium potassium bronze in this case instead of a potassium bronze. For example, from a starting material mixture consisting of potassium carbonate and tungsten(VI) oxide in the ratio of 1 : 2 a potassium bronze $K_{0.41}WO_3$ was produced, while from a starting material containing potassium salt and tungsten oxide in approximately the same ratio as above and additional sodium carbonate in such a small amount as a twentieth of the amount of potassium

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[10] A. Magnéli, *Ark. Kemi.*, **1**, 213 (1949).

[11] A. D. Wadsley, "Nonstoichiometric Compounds," ed. by L. Mandelcon, Academic Press, New York (1964), p. 98.

salt (No. 15, Table 1) a sodium potassium bronze $Na_{0.12}K_{0.43}WO_3$ was prepared in preference to the tetragonal potassium bronze. Brimm *et al.* similarly found that incorporation of any potassium into the structure of cubic sodium bronzes led exclusively to tetragonal bronzes. Therefore, it might be presumed that sodium ions were inserted into the K_yWO_3 host lattice which belonged to the tetragonal system, so that incorporation of sodium in the interstitial spaces existing in the host lattice stabilized the tetragonal crystal structure.

The lattice constant *a* of cubic sodium bronzes Na_xWO_3 is known to be linearly proportional to the *x* value as expressed by $a=0.0819x+3.7846$.[12] In other words, the WO_3 host lattice was expanded in accordance with the increase of the sodium concentration in the lattice. A similar result was observed with respect to potassium bronzes, because the reported *y* values of some tetragonal potassium bronzes K_yWO_3 proved to be in a parallel relation to the lattice constants of their crystals.[10,13]

It may be reasonable to presume that the potassium ions, larger than the sodium ions, in the crystal would influence more decisively the host lattice and might determine the size. The lattice constants, *a* and *c*, measured by the X-ray powder method are shown in Table 1. The value of c/a was unequivocally 0.312, so that, for the sake of simplicity, plotting in Fig. 1 was only for the constant *a*.

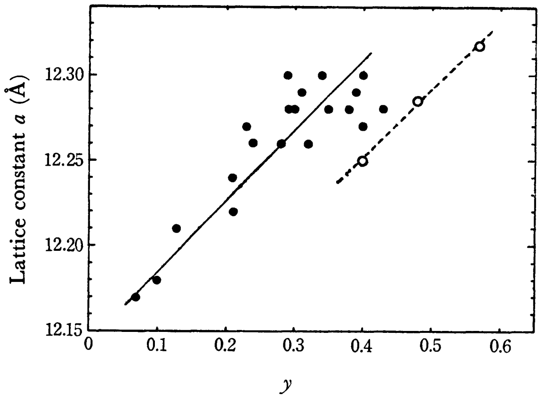

Fig. 1. Lattice constant *a* as a function of *y*.
● of tetragonal $Na_xK_yWO_3$
○ of tetragonal K_yWO_3[13,14]

The variation of the lattice constant *a* for $Na_xK_yWO_3$ crystal is shown as a function of *y* in Fig. 1. The lattice constant *a* reported of tetragonal potassium bronzes, K_yWO_3, for $y=0.40-0.57$[10,13] is also shown by open circles. The lattice constant for sodium potassium bronzes represented by solid circles, though it diverges more for larger values of *y*, seems to vary in the linear relation to *y* within the range in which measurement was made, as shown by the full line. The inclination of the line is approximately parallel to that of the broken line which shows the linear variation concerning potassium bronzes. For the same value of *y*, the lattice constant of a sodium potassium bronze is larger than that of a potassium bronze, presumably due to the sodium ions which are incorporated in the corresponding potassium bronze. Extrapolation of the full line to $y=0$ suggests that the extremity of sodium potassium bronze, where the potassium content diminishes to null, would have the lattice constant 12.14 Å. This value may be considered to be not inconsistent with 12.1 Å reported by Magnéli[14] for the lattice constant of a tetragonal sodium bronze because of larger error involved.

Although a linear relationship exists as stated above between the lattice constant *a* and *y* of the sodium potassium bronzes, no correlation was found between the lattice constant *a* and *x*. Therefore it may be concluded that, in determining the structure of sodium potassium bronzes, the role of *y*, or of the potassium content, is more important than that of *x*, or of the sodium content.

Crystals of tetragonal potassium bronzes K_yWO_3 are stable for *y* values larger than 0.14.[3] The *y* values with which crystals of sodium potassium bronzes are stable extend from over 0.4 to less than 0.1. In other words, a tetragonal form of potassium bronze crystals has been made stable for smaller *y* values by introducing sodium ions into the structure.

The color of crystals of sodium potassium bronzes can be related to their lattice constants. Thus, as seen in Table 1, it varies from reddish to bluish as the lattice constant *a* is decreased. The same inclination was observed with sodium bronzes, including cubic and tetragonal.[15,16] Color referred to in this paper involves the relevant regular reflectance spectrum, which will be discussed elsewhere in the near future.

The density of eleven samples of sodium potassium bronzes, whose *x* and *y* values varied from 0.22 to 0.58 and from 0.07 to 0.39, respectively, was 7.15 g/cm³ within an error of 0.03. This value argees with the density of tetragonal potassium bronze, 7.18±0.03 g /cm³ for $K_{0.40}WO_3$, by Sienko and Morehouse.[13]

The number of $Na_xK_yWO_3$ unit included in a unit cell of the crystal can be calculated from the observed density and lattice constants. The calculated value of the number for eleven different sodium potassium bronzes was 10, which agrees with

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[12] B. W. Brown and E. Banks, *J. Amer. Chem. Soc.*, **76**, 963 (1954).

[13] M. J. Sienko and S. M. Morehouse, *Inorg. Chem.*, **2**, 485 (1963).

[14] A. Magnéli, *Ark. Kemi.*, **1**, 269 (1949).

[15] M. E. Straumanis, *J. Amer. Chem. Soc.*, **71**, 679 (1949).

[16] G. Hägg, *Z. Phys. Chem.* (Leipzig), **B29**, 192 (1935).

that of the tetragonal potassium bronzes published by Magnéli(10) and by Brimm *et al.*(3)

In conclusion, the close resemblance of tetragonal sodium potassium bronzes as a whole to tetragonal potassium bronzes, instead of to sodium bronzes, with respect to color, lattice constants, density and the related quantity, has convenced us that the crystal lattices of the sodium potassium bronzes are mainly decided by the lattices of the corresponding potassium bronzes, and that the sodium ions are incorporated and play a less important role in determining the structure of the crystal.

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