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Short Communications

Note on the Thermal Expansion of the Wolfram Bronzes of Potassium, Rubidium and Cesium

PER-ERIK WERNER, PEDER KIERKEGAARD and ARNE MAGNÉLI

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

The bronze samples used in this investigation were prepared by reducing mixtures of alkali carbonate and wolfram trioxide with hydrogen gas at about 600°C [1]. The products were purified by boiling alternately with concentrated alkali carbonate solution, concentrated hydrochloric acid and aqua regia. The chemical analysis was in most cases confined to a determination of the alkali content by heating the bronze in a stream of hydrogen chloride gas and oxygen at about 500°C for up to 5 h and titrating the residual alkali chloride according to Mohr. In some instances, the wolfram content was also determined [2].

X-Ray investigation of the preparations was carried out with powder methods using a Guinier camera with strictly monochromatized CuKa_1 radiation for the room temperature work and employing techniques described earlier [3]. The accuracy of the unit cell parameters thus obtained should be better than that previously reported by one of the present authors. The data given in Table 1 were thus obtained.

The studies at elevated temperatures were made using a Norelco diffractometer (CuK radiation) provided with a vacuum furnace producing a maximum temperature

Table 2. Coefficients of linear thermal expansion of wolfram bronzes.

Sample	Axis	Temperature region	β(/°C) × 10^6
$K_{0.30}WO_3$	*a*	20–545°C	(6 ± 1)
		545–750°C	−(12 ± 3)
	c	20–750°C	(15 ± 3)
$Rb_{0.27}WO_3$	*a*	20–500°C	(7 ± 2)
		700–900°C	0
		900–970°C	−(6 ± 3)
	c	20–970°C	(12 ± 3)
$Cs_{0.31}WO_3$	*a*	20–720°C	(2.0±0.7)
	c	20–720°C	(4 ± 1)
$K_{0.45}WO_3$	*a*	20–765°C	(4.8±0.5)
	c	20–765°C	(5 ± 2)
$K_{0.52}WO_3$	*a*	20–740°C	(4.8±0.5)
	c	20–740°C	(3 ± 1)

Table 1. Unit cell dimensions of wolfram bronzes.

Sample	Structural type	Unit cell dimensions at room temperature	
		a Å	*c* Å
$K_{0.30}WO_3$	hexagonal [5]	7.385 ± 0.002	7.513 ± 0.005
$Rb_{0.27}WO_3$	»	7.394 ± 0.002	7.516 ± 0.004
$Cs_{0.31}WO_3$	»	7.406 ± 0.002	7.608 ± 0.004
$K_{0.45}WO_3$	tetragonal [4]	12.297 ± 0.004	3.836 ± 0.002
$K_{0.52}WO_3$	»	12.308 ± 0.003	3.842 ± 0.001

of the specimen of more than 1 000°C [6]. The coefficients of linear thermal expansion β found for the various specimens are listed in Table 2.

Data on the thermal expansion of cubic sodium wolfram bronze specimens from room temperature to 600°C have been reported by Rosen, Post and Banks [7], who also studied the thermal expansion of wolfram trioxide within this interval [8]. They found that cubic sodium bronzes show expansion coefficients of $(11.8 \pm 0.4) \times 10^{-6}$/°C that vary with the content of sodium. The coefficients change sharply at the transition temperatures to values around 4.5×10^{-6}/°C which vary with the sodium content. Wolfram trioxide shows a similar transition near 330°C which manifests itself as a change in the low-temperature monoclinic structure to an orthogonal, very probably orthorhombic, form above this temperature. The coefficients of expansion of the *a* and *c* axes are both close to 13×10^{-6}/°C below 300°C and about 18×10^{-6}/°C for the high-temperature form. In the *b* direction, however, the transformation of low- to high-temperature structure is accompanied by a change in the expansion coefficient from 14×10^{-6}/°C to -1.3×10^{-6}/°C.

The present study has given results for the tetragonal potassium wolfram bronze samples which are of the same magnitude as those obtained by Rosen, Post and Banks [7] for the sodium bronze above the transition temperature.

The anomalous thermal expansion behaviour of hexagonal potassium wolfram bronze at 545°C is rather similar to those occurring in the cubic sodium bronzes and in wolfram trioxide. This may indicate similarities in the so far unknown transitional mechanisms.

It is obvious from Table 1 that the unit cell dimensions of the hexagonal potassium and rubidium wolfram bronzes are almost exactly the same and that the cesium bronze unit is only slightly larger. This indicates that the wolfram and oxygen atoms form a rather rigid threedimensional network, the interstices of which should be of appropriate size to accomodate the potassium or rubidium atoms while the cesium atoms cause a slight expansion of the holes [5]. These minor structure differences may be associated with the differences in thermal expansion shown by the three hexagonal bronzes (*cf.* Table 2). Thus the potassium and rubidium compounds behave analogously up to about 500°C. The change in the rubidium compound is certainly not an abrupt one as in the potassium bronze but extends over a wide temperature interval. However, above 900°C, the two bronzes again behave similarly. The cesium bronze on the other hand shows a thermal expansion which is substantially less than those of the potassium and rubidium compounds.

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