
**STRUCTURE
OF INORGANIC COMPOUNDS**

Dedicated to the 80th Birthday of L.A. Shuvalov

Structure Type of Hexagonal Tantalum Bronzes with Variable Composition $K_6Ta_{6+z}O_{15}F_6(F, O)_y$: $Ta^{(5-\delta)+}$ Bronzes and Ta^{5+} Compounds

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Abstract—The structure type of hexagonal compounds with the variable composition $K_6Ta_{6+z}O_{15}F_6(F, O)_y$, where $Z \leq 1$ and $y \leq 3$ (sp. gr. $P6/m$, $a \sim 13.12 \text{ \AA}$, $c \sim 3.86 \text{ \AA}$) has been studied. Based on the structural data for a crystal of the Ta^{5+} -containing compound and two crystals of $Ta^{(5-\delta)+}$ -containing bronzes formed at the cathode during electrolysis of salt melts containing Ta^+ cations, it was established that the bronze formation is associated with the interstitial defects of intercalated Ta cations. The scheme of reduction of Ta cations at the cathode is suggested, and the formulas of the compounds are obtained with due regard for partial Ta reduction to various integral oxidation degrees. The crystals of the colorless transparent Ta^{5+} -containing compound of the composition $K_6Ta_{6.27}^{5+}O_{15}F_{7.4}$, brown semitransparent *partly reduced* Ta^+ -containing bronze of the composition $K_6Ta_{6.33}^{5+}Ta_{0.55}^+O_{15}F_{8.2}$, and dark gray metal-like *completely reduced* Ta^+ -containing bronze of the composition $K_6Ta_6^{5+}Ta^+O_{15}F_7$ are studied experimentally. © 2004 MAIK “Nauka/Interperiodica”.

INTRODUCTION

A decrease of the maximum reduction degree of B elements in perovskite-like and structurally related $A_{1-\Delta}B_{1+Z}(O, F)_{3\pm y}$ compounds (where A is an alkali metal and B is a transition metal from groups V or VI) gives rise to the properties unusual for complex or fluoride oxides, such as metallic or intense color, loss of transparency, metallic luster, and metallic or semiconductor conductivity [1]. In distinction from the isostructural compounds containing one or several transition metals in the maximum degree of oxidation, these compounds are called oxide bronzes, hereafter simply referred to as bronzes. Usually, to each complex oxide there correspond several oxide bronzes with different physical (optical and electric) properties depending on the degree of reduction of transition metal [1]. As a rule, the chemical composition of bronzes includes at least one element from group VI, e.g., W, (W, Nb), (W, Ta) bronzes, and the average degree of oxidation of the B element becomes higher than five. The degree of reduction of the transition metal in these structures is controlled by partial filling of the alkali-metal positions [1]. We showed [2] that the positions of the alkali metal in Ta bronzes with a degree of Ta oxidation less than

five are fully occupied. Since there is no information on the structural processes explaining the reduction of the tantalum oxidation degree, we decided to systematically study the structures of tantalum bronzes and compare the data obtained with the corresponding data for the isostructural Ta-containing compounds (for brevity, hereafter simply called Ta^{5+} compounds). Earlier, within this program, we studied in detail the cubic perovskite-like structure of the black bronze $KTa_{1+z}O_3$ ($z \sim 0.107$) possessing semiconductor properties [2]. Comparing the data obtained with the structural characteristics of a transparent dielectric $KTaO_3$ crystal [3], we found that a decrease in the averaged degree of tantalum oxidation in the bronze (partial reduction) results in the formation of substitutional defects (about 9% K cations per Ta–Ta dumbbell), which explains the semiconductor properties, loss of transparency, and metal-like appearance of the crystals. The establishment of these structural characteristics became possible because of the use of precision experimental and computational methods [2, 3].

The structure of the hexagonal bronze–conductor of the composition $K_6Ta_{6.5}O_{15+x}F_{6+y}$ [4] is compared with the structure of its dielectric analogue

$K_6Ta_{6.5}O_{14.5}F_{9.5}$ [5] refined in a rather crude approximation. As a result, the conclusions drawn in [4] are not complete.

The crystals of analogous hexagonal tantalum bronzes obtained in our study and having different colors and transparencies and the crystals of newly synthesized Ta^{5+} compound allowed us to perform comparative structural studies by the same methods. As a result, we obtained new data on the structure type and the effect of the degree of tantalum oxidation and their effect on the fine details of the crystal structure and the optical characteristics of these crystals. The comparative analysis of newly established structural characteristics was performed based on the data obtained and the known data [4, 5]. The results of this analysis are considered below.

EXPERIMENTAL

Synthesis. Two types of tantalum bronzes—dark-gray metal-like nontransparent crystals with metallic luster (bronze **I**) and brown semitransparent crystals (bronze **II**)—were obtained from the melted salt $K_2TaOF_5-(KF + NaF + LiF)_{out}$ system with the use of a soluble TaO anode by electrochemical deposition at a molybdenum cathode. Electrolysis was performed at the current density $D_c = 0.15 \text{ A/cm}^2$ and a temperature of 750°C . The synthesis of tantalum and Ta-containing compounds was described in detail elsewhere [3]. Both types of crystals were formed in one experiment. X-ray diffraction analysis (DRON-3M diffractometer, MoK_α radiation) of the powder prepared from the cathode product indicated that all the crystals were hexagonal tantalum bronzes, one of which was studied in detail earlier [4]. Both types of crystals had the habit of elongated hexagonal prisms or their fragments. It should be emphasized that the cathode product consisted of brown crystals of different shades and degrees of transparency. Against the background of brown crystals, there were also visually distinguishable homogeneous dark-gray metal-like nontransparent crystals. The electrolyte crystallized near the cathode also contained transparent crystals with a similar habit (**III**) whose diffraction patterns indicated the same structure type. The formation of crystals **III** without any contact with the cathode and their transparency led to the conclusion that tantalum in their composition has the same degree of oxidation (5+) as in the K_2TaOF_5 salt used in electrolysis.

It is also important to note that the formation of hexagonal bronzes at the cathode in electrolysis of the above salt melts is a poorly reproducible process even if all the controllable parameters of electrolysis, such as the melt temperature, current density, and concentration of the K_2TaOF_5 salt, are maintained constant. In addition, transparent crystals of this type were also formed during crystallization on a cathode of tetragonal

(structure type of tetragonal W-bronze) and cubic (perovskite type) bronzes.

Chemical analysis. Chemical microanalysis (ARL-SEMQ analyzer (15 kV, 25 nA) equipped with EDAX (12 kV, 100 nA)) showed that the crystals grown contained K, Ta, F, and O. No traces of Na were revealed. The accuracy of the microanalysis for each type of crystal was relatively low because of the varying Ta/K ratio (Table 1). However, one can clearly see the general tendency of an increase in the tantalum content in the row “transparent crystals **III**—brown semitransparent bronze **II**—dark-gray metal-like bronze **I**” (Table 1). Within the experimental accuracy, the fluorine content (7–8 wt %) is independent of the type of crystal. The evaluation of the chemical composition based on the refined structural data (Table 1) confirms these data.

Single-crystal diffraction experiment. The structural studies were performed on selected **I**, **II**, and **III** single crystals having the shape of hexagonal prisms with the well formed $\{hk0\}$ and $\{001\}$ crystal faces. X-ray diffraction experiments on all three types of single crystals were performed on a KM4 diffractometer with a CCD detector (MoK_α radiation). The main characteristics of the experiments and the unit-cell parameters of the crystals are indicated in Table 2. The analysis of the reciprocal-space sections did not reveal any satellite reflections or reflections that would indicate a multiple increase of any lattice parameter for any of the crystals.

STRUCTURE REFINEMENT

All the structural computations were performed using the JANA2000 program system [6]. The characteristics of the refinement are indicated in Table 2. The corresponding parameters of the atomic positions are listed in the upper part of Table 3, and the interatomic distances, in Table 4.

The refinement method was described in detail in the structure determination of the analogous compound—black hexagonal bronze [4]. The atomic coordinates of the structure framework borrowed from [4] [Ta(1), K, O(1), O(2), O(3), and F(1)] were refined in the full-matrix anisotropic approximation of atomic thermal vibrations within the sp. gr. $P6/m$. The F(1) position of this structure type was unambiguously established earlier [4] from the balance of valence strengths at anions (calculated by the methods suggested in [7]) and was confirmed in the present study (Table 5). The successive refinement of the occupancies of the Ta(1) and K positions indicated their complete filling (within the computation accuracy).

The partly occupied Ta(2) position on the sixfold axis was established from the residual synthesis calculated from the refined positions of the framework atoms. Pronounced displacements of Ta(2) atoms along the z axis were refined either by splitting the atomic position along this axis or by refining the components

Table 1. Characteristics of the chemical composition of $K_6Ta_{6+z}O_{15}F_6(O, F)_y$ compounds. **I** indicates crystals of metal-like bronze; **II**, crystals of brown semitransparent bronze; and **III**, colorless transparent crystals of the Ta^{5+} -containing compound

	I	II	III
Microanalysis data			
Atomic Ta/K ratio	1.10–1.20	1.08–1.16	1.03–1.10
F content	7–8 wt % (20–23 at. %)		
Refined structural data			
Chemical formula*	$K_6Ta_{6+0.487+z_1+z_2+z_3}O_{15}F_6(O, F)_{1.1}$	$K_6Ta_{6+0.516+z_1+z_2+z_3}O_{15}F_6(O, F)_{2.18}$	$K_6Ta_{6+0.271}O_{15}F_{6+1.4}$
Number of atoms Ta_{int} in the $M(1)$, $M(2)$, and $M(3)$ positions	$z_1 + z_2 = 0.20(8)$; $z_3 = 0.36(6)$; $z = z_1 + z_2 + z_3 = 0.56(14)$	$z_1 + z_2 = 0.24(8)$; $z_3 = 0.12(6)$; $z = z_1 + z_2 + z_3 = 0.36(14)$	
Chemical composition with allowance for interstitial defects, Ta_{int}	$K_6Ta_{7.05}O_{15}F_6(O, F)_{1.1}$	$K_6Ta_{6.88}O_{15}F_6(O, F)_{2.18}$	$K_6Ta_{6.27}O_{15}F_{7.4}$
The most probable composition of I and II	$K_6Ta_7O_{15}F_7 = K_6Ta_6^{5+}Ta^+O_{15}F_7$	$K_6Ta_{6.88}O_{15}F_{8.2} =$ $K_6Ta_{6.33}^{5+}Ta_{0.55}^+O_{15}F_{8.2}$	
Atomic Ta/K ratio	1.77	1.15	1.05

* The given values correspond to the refinement of the main positions of the structure with no account for intercalated Ta atoms (see Table 3).

Table 2. Main characteristics of diffraction experiments and refinement of structures **I**, **II**, and **III**

	I	II	III
X-ray experiment			
Diffractometer	KM4CCD		
Radiation	Mo K_α		
Range of measurements, $\sin\theta/\lambda_{max}$	0.8	0.8	0.8
Number of measured reflections	30131	30216	29494
Number of crystallographically independent reflections with $I > 6\sigma(I)$	800	780	680
μ , cm^{-1}	31.82	31.73	30.56
Allowance for absorption	Numerical integration over the real shape of crystal		
R_{av}	0.097	0.075	0.087
Sp. gr.	$P6/m$	$P6/m$	$P6/m$
Unit-cell parameters a , c (\AA), and V (\AA^3)	13.123(1), 3.8622(4); 575.995	13.132(1), 3.8610(4); 576.606	13.110(1), 3.8625(4); 574.899
d_x , g/cm^3	5.457	5.381	5.055
Refinement characteristics*			
$R(F)$, $wR(F)$	0.0333, 0.0447	0.0318, 0.0423	0.0273, 0.0361
Weighting scheme	$w = 1/\sigma(F)^2$		
GOF	2.90	2.80	1.32
Parameter of isotropic extinction	0.0169(3)	0.0122(3)	0.0148(2)
ρ_{max} , ρ_{min} , $e/\text{\AA}^3$	3.83, -1.97	3.51, -1.83	2.11, -2.14

* Values corresponding to the refinement of the main structural positions with no allowance for intercalated Ta atoms (see Table 3).

of the 6th rank tensor of anharmonic vibrations. The zero values of the C and E tensor components (because of the position symmetry) added eight parameters that should be refined independently, with the ratio of the number of reflections to the number of the parameters

to be refined exceeding 15. The characteristics of the refinement quality of these two variants were practically equivalent, and the position splitting was very small (maximum $Ta(2)$ – $Ta(2)$ distance 0.15 \AA for crystals **III**), which did not allow us to select unambigu-

Table 3. Atomic parameters in structures **I**, **II**, and **III**

Atomic positions and their characteristics	I	II	III
Main structural positions			
K [6j (x y 0)]:			
<i>p</i> ; <i>x</i> , <i>y</i>	1; 0.6566(1), 0.9127(1)	1; 0.6568(1), 0.9131(1)	1; 0.6584(1), 0.9128(1)
U_{eq}	0.0318(5)	0.0332(5)	0.0376(5)
U_{11} , U_{22}	0.0468(7), 0.0209(5)	0.0465(8), 0.0236(6)	0.0562(8), 0.0241(6)
U_{33} , U_{12} , Å ²	0.0191(5), 0.0104(5)	0.0198(5), 0.0101(6)	0.0225(5), 0.0124(6)
Ta(1) [6k (x y 0.5)]:			
<i>p</i> ; <i>x</i> , <i>y</i>	1; 0.36996(1), 0.84413(1)	1, 0.36989(1), 0.84412(1)	1, 0.36986(1), 0.84454(1)
U_{eq}	0.0093(2)	0.0121(2)	0.0126(2)
U_{11} , U_{22}	0.0099(3), 0.0064(3)	0.0129(3), 0.0099(3)	0.0129(3), 0.0103(3)
U_{33} , U_{12} , Å ²	0.0114(3), 0.0040(3)	0.0123(3), 0.0047(3)	0.0148(3), 0.0060(3)
O(1) [6k (x y 0.5)]:			
<i>p</i> ; <i>x</i> , <i>y</i>	1; 0.4659(2), 0.7774(2)	1; 0.4681(2), 0.7788(2)	1; 0.4667(2), 0.7767(2)
U_{eq}	0.024(1)	0.026(1)	0.025(1)
U_{11} , U_{22}	0.010(1), 0.012(2)	0.018(1), 0.008(2)	0.014(1), 0.010(2)
U_{33} , U_{12} , Å ²	0.050(2), 0.007(1)	0.054(2), 0.009(1)	0.050(2), 0.005(1)
O(2) [3g (0.5 0 0.5)]:			
<i>p</i> ; U_{eq}	1; 0.038(2)	1; 0.040(2)	1; 0.032(2)
U_{11} , U_{22}	0.012(2), 0.004(2)	0.015(2), 0.012(2)	0.013(2), 0.003(2)
U_{33} , U_{12} , Å ²	0.087(4), -0.004(2)	0.089(4), -0.001(2)	0.067(4), -0.006(2)
O(3) [6j (x y 0)]:			
<i>p</i> ; <i>x</i> , <i>y</i>	1; 0.6465(3), 0.1513(4)	1; 0.6446(3), 0.1512(4)	1; 0.6465(3), 0.1506(4)
U_{eq}	0.044(2)	0.045(2)	0.042(2)
U_{11} , U_{22}	0.064(3), 0.081(3)	0.069(3), 0.073(3)	0.061(3), 0.074(2)
U_{33} , U_{12} , Å ²	0.000(8), 0.046(2)	0.000(9), 0.042(2)	0.000(5), 0.039(2)
F(1) [6k (x y 0.5)]:			
<i>p</i> ; <i>x</i> , <i>y</i>	1; 0.6530(2), 0.7412(2)	1; 0.6531(2), 0.7417(2)	1; 0.6547(2); 0.7420(2)
U_{eq}	0.025(1)	0.026(1)	0.028(1)
U_{11} , U_{22}	0.015(1), 0.023(1)	0.011(1), 0.023(1)	0.020(1), 0.023(1)
U_{33} , U_{12} , Å ²	0.038(2), 0.009(1)	0.042(2), 0.006(1)	0.045(2), 0.013(1)
Ta(2)* [1b (0 0 0.5)]:			
<i>p</i> ; U_{eq}	0.487(1); 0.0291(1)	0.516(1); 0.0393(1)	0.271(1); 0.066(4)
$U_{11} = U_{22}$, U_{33}	0.0104(8), 0.067(2)	0.022(1), 0.073(3)	0.016(2), 0.16(1)
U_{12} , Å ²	0.0052(4)	0.0112(7)	0.008(1)
D_{1111} , D_{1133}	-0.0013(1), -0.015(1)	-0.0000(5), -0.017(2)	-0.0022(6), -0.020(7)
D_{3333} , Å ²	-0.21(6)	-0.21(11)	4.0(9)
F_{111111} , F_{111112}	-0.00025(3), -0.00011(2)	0.000(1), 0.00004(6)	-0.0005(1), -0.00020(8)
F_{111122}	-0.00005(2)	0.00003(5)	-0.00014(7)
F_{111133} , F_{113333}	-0.0010(2), -0.020(3)	-0.0014(4), -0.024(5)	-0.0031(9), -0.02(3)
F_{333333} , Å ²	-0.6(2)	-0.8(4)	11(4)
F(2) [12l (x y z)]:			
<i>p</i>	0.092(2)	0.182(2)	0.113(2)
<i>x</i> , <i>y</i> , <i>z</i>	0.038(2), 0.134(1), 0.188(6)	0.036(2), 0.141(2), 0.195(4)	0.037(2), 0.111(2), 0.100(4)
U_{iso}	0.08(1)	0.093(8)	0.055(6)
Positions of intercalated Ta atoms			
$M(1)$ [2e (0 0 z)]:			
<i>p</i> ; <i>z</i> ; $U_{\text{eq}} = 0.01$ Å ²	0.025(8); 0.127(2)	0.03(1); 0.122(2)	
$M(2)$ [6k (x y 0.5)]:			
<i>p</i> ; <i>x</i> , <i>y</i> ; $U_{\text{eq}} = 0.01$ Å ²	0.025(8); 0.121(2), 0.046(2)	0.03(1); 0.115(2), 0.046(2)	
$M(3)$ [6k (x y 0.5)]:			
<i>p</i> ; <i>x</i> , <i>y</i> ; $U_{\text{eq}} = 0.01$ Å ²	0.06(1); 0.677(2), 0.888(2)	0.02(1); 0.685(2), 0.892(2)	

* Position was refined in the anharmonic approximation of atomic thermal vibrations. The independent values of $D \times 10^4$ and $E \times 10^6$ are given.

Table 4. Interatomic distances (Å) in structures **I**, **II**, and **III**

	I	II	III
Framework [Ta(1)O ₅ F] octahedron			
Ta–O(1)	1.859(4) 1.989(3)	1.872(4) 1.994(3)	1.878(4) 1.977(3)
Ta–O(2)	1.899(1)	1.915(1)	1.894(1)
Ta–O(3)	1.948(1) × 2	1.944(1) × 2	1.947(1) × 2
Ta–F(1)	2.052(4)	2.055(4)	2.062(4)
Framework [K ₄ F ₄] polyhedron			
K–O(1)	2.950(2) × 2	2.934(2) × 2	2.958(2) × 2
K–F(1)	2.948(2) × 2 2.776(2) × 2	2.947(2) × 2 2.777(2) × 2	2.939(2) × 2 2.767(2) × 2
K–O(3)	3.19, 3.03	3.19, 3.04	3.20, 3.06
Channel [Ta(2)F ₆] statistical prism			
Ta(2)–F(2)	1.98(2) × 6	2.04(2) × 6	2.00(2) × 6
Framework–channel bonds			
K–F(2)	2.82 × 0.18 2.90 × 0.18	2.92 × 0.36 2.95 × 0.36	3.01 × 0.22 3.06 × 0.22

Table 5. Balance of valence strengths at framework [K₆Ta₆O₁₅F₆] anions in structures **I**, **II**, and **III**

Anions		Ta(1)	K	Total charge at anions
O(1)	I	1.179 + 0.830	0.110 × 2	2.229
	II	1.139 + 0.819	0.114 × 2	2.186
	III	1.120 + 0.857	0.107 × 2	2.191
O(2)	I	1.058 × 2		2.116
	II	1.014 × 2		2.028
	III	1.073 × 2		2.146
O(3)	I	0.927 × 2	0.088 + 0.057	1.999
	II	0.937 × 2	0.086 + 0.057	2.017
	III	0.930 × 2	0.081 + 0.055	1.996
F(1)	I	0.628	0.075 × 2 + 0.120 × 2	1.018
	II	0.623	0.076 × 2 + 0.120 × 2	1.015
	III	0.611	0.077 × 2 + 0.123 × 2	1.011

ously the true variant. The data in Tables 1 and 2 are given for the variant of the anharmonic approximation of atomic displacements for all three crystals. However, we can not exclude possible splitting of the Ta(2) position, especially for crystals **III**.

The F(2) position of the anionic environment of Ta(2) atoms was determined from the residual electron densities calculated within two space groups, $P6/m$ and $P\bar{6}$. In the sp. gr. $P\bar{6}$, the distribution of the residual electron density indicated the existence of a sixfold axis for all three crystals, which uniquely indicated the sp. gr. $P6/m$. Partial delocalization of the F(2) position, which manifests itself in high values of atomic thermal

displacements and in the existence of regions with elevated residual electron density, was studied in detail in [4] and confirmed in this study for all three crystals. The refinement of the anisotropy of atomic displacements gave the negative U_{33} components for crystals **III**. Therefore, we returned to the isotropic coefficients for all three crystals. For crystals **III**, the requirement of electroneutrality at the known degree of Ta ion oxidation (Ta⁵⁺) uniquely indicated the filling of the F(2) position solely with F ions. One cannot exclude possible partial replacement of F by O atoms in this position for crystals **I** and **II**, but this would practically not influence the refinement characteristics and, therefore, cannot unambiguously be established in the refinement.

RESIDUAL ELECTRON DENSITY

Comparing the residual electron density for crystals of bronzes **I** and **II** with those for transparent crystals **III**, we see that the latter are characterized by additional maxima $M(1)$, $M(2)$, and $M(3)$ (Figs. 1, 2). The electron-density values at these maxima are ~ 2.0 e/Å³ at $M(1)$ for both bronzes, 2.6 and 3.3 e/Å³ at $M(2)$ for bronzes **I** and **II**, and 3.8 and 3.5 e/Å³ at $M(3)$ for bronzes **I** and **II**, respectively. The exact localization of these maxima with approximately equal coordinates for both bronzes and their absence for the transparent crystals allowed us to identify the maxima with additional (intercalated) atoms—interstitial defects.

The requirement of electroneutrality of the compounds with the reduced degree of tantalum oxidation in **I** and **II** excludes anion intercalation. Therefore, the “intercalated position” might be occupied by either K or Ta cations. According to the chemical analysis, $(\text{Ta}/\text{K})_{\text{obs}} > 1.08$ (Table 1). For the basic atoms of the structure, this ratio has the value $[\text{Ta}(1) + \text{Ta}(2)]/\text{K} = 1.8$ and 1.09 for **I** and **II**, respectively. The additional K cations would decrease this ratio, but this is inconsistent with the microanalysis data. However, the assumption about possible intercalation of Ta cations in the bronze structures would explain the increase in Ta content in bronzes indicated above in comparison with the Ta content in transparent Ta⁵⁺ compound.

The allowance for the additional atomic positions with low occupancies with Ta_{int} atoms slightly reduces the reliability factors of the structural refinement of bronzes **I** and **II** and removes the maxima of the residual electron density from the syntheses. The refined characteristics of these positions are indicated in the lower part of Table 3.

The refinement shows that the general formula of all three crystals studied can be written as K₆Ta_{6+z}O₁₅F₆(F, O)_y. The values of the variable parameters and their notation are given in Table 1. The necessary corrections to these data are considered and discussed in the next section.

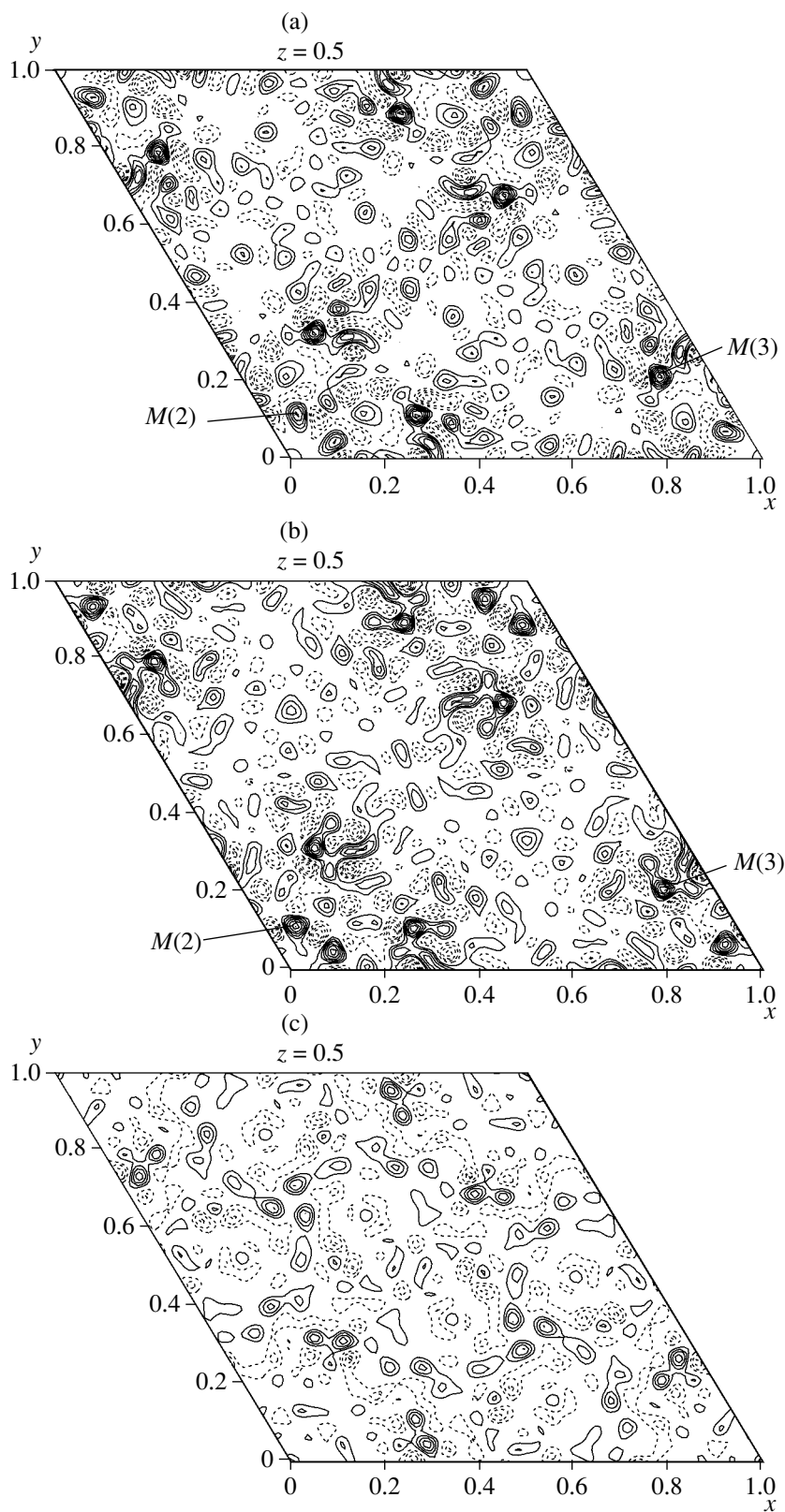


Fig. 1. $(xy\ 0.5)$ section of the residual electron-density for $K_6Ta_6+zO_{15}F_6(F, O)_y$ crystals: (a) bronze **I**, (b) bronze **II**, and (c) Ta^{5+} -containing compound. Isolines are separated by $0.5\ e/\text{\AA}^3$. The $M(2)$ and $M(3)$ maxima are identified with the interstitial defects of tantalum cations.

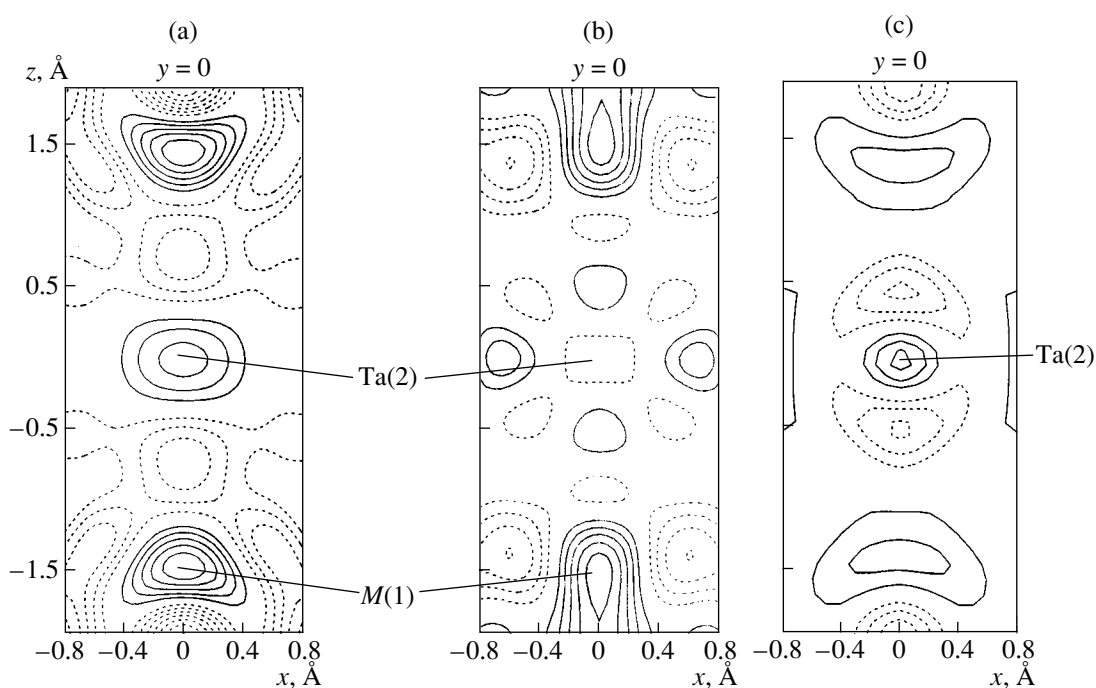


Fig. 2. (xOz) section of the residual electron-density for $K_6Ta_{6+z}O_{15}F_6(F, O)_y$ crystals: (a) bronze **I**, (b) bronze **II**, and (c) Ta^{5+} -containing compound. Isolines are separated by $0.25 e/\text{\AA}^3$. The Ta(2) position is indicated. The M(1) maximum is identified with interstitial defects of tantalum cations.

DISCUSSION OF RESULTS

Characteristics of the $K_6Ta_{6+z}O_{15}F_6(F, O)_y$ structure type. Comparing the structures of the three crystals studied with the structures of two structures determined earlier [4, 5], we established the main characteristics of the structure type of hexagonal tantalum bronzes of the variable composition $K_6Ta_{6+z}O_{15}F_6(F, O)_y$ with the unit-cell parameters $a \sim 13.12 \text{ \AA}$ and $c \sim 3.88 \text{ \AA}$, sp. gr. $P6/m$. Figure 3 shows this structure projected along the sixfold axis.

The $[Ta(1)O_5F(1)]$ octahedra with the central Ta(1) atom lying in the m plane ($z = 0.5$) form an open framework with wide (about 6 \AA in diameter) hexagonal channels. The framework is complemented with K atoms also located in the m plane ($z = 0$) in the channel walls and characterized by the trigonal–prismatic environment of O and F(1) atoms. The balance of valence strengths at anions (Table 5) shows that this coordination is complemented with two, more distant, O(3) atoms (at distances of ~ 3.0 and $\sim 3.2 \text{ \AA}$). The positions of all the main atoms [Ta(1), K, O(1), O(2), O(3), and F(1)] in all the crystals studied have close values of all the parameters, including the coefficients of anisotropic atomic displacements. Therefore, they all are considered as framework atoms. The chemical formula of the framework can be written as $[K_6Ta_6O_{15}F_6]$; the framework has the constant composition and structure in all the crystals studied, including those described in [4, 5].

The partially occupied Ta(2) and F(2) positions are situated in the hexagonal channels of the structure (Figs. 3, 4). The Ta(2) atom is located on the sixfold axis of the channel at the same level as the Ta(1) atom, $z = 0.5$. The atoms in this position are partly delocalized (up to splitting of the position, with the maximum amplitude along the sixfold axis being of about 1 \AA [5]). The F(2) atoms surround the Ta(2) atom statistically and occupy the positions of the hexagonal prism. However, this prism cannot exist locally because of too short F(2)–F(2) contacts ($\sim 1.5 \text{ \AA}$) in the basis. Therefore, this prism can be considered as a result of the superposition of two local trigonal prisms or two deformed octahedra (trigonal antiprisms). The atoms in the F(2) position are delocalized more pronouncedly than atoms in the Ta(2) position, which is seen from too high values of the atomic-displacement parameters and the existence of rather large area of elevated residual electron density, which was indicated in [5] and discussed in detail in [4]. Despite the fact that the coordinates of the F(2) position differ from crystal to crystal (Table 3, Fig. 4), the Ta(2)–F(2) distances have the same values, $\sim 2.0 \text{ \AA}$ (Table 4). The chemical formula of the structural unit located in the channel can be written as $[Ta_x(F, O)_y]$. It should be noted that this unit does not necessarily contain oxygen (crystal **III**). In the crystals known, $0.27 < x < 0.52$ and $1 < y < 2.5$. Thus, the channel has a variable composition and structure.

One of the characteristic features of the structure type of hexagonal tantalum bronzes is the noticeable

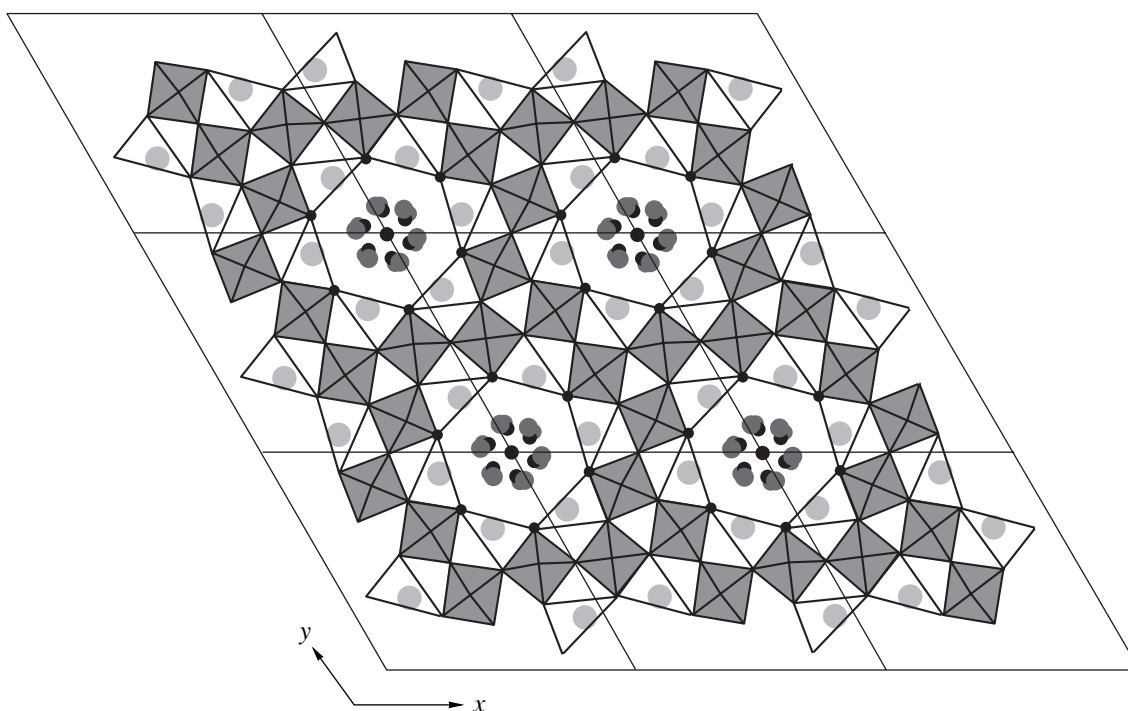


Fig. 3. $K_6Ta_6+zO_{15}F_{6+y}$ structure projected along the sixfold axis. The structure framework is built by $[Ta(1)O_5F(1)]$ octahedra and K atoms (depicted by large gray circles). The central atoms of octahedra, Ta(1), are located at a height of $z = 0.5$; the K atoms are located at a height of $z = 0$. The F(1) atoms are shown by black dots. Black circles in the centers of hexagonal channels show partly occupied Ta(2) positions. The statistical environment of Ta(2) atoms with F(2) atoms (dark gray circles) is shown as the superposition of the positions found in five crystals: **I**, **II**, and **III** (present study) and two crystals studied earlier [3, 4]. Thin lines show projections of the coordinate axes of nine unit cells.

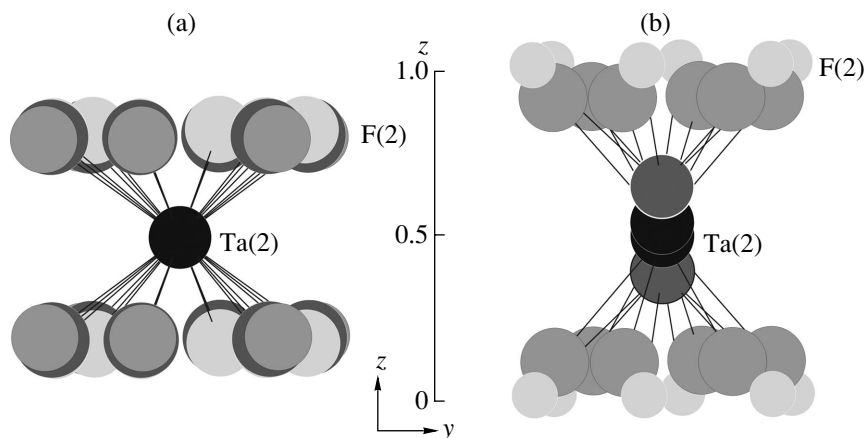


Fig. 4. Channels in the $K_6Ta_6+zO_{15}F_{6+y}$ structures: (a) bronzes; F(2) positions in crystals **I** and **II** (present work) and crystal studied in [4] are shadowed differently; (b) Ta^{5+} -containing compounds; Ta(2) and F(2) positions are indicated by more intense color for crystal **III** and less intense color for a crystal studied in [5].

change in the positions of channel atoms (mobility) with respect to the framework both within one structure (partial delocalization of F(2) atoms and anharmonicity of atomic displacements or splitting of the Ta(2) position) and in the transition from one crystal to another (the change in the coordinates of the F(2) position) (Figs. 3, 4). This is associated with the fact that the Ta(2) cations located along the channel axis are not

related to the framework anions (the minimum Ta(2)–F(1) distance is ~ 4.1 Å), whereas the channel F(2) anions and the framework cations form K–F(2) bonds statistically distributed over the channel with the low probability of their existence (0.1–0.2) determined by partial filling of the F(2) position (Table 3). Partial delocalization of F(2) and splitting of the Ta(2) position within one crystal are possible because of a possible

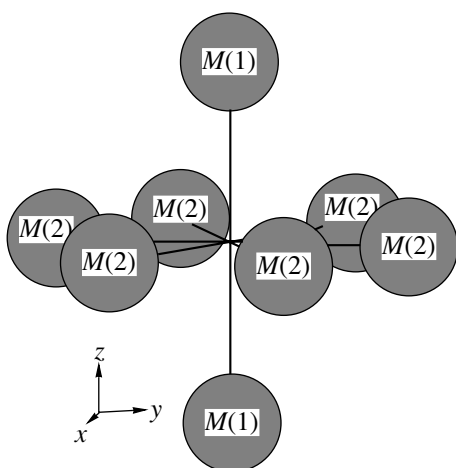


Fig. 5. Space–time cluster of interstitial defects— Ta_{int} cations—with the center in the vacant $Ta(2)$ position in structures of bronzes (interstitial defects of the first-type).

rotation of the K – $F(2)$ – $Ta(2)$ rigid unit: if one end of the chain (the K atom) is fixed, the other end of the chain [$Ta(2)$ atom, which is displaced along the channel axis] and its middle point [$F(2)$ atom] can also change their positions as was considered in detail elsewhere [4]. The causes of the variation of the coordinates of the $F(2)$ atom from crystal to crystal are explained by interstitial defects considered below.

Thus, the main characteristics of the structure type considered above—a framework having the constant composition and structure and the channels of the variable compositions mobile with respect to the framework—are independent of the degree of tantalum oxidation.

Differences in the structures refined. Crystals **I**, **II**, and **III** and the crystals described earlier [4, 5] have different compositions, different states of Ta-ion oxidation, and different optical properties (color and transparency). Therefore, it is interesting to consider not only the common features of the structure type but also the individual features of various crystals. The differences in their structures manifest themselves, first of all, in the statistical filling of hexagonal channels with $Ta(2)$ and $F(2)$ atoms (Figs. 3, 4).

The occupancies of the $Ta(2)$ positions are 0.487(1) and 0.516(1) in bronzes **I** and **II**, respectively, whereas in crystal **III**, the occupancy of this position is almost two times lower, 0.271(1). There is no one-to-one correspondence between the occupancies of the $Ta(2)$ and $F(2)$ positions: to the minimum occupancy of the $Ta(2)$ position there corresponds the intermediate occupancy of the $F(2)$ position (Table 3). In a crystal of black bronze studied in [4], the $Ta(2)$ position has the same coordinates as in bronzes **I** and **II**, but its occupancy is lower, 0.45(1). The coordinates (0.038 0.131 0.171) and occupancy [$p = 0.13(4)$] of the $F(2)$ position in the crystal studied in [4] differ from those obtained in the

present study (Fig. 4a, Table 3), but the $Ta(2)$ – $F(2)$ distances are the same, ~ 2.0 Å.

In transparent crystals studied in [5], the $Ta(2)$ atom was located in the split position with a $Ta(2)$ – $Ta(2)$ distance of 1.0 Å and occupancy of 0.5. This value is approximately two times higher than in analogous transparent crystals **III**. The data obtained in this study show that this position may also be split in crystals **III**, but with a much shorter $Ta(2)$ – $Ta(2)$ distance, ~ 0.15 Å (Fig. 4b). The $F(2)$ position was more precisely localized in the sp. gr. $P\bar{6}$ in [5], but we failed to localize this position in crystals **III**. However, despite the fact that the coordinates of this position obtained in [5] do not coincide with any of the variants in our study (Fig. 4b), the $Ta(2)$ – $F(2)$ distances are also equal to ~ 2.0 Å.

The mobility of atoms in channels (high values of the atomic thermal displacements of $Ta(2)$ and partial delocalization of $F(2)$ atoms) is a characteristic feature of all the crystals, although the mobility of $Ta(2)$ atoms is considerably higher in Ta^{5+} compounds than in bronzes (Fig. 4, Table 3). These discrepancies have not been interpreted because of interstitial defects in the bronze structures.

Interstitial defects and their influence on structural characteristics. Now, proceed to the experimental data which were obtained only in the present study (no similar data were considered in [4, 5]).

Analysis of residual electron-densities revealed additional intercalated tantalum atoms (cations), Ta_{int} , in the structures of bronzes **I** and **II** [$M(1)$, $M(2)$, and $M(3)$ positions in Figs. 1a, 1b and 2a, 2b] and showed their absence in the structure of compound **III** (Figs. 1c, 2c). The low occupancies of the intercalation positions ($pM(1) = pM(2) \sim 0.03$ and $pM(3) = 0.02$ and 0.06 , Table 3) refined at the fixed value of the of thermal-displacement parameters ($U_{\text{eq}} = 0.01$ Å²) result in low accuracy of the concentration of interstitial defects determined ($z = z_1 + z_2 + z_3$ in Table 1, where z_i is the number of Ta_{int} atoms in the $M(i)$ position per formula unit). Nevertheless, the Ta/K ratios obtained with due regard for Ta_{int} agree better with the data of chemical analysis performed without allowance for Ta_{int} atoms.

The positions of the interstitial defects Ta_{int} can be divided into two groups having different occupancies and different crystal-chemical function. The first group is formed by the $M(1)$ and $M(2)$ positions in the structure channels. These positions form a hexagonal bipyramidal cluster with the center coinciding with the position of the $Ta(2)$ atom (Fig. 5). This cluster can be represented as the superposition of four Ta – Ta dumbbells whose centers are located at one point and the Ta – Ta distances range from 2.7 to 2.9 Å. One dumbbell is oriented along the sixfold axis, whereas the three other dumbbells are located in the perpendicular plane at an angle of 60° to one another. The simultaneous presence of any two dumbbells of the four with the center at the same local point is low probable because of too short

(less than 1.3 Å) interatomic distances. Therefore, the cluster configuration of the defects of the first group can be considered as a result of averaging of the statistical distribution of Ta_{int} atoms over the eight vertices of the cluster. The location of the atom at the $Ta(2)$ position excludes the formation of a defect cluster around this local point. The crystal-chemical features of the interstitial defects of the first group can be formulated in the following way. (i) Ta_{int} atoms do not form anomalously short distances with atoms from any fully occupied position of the structure and (ii) Ta_{int} atoms form short distances with the atoms in the partially $Ta(2)$ (~1.3 Å) and $M(3)$ (~2.3 Å) positions.

The second type of interstitial defects is determined by the $M(3)$ position. Similar to K atoms, this position belongs to the framework walls limiting the channel space and, therefore, can be considered as the framework position complementing the plane of location of the basic tantalum atoms, $Ta(1)$ and $Ta(2)$, to the configuration of a close packed layer (Fig. 6). The distances between the main $Ta(1)$ atoms in this plane range within 3.65–3.82 Å. The $M(3)$ – $Ta(1)$ (3.09–3.77 Å) and $M(3)$ – $Ta(2)$ (3.64–3.73 Å) distances are comparable to the $Ta(1)$ – $Ta(1)$ distances in the plane. The centers of the statistical clusters considered above are also located in this plane. For further analysis, one should bear in mind that the positions of the first type of defects, $M(2)$, are located between the vacant $Ta(2)$ positions and the position of the interstitial defects of the second type, $M(3)$ (Fig. 6). The crystal-chemical characteristic of the interstitial defects of the second type is anomalously short distances to the completely filled positions of K atoms, K – $M(3)$ ~ 2.0 Å, which are equal to the sum of the ionic radii of K^+ and Ta^{5+} . We also observed anomalously short Ta – Ta_{int} distances (1.4 Å) in the crystals of the β -Ta tetragonal modification of metallic tantalum [8].

In the tantalum bronzes under consideration, the intercalated atoms in the β -Ta structure complement the plane of location of the main atoms to a close packed plane, with the average Ta – Ta distance in the plane being of about 2.8 Å (the distances range from 2.68 to 2.98 Å).

The mobility of channel atoms correlates with the concentration of defects of the second type in bronzes **I** and **II**: the thermal parameters of both $Ta(2)$ and $F(2)$ are much higher than those in bronze **III**, where the occupancy of the $M(3)$ positions is three times lower than in bronze **I** (Table 3). This correlation can be explained in the following way. The framework–channel interaction may occur only via the formation of K – $F(2)$ bonds. Thus, the mobility of the channel atoms depends on the strength of this interaction characterized by the corresponding bond lengths. In the Ta^{5+} compounds, the total charge of the framework of the $K_6Ta_6O_{15}F_6$ structure is zero and the lengths of the K – $F(2)$ bonds exceeding 3.01 Å (crystal **III**, Table 4) indicate the van der Waals nature of the framework–channel interaction. Since the balance of the valence strengths at the framework anions (Table 5) calculated using the data for Ta^{5+} does not allow one to distinguish between bronzes **I** and **II**, on the one hand, and compound **III**, on the other hand, it is possible to draw the conclusion that tantalum occupying the main positions of the framework has the maximum oxidation degree (Ta^{5+}) of all three structures. In this case, the Ta cations incorporated into $M(3)$ give rise to the total positive charge of the framework which should be compensated with the negative charge of the structural unit located in the channel and an increase in the ionic component of the interaction between the framework K cations and the channel $F(2)$ anions, i.e., by shortening of the K – $F(2)$ distances. Indeed, the bond length shorter in **I** in

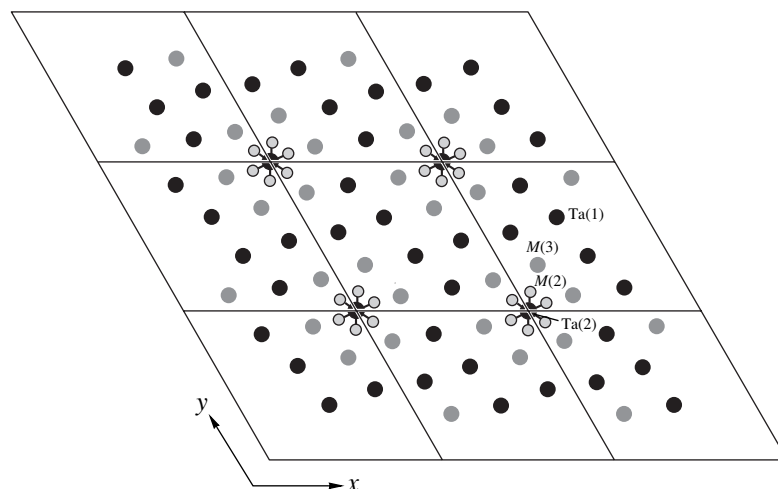


Fig. 6. Distribution of Ta_{int} cations in the $(xy0.5)$ plane. Interstitial defects of the second type ($M(3)$ position) are shown by dark gray circles and complement the main $Ta(1)$ and $Ta(2)$ positions (black circles) to a close packed layer. Interstitial defects of the first type ($M(2)$ position shown by light gray circles) are located along the paths of cation migration from the $Ta(1)$ to $M(3)$ position.

comparison with the bond length formed in **II** corresponds to a higher concentration of interstitial defects in $M(3)$ (Table 3). Taking into account the structural rigidity and the charge balance of the framework and, in principle, possible dynamics of channel atoms, one can assume that shortening of K–F(2) distances is explained by the displacement of F(2), which was really observed experimentally: at close K coordinates, the minimum length of the K–F(2) bond decreased from 3.01 Å in **III** to 2.82 Å in **I** and 2.92 Å in **II** because of the differences in the coordinates of the F(2) atoms (Table 3).

Thus, the change in the coordinates of the F(2) atoms observed in different crystals (Table 3) is the necessary condition for attainment of the optimum K–F(2) distances for each structure (Table 4) and is determined by the positive charge of the framework dependent, in turn, on the concentration of the second-type interstitial defects in $M(3)$. On the other hand, the lower the number of these defects (i.e., the lower the occupancy of the $M(3)$ position), the weaker the framework–channel interaction (i.e., the longer the K–F(2) bonds) and, therefore, the higher the mobility of atoms in the channel (i.e., the higher the values of the atomic-displacement parameters of the channel atoms). The experimental data (Table 3) confirm the above thesis: the atomic displacements of the Ta(2) atoms are minimal in **I**, somewhat more pronounced in **II**, and may reach the values resulting in splitting of this position in **III**.

Thus, the major differences between **I**, **II**, and **III** crystals—different mobilities and coordinates of Ta(2) atoms—are associated with the incorporation of positive interstitial defects Ta_{int} into the structure framework. An increase in the displacement parameter of F(2) atoms in bronzes **I** and **II** in comparison with its value in **III** can readily be understood if one takes into account the specific features of reduction of Ta^{5+} ions at the cathode considered below.

Characteristics of compounds formed due to reduction at the cathode. Reduction at the cathode may take place only at a certain potential corresponding to the attainment by some ions in the electrolyte of a certain reduced state. Therefore, all the cathode products obtained as a result of any reduction process in one experiment may contain a chemical element only in two oxidation states—one corresponding to the initial state, and the other corresponding to the reduced state. For ionic–covalent compounds, only the integral values of the oxidation degree have physical sense.

We consider the bronze formation associated with reduction of pentavalent tantalum ions at the cathode. In the general case, in addition to the initial Ta^{5+} ion, one can expect the formation of crystals containing any of the reduced Ta^{4+} , Ta^{3+} , Ta^{2+} , and Ta^{+} ions and also atomic Ta^0 .

Taking into account that the crystals of bronzes **I** and **II** were obtained in one electrochemical experiment, we assume that all the reduced $Ta^{(5-\delta)+}$ ions in

both crystals are in the same oxidation degree (the same integral parameter δ). The possible stoichiometric bronze compositions are obtained with due regard for the above characteristics of their formation at the cathode.

Scheme of formation of hexagonal tantalum bronzes at the cathode. As we have already mentioned, transparent crystals **III** not containing reduced tantalum ions were obtained simultaneously with crystals of bronzes **I** and **II**, which contain partly reduced tantalum. Under a microscope, among the crystals obtained in one batch, we also observed some crystals having the shape of hexagonal prisms with brown faces and radially colored basis—from the colorless center to the intense brown perimeter. Cleaving these crystals, we revealed that their bulk also had similar zonal structure. The middle parts of other elongated prismatic crystals had a clear boundary between the colorless center and brown periphery. These visual observations led to the conclusion that crystals of these bronzes could be formed because of reduction of tantalum ions in the already formed crystals of Ta^{5+} compounds in direct contact with the cathode. This reduction seemed to be possible because of the mobility of reducible tantalum ions in the channel. The reduction mechanism can be represented by the following sequence. Fluctuations of the melt composition in the region near the cathode give rise to nucleation and subsequent growth of crystals of the Ta^{5+} compound. The contact between the crystal and cathode results in reduction, first of all, of Ta^{5+} cations in the structure channels, because these cations are screened by anions to a lesser degree than other Ta^{5+} cations (the statistical character of anion distribution in the partly occupied F(2) position around Ta(2) cations). As a result, the channels acquire a negative charge, which is compensated because some F(2) anions migrate into the melt, whereas some Ta^{5+} cations move from the melt to the channels and also because partly reduced $Ta^{(5-\delta)+}$ cations migrate from the channels to the $M(3)$ position in the framework. The cations in the $M(3)$ position charge the framework and, thus, intensify the interaction between the framework and the channel via formation of K–F(2) bonds. This results in a lower mobility of F(2) anions and blocking of their migration to the melt with an increase of the framework charge, i.e., with an increase in the number of cations in $M(3)$. The capture of Ta^{5+} ions from the melt, their motion along the channel, and their reduction at the cathode are limited by the unvarying number of ions. On the other hand, the velocity of Ta^{5+} migration (or the rate of electron exchange between oppositely charged tantalum cations) along the channel axis is lower, the larger the number of reduced $Ta^{(5-\delta)+}$ ions located along this axis. When all the channel cations in the crystal bulk are reduced to Ta^{5+} , the reduction process ceases and the crystal becomes *completely reduced* $Ta^{(5-\delta)+}$ bronze (depending on the conditions of electrolysis, δ may take one of integral values 1, 2, 3, or 4).

The other limiting parameter of the reduction processes is the duration of the contact between the cathode and crystal. If the reduction process is interrupted, the crystals formed can also contain unreduced Ta^{5+} cations in the structure channels. Hereafter, these crystals are called partly reduced $\text{Ta}^{(5-\delta)+}$ bronzes. Obviously, the degree of completeness of the reduction process can vary even within one crystal because of the anisotropy of conductivity (only along the hexagonal axis) and different areas of the crystal–cathode and crystal–melt contacts in different parts of the crystal. The formation of bronze crystals with different degree of the completeness of the reduction process in single experiment is explained by different influence of each of the parameters limiting reduction of randomly oriented growing crystals.

Within the framework of the above scheme of reduction, the $M(1)$ and $M(2)$ maxima of the residual electron density interpreted as interstitial defects of the first type correspond to the highest probability of encountering cations on the paths of their migration from the $\text{Ta}(2)$ positions: $M(1)$ indicates migration of tantalum along the channel axis, and $M(2)$, migration of tantalum into the framework (into $M(3)$). Since the multiplicity of the $\text{Ta}(2)$ position is unity and the interstitial defects arise as a result of redistribution of cations occupying this position, the total number of cations in the $\text{Ta}(2)$, $M(1)$, $M(2)$, and $M(3)$ positions (Z in Table 1) should not exceed unity. This is confirmed (within the accuracy of standard deviations) by the results obtained for bronzes **I** ($Z = 1.05(14)$) and **II** ($Z = 0.88(14)$).

The mechanism of tantalum reduction suggested here allows one to interpret higher U_{eq} values of $\text{F}(2)$ anions in bronzes in comparison with the analogous values in the Ta^{5+} compound and also different occupancies of the $M(1)$, $M(2)$, and $M(3)$ positions, because, in fact, various stages of the reduction process in these bronzes are fixed. The following characteristics obtained for bronze **II** indicate that the intermediate stage of the reduction process in this bronze is fixed:

—the concentration of the interstitial defects in $M(3)$ is lower (hereafter, $z_3 = 0.12$ atoms per unit cell) than the concentration of atoms in the $M(2)$ and $M(1)$ positions along the migration paths ($z_1 + z_2 = 0.24$);

—the highest possible value of the displacement parameter of the $\text{F}(2)$ atom ($U_{\text{iso}} = 0.093 \text{ \AA}$), which reflects its pronounced delocalization at the moment of cessation of crystal formation;

—the maximum number of $\text{F}(2)$ anions (2.2) at a low number of tantalum cations ($6 + Z = 6.88$) in the unit cell.

On the contrary, the state of bronze **I** was estimated to be close to the state of complete reduction because of the following:

—a higher defect concentration in $M(3)$ ($z_3 = 0.36$) than in $M(2)$ and $M(1)$ ($z_1 + z_2 = 0.20$);

—a lower value of the displacement parameter of $\text{F}(2)$ ($U_{\text{iso}} = 0.08 \text{ \AA}$);

—the minimum number of $\text{F}(2)$ anions (1.1) at the maximum possible number of tantalum cations ($6 + Z = 7$) in the unit cell.

Chemical formula of the compounds with the variable composition $\text{K}_6\text{Ta}_{6+z}\text{O}_{15}\text{F}_6(\text{F}, \text{O})_y$ (theoretical analysis). The composition of the compounds with the structure type studied can be considered at several levels:

$$\begin{aligned} & \text{K}_6\text{Ta}_{6+z}\text{O}_{15}\text{F}_6(\text{F}, \text{O})_y \\ &= \text{K}_6\text{Ta}_{6+x+z}\text{O}_{15}\text{F}_6(\text{F}, \text{O})_y \quad (1) \\ &= [\text{K}_6\text{Ta}_6\text{O}_{15}\text{F}_6\{\text{Ta}_{z_3}\}][\text{Ta}_x(\text{F}, \text{O})_y\{\text{Ta}_{z_1+z_2}\}]. \end{aligned}$$

Square brackets show the compositions of the framework and the channel. Hereafter, the curly brackets indicate Ta_{int} atoms whose total number, $\text{Ta}_{\text{int}} - z = z_1 + z_2 + z_3$, is represented as a sum of the atoms in the $M(1)$, $M(2)$, and $M(3)$ positions. The total variable number of tantalum atoms in the structure, $Z = x + z$, is, (x), the sum of the basic atoms in the partially occupied $\text{Ta}(2)$ position, (x), of multiplicity 1 and the total number of Ta_{int} atoms, (z), and y is the number of atoms in partly occupied $\text{F}(2)$ position of multiplicity 12.

Compounds of pentavalent tantalum ($\delta = 0$). The results obtained in the present study show that Ta^{5+} compounds contain no interstitial defects. Thus, relation (1) can be written in the simplified form as

$$\begin{aligned} & \text{K}_6\text{Ta}_{6+x}\text{O}_{15}\text{F}_6(\text{F}, \text{O})_y \quad (2) \\ &= [\text{K}_6\text{Ta}_6\text{O}_{15}\text{F}_6][\text{Ta}_x(\text{F}, \text{O})_y]. \end{aligned}$$

The framework composition $[\text{K}_6\text{Ta}_6\text{O}_{15}\text{F}_6]$ is constant and its total charge is zero. The variable composition of the compounds is explained by partial occupancy of the position in the channel $[\text{Ta}(2) = x\text{Ta}$ and $\text{F}(2) = y(\text{F}, \text{O})]$ and the chemical composition of its anionic component, which admits the above variations.

The ranges of x and y variation can be evaluated proceeding from the crystal-chemical limitations imposed on the $\text{F}(2)$ position of multiplicity 12 in which the atoms form the first coordination sphere of $\text{Ta}(2)$ with due regard for the total charge balance of cations and anions located in the channel. As has already been noted, in fact, the 12-vertex hexagonal $[\text{Ta}(2)\text{F}(2)_{12}]$ prism corresponding to the complete occupancy of the $\text{F}(2)$ position cannot exist because of too short $\text{F}(2)$ – $\text{F}(2)$ contacts ($\sim 1.3 \text{ \AA}$) in its basis. The possible statistical $[\text{Ta}(2)\text{F}(2)_6]$ polyhedra (trigonal prism and antiprism) corresponds to 50% occupancy of this position. However, these polyhedra can be formed only in every second unit cell (or even more seldom) because of too short $\text{F}(2)$ – $\text{F}(2)$ contacts between the polyhedra

($\sim 1.5 \text{ \AA}$). Therefore, the occupancy of this position is $pF(2) \leq 0.25$ and $0 < y = 12 \times pF(2) \leq 3$.

The condition of channel electroneutrality is written as $5x = y + y(O) = 2y(O) + y(F)$, where the total number of anions, $y = y(O) + y(F)$, is represented as the sum of the numbers of O and F ions. It follows from the above equation that $y = 5x - y(O)$. Considering two possible limiting chemical compositions of the anionic position (F or O), we obtain the following condition of electroneutrality of the channel valid for any mixed composition of the F(2) position

$$5x/2 \leq y \leq 5x, \quad (3)$$

where the lower limit y corresponds to the presence in the channel solely of divalent O anions, $[\text{Ta}_x\text{O}_{2.5x}]$, whereas the upper limit, solely to the presence of monovalent F anions, $[\text{Ta}_x\text{F}_{5x}]$. This signifies that the channel can contain different number y of anions (depending on their kind) at the same occupancy $\text{Ta}(2) = x$.

The value of the local coordination number of Ta(2) atoms averaged in space and time, $(\text{cn})_{\text{av}}$, equal to the ratio of the number of anions, y , to the number of cations, x , is obtained from Eq. (3) as $2.5 \leq [(\text{cn})_{\text{av}} = y/x = 5 - y(O)/x] \leq 5$. The latter condition signifies that the maximum number of anions per Ta(2) atom cannot exceed five. Therefore, the $[\text{Ta}(2)\text{F}(2)_6]$ polyhedron is always of a statistical nature. It is logical to assume that the probability of the structure-type stabilization considered here is higher, the higher the occupancy of the vertices of this polyhedron, i.e., the closer the $(\text{cn})_{\text{av}}$ value is to six. Obviously, the minimum possible value of $(\text{cn})_{\text{av}}$ equal to 2.5 corresponds to filling of the anionic position with only O ions, whereas the maximum possible value, $(\text{cn})_{\text{av}} = 5$, corresponds to filling of this position with only F ions at $y = y(F) = 5x$.

Now, evaluate the occupancies of the Ta(2) position, x , at which the value of $(\text{cn})_{\text{av}}$ is close to the maximum possible value. It can readily be shown that

—if $0 < x \leq 0.6$, the F(2) position can be filled solely with F anions irrespectively of the x value, $y = y(F) = 5x$. The O ions which reduce the $(\text{cn})_{\text{av}}$ value can have any relative concentration ranging from zero [$y = y(F) = 5x$] to the complete filling of the F(2) position with oxygen [$y = y(O) = 5x/2$]. At the fixed concentration of O ions, the higher the x value, the less the influence of the present oxygen on the $(\text{cn})_{\text{av}}$ of Ta(2) atoms;

—if $0.6 < x \leq 1$, this structure type can be formed without oxygen anions, because $3 < 5x = y + y(O) \leq 5$ and $y \leq 3$. In this case, with an increase in x from 0.6 to 1.0, the possible number of F ions decreases from 5 to zero and, therefore, the maximum possible value of $(\text{cn})_{\text{av}}$ decreases from 5 to 2.5.

The above estimation shows that the probability of the structure-type stabilization is higher in the range $0 < x \leq 0.6$ and that there is no oxygen in the F(2) position; the probability decreases with an increase in x

from 0.6 to 1.0. The closer x is to 0.6, the higher the probability that the F(2) position is filled not only with F ions but also with a small amount of oxygen. Thus, for the Ta^{5+} compounds, the limitations imposed on the stoichiometry in formula (2) are: $y \leq 3$, $x = [y(F) + 2y(O)]/5 \leq 1$, where $y(F) + y(O) = y$. The most probable compositions are $\text{K}_6\text{Ta}_{6+x}\text{O}_{15}\text{F}_{6+5x} = [\text{K}_6\text{Ta}_6\text{O}_{15}\text{F}_6][\text{Ta}_x\text{F}_{5x}]$ with the subscripts x ranging within $0 < x \leq 0.6$.

It should be emphasized that the formula $\text{K}_6\text{Ta}_{6.5}\text{O}_{14.5}\text{F}_{9.5} = [\text{K}_6\text{Ta}_6\text{O}_{12.688}\text{F}_{8.312}][\text{Ta}_{0.5}\text{O}_{1.812}\text{F}_{1.188}]$ given in [5] for transparent Ta^{5+} compounds is somewhat erroneous. This can be explained by the fact that the balance of the valence strengths at framework anions, which allows one to unambiguously localize the F and O atoms (Table 5) and, thus, adequately determine the framework charge and write its formula, was not estimated in [5]. According to Eq. (3), the coefficient $p\text{Ta}(2) = 0.5$ ($x = 0.5$) determined in [5] can correspond to the number of anions in the channel ranging within $1.25\text{O} \leq y \leq 2.5\text{F}$ but not to $y = (1.812\text{O} + 1.188\text{F}) = 3(\text{F}, \text{O})$, as was indicated in [5]. Thus, the most probable formula of Ta^{5+} compound studied in [5] is $[\text{K}_6\text{Ta}_6\text{O}_{15}\text{F}_6][\text{Ta}_{0.5}\text{F}_{2.5}] = \text{K}_6\text{Ta}_{6.5}\text{O}_{15}\text{F}_{8.5}$. The refinement of structure **III**, another example of a Ta^{5+} compound, showed that the F(2) position did not contain any oxygen because $y \sim 5x$ and $[\text{K}_6\text{Ta}_6\text{O}_{15}\text{F}_6][\text{Ta}_{0.27}\text{F}_{1.4}] = \text{K}_6\text{Ta}_{6.27}\text{O}_{15}\text{F}_{7.4}$. Thus, the compositions of both Ta^{5+} compounds confirm the conclusion about the stabilization of the structure type in the absence of oxygen in the channel.

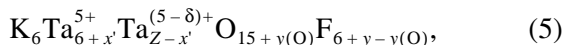
Compounds containing $\text{Ta}^{(5-\delta)+}$ ions with reduced degree of oxidation (bronzes). The variable composition of bronzes depends not only on the variations in the channel composition but also on the variable number of Ta_{int} atoms, which are absent in the Ta^{5+} compounds. The composition of the $[\text{K}_6\text{Ta}_6\text{O}_{15}\text{F}_6\{\text{Ta}_{z3}\}]$ framework has a variable component $z3$ equal to the number of Ta_{int} atoms in the $M(3)$ position, which is related to the total positive charge of the framework. Therefore, the charge of the structure channel $[\text{Ta}_x(\text{F}, \text{O})_y\{\text{Ta}_{z1+z2}\}]$ is opposite to the charge of the framework. To estimate the variable parameters in formulas (1), we have to write the electroneutrality condition of the structure.

The positive charge of the framework due to $\text{Ta}_{\text{int}}^{(5-\delta)+}$ in the $M(3)$ position equals $(5-\delta)z3$. The negative charge of the channel is associated with the complete or partial reduction of Ta^{5+} in the Ta(2) position and incorporation of $\text{Ta}_{\text{int}}^{(5-\delta)+}$ ions with a reduced oxidation degree into the $M(1)$ and $M(2)$ positions. Therefore, the equation of compound electroneutrality can be written as

$$y + y(O) = (5 - \delta)(Z - x') + 5x', \quad (4)$$

where $y(O) \leq y$. The left-hand side of Eq. (4) describes the total charge of the channel anions that neutralize the total charge of cations in the partly occupied positions in the right-hand side of the equation; x' is the number of unreduced Ta^{5+} ions in the Ta(2) position.

It is seen from Eq. (4) that the total varying number Z of cations is controlled, first of all, by the number y of anions and, at the given y value, depends on the degree of reduction of tantalum ions, δ , and not on the number x of reduced $Ta^{5+x'}$ ions in the position Ta(2). Taking into account that $Z \leq 1$, we find from Eq. (4) that $y(O) \leq 2.5$. Thus, the compositions of bronzes with the structure type considered here can be written as



where $\delta = 1, 2, 3, 4$, or 5 , $y \leq 3$ is the total variable number of (F, O) anions, including $y(O) \leq 2.5$ oxygen ions, and $Z \leq 1$ is the total variable number of tantalum cations, including $x' = (y + y(O) - (5 - \delta)Z)/\delta$ unreduced Ta^{5+} cations, where $0 \leq x' < 1$. For completely reduced bronzes, $x' = 0$ by definition, and the corresponding bronzes have the composition $K_6 Ta_6^{5+} Ta_Z^{(5-\delta)+} O_{15+y(O)} F_{6+y-y(O)}$.

All the variable parameters in the generalized composition described by formula (5) depend on the degree of reduction of tantalum ions (δ) and presence of oxygen anions in F(2). It is also interesting to consider three additional particular cases: maximum reduction of some Ta^{5+} ions up to Ta^0 ($\delta = 5$); absence of oxygen in the structure channels ($y(O) = 0$); and the combination of the first two conditions.

If reduction proceeds up to Ta^0 ($\delta = 5$), the presence of anions depends only on the unreduced Ta^{5+} ions in the Ta(2) position, $x' = y/5 + y(O)/5$. Then, formula (5) is simplified to $K_6 Ta_{6+x'} Ta_{Z-x'}^0 O_{15+5x'-y} F_{6+2y-5x'}$. In this case, the completely reduced bronze has no anions in the channels: $K_6 Ta_6^{5+} Ta_Z^0 O_{15} F_6 = [K_6 Ta_6^{5+} O_{15} F_6 Ta_{z3}^0][Ta_{Z-z3}^0]$.

This variant differs from Ta^{5+} compounds only by the presence of interstitial defects—neutral Ta_{int} atoms. The total charge of the framework is zero, which explains the high mobility of ions and atoms in the channel.

The absence of oxygen ions in the channel corresponds to the composition $K_6 Ta_{6+x'} Ta_{Z-x'}^{(5-\delta)+} O_{15} F_{6+y}$, where $\delta = 1, 2, 3, 4$, or 5 ; $y \leq 3$, $Z \leq 1$ is the total variable number of Ta cations, including $x' = (y - (5 - \delta)Z)/\delta$ unreduced Ta^{5+} cations, $0 \leq x' < 1$, $Z \leq y/(5 - \delta)$, if $\delta \neq 5$. With the same number of anions in the channel (y), the number of unreduced Ta^{5+} ions in the Ta(2) position (x') is less than in the presence of oxygen, which corresponds to a higher $(cn)_{av}$ of Ta and stabilizes the structure. Therefore, these compositions are more probable.

At the maximum possible tantalum reduction ($\delta = 5$) and in the absence of oxygen in the structure channels,

the composition described by (5) becomes $K_6 Ta_{6+0.2y} Ta_{Z-0.2y}^0 O_{15} F_{6+y} = [K_6 Ta_6^{5+} O_{15} F_6 \{Ta_{z3}^0\}] \cdot [Ta_{0.2y}^{5+} Ta_{Z-z3-0.2y}^0 F_y]$. In terms of crystal chemistry, the compounds with such compositions are highly probable because $(cn)_{av} = 5$, i.e., is close to six for Ta^{5+} ions in the Ta(2) position and intercalation of neutral Ta atoms into the structure. Proceeding from the degree of tantalum reduction, i.e., the δ parameter, the type of compounds considered here can be related to $Ta^{(5-\delta)+}$ bronzes, with due regard for the fact that only some tantalum ions are reduced.

The occupancies of the Ta(2), F(2), and Ta_{int} positions correspond to the following compositions: $[K_6 Ta_6 O_{15} F_6 \{Ta_{0.36(6)}\}][Ta_{0.487(1)}(F, O)_{1.10(2)} \{Ta_{0.20(8)}\}]$ for bronze **I** and $[K_6 Ta_6 O_{15} F_6 \{Ta_{0.12(6)}\}][Ta_{0.516(1)}(F, O)_{2.18(2)} \{Ta_{0.20(8)}\}]$ for bronze **II**. With due regard for the condition $Z \leq 1$, the composition of bronze **I** is $[K_6 Ta_6 O_{15} F_6 \{Ta_{0.34}\}][Ta_{0.49}(F, O)_{1.1} \{Ta_{0.17}\}]$. The anion composition in the channels can be refined with an accuracy of the determination of possible degrees of oxidation of reduced tantalum ions by Eqs. (4) and (5).

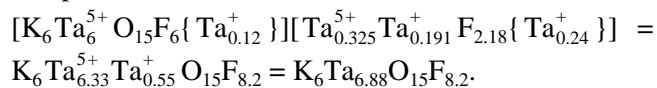
Estimation of oxidation degree of tantalum in bronzes I and II. First of all, we should like to note that no reduction of Ta^{5+} ions to Ta^0 ($\delta = 5$) is possible in **I** and **II**, because the shortening of the K–F(2) distances in comparison with analogous distances in **III** would indicate the existence of charges of both channel and framework, i.e., the presence of cations instead of neutral atoms in the $M(3)$ position. Substitution of $x, y, z1, z2$, and $z3$ values obtained for **I** (Table 1) into Eq. (4) with due regard for the fact that $y(O) \leq y = 1.1$ yields $\delta \geq 3$. Therefore, in order to determine the most probable degree of tantalum reduction in bronzes **I** and **II**, one has to consider two possible cases of correspondence of formula (5) to the chemical composition obtained, i.e., $\delta = 3$ and $\delta = 4$.

If $\delta = 3$, some Ta^{5+} ions are reduced to Ta^{2+} , i.e., **I** and **II** are Ta^{2+} bronzes. With due regard for the errors in the determination of the position occupancies, formula (5) can be written as $[K_6 Ta_6^{5+} O_{15} F_6][Ta_{0.34}^{2+}][Ta_{0.49}^{2+} O_{1.0} \{Ta_{0.17}^{2+}\}]$ for bronze **I** and $[K_6 Ta_6^{5+} O_{15} F_6 \{Ta_{0.12}^{2+}\}][Ta_{x'}^{5+} Ta_{0.52-x'}^{2+} O_{3x'-0.42} F_{2.6-3x'} \{Ta_{0.24}^{2+}\}]$ for bronze **II**, where x' is the number of unreduced Ta^{5+} ions in the Ta(2) position ranging from 0.14 (no oxygen in channels) to 0.52 (mixed anionic composition of channels). The two limiting compositions of the channels in **II** are $[Ta_{0.14}^{5+} Ta_{0.38}^{2+} F_{2.18} \{Ta_{0.24}^{2+}\}]$ and $[Ta_{0.52}^{5+} O_{1.13} F_{1.05} \{Ta_{0.24}^{2+}\}]$. In this case, **I** is the completely reduced Ta^{2+} bronze containing no F anions in the channels and **II** is the partly reduced Ta^{2+} bronze containing at least 1.05 F anions in the channels.

If $\delta = 4$, some Ta^{5+} ions are reduced to Ta^+ , i.e., **I** and **II** are Ta^+ bronzes. Bronze **I** has the composition $[\text{K}_6\text{Ta}_6^{5+}\text{O}_{15}\text{F}_6\{\text{Ta}_{0.34}^+\}][\text{Ta}_{x'}^{5+}\text{Ta}_{0.49-x'}^+\text{O}_{4x'-0.1}\text{F}_{1.2-4x'}\{\text{Ta}_{0.17}^+\}]$, where, with an increase in the oxygen content in the channel from 0 to 1.1, x' varies from 0 (or, more precisely, from 0.025) to 0.3. The limiting compositions of the channels are approximately $[\text{Ta}_{0.49}^+\text{F}_1\{\text{Ta}_{0.17}^+\}]$ and $[\text{Ta}_{0.3}^{5+}\text{Ta}_{0.19}^+\text{O}_{1.1}\{\text{Ta}_{0.17}^+\}]$. Bronze **II** has the composition $[\text{K}_6\text{Ta}_6^{5+}\text{O}_{15}\text{F}_6\{\text{Ta}_{0.12}^+\}][\text{Ta}_{x'}^+\text{Ta}_{0.516-x'}^+\text{O}_{4x'-1.3}\text{F}_{3.48-4x'}\{\text{Ta}_{0.24}^+\}]$, where, with an increase in the oxygen content in the channel from 0 to 0.764, x' varies from 0.325 to 0.516. The limiting compositions of the channels are $[\text{Ta}_{0.325}^{5+}\text{Ta}_{0.191}^+\text{F}_{2.18}\{\text{Ta}_{0.24}^+\}]$ and $[\text{Ta}_{0.516}^{5+}\text{O}_{0.764}\text{F}_{1.416}\{\text{Ta}_{0.24}^+\}]$. In this case, **I** is the Ta^+ bronze with an arbitrary ratio of F anions to O cations in the channels. This bronze is completely reduced if it has no oxygen in the channels. Partly reduced Ta^+ bronze **II** contains at least 1.416 F anions in the structure channel.

Formally, both above variants of tantalum reduction are possible. However, in Ta^{2+} bronzes ($\delta = 4$), the channels of structure **I** should contain solely O anions. Since, during reduction, the anions leave the structure, the initial structure of the crystal should contain no F anions, which would correspond to the channel composition $[\text{Ta}_x^{5+}\text{O}_{2.5x}]$ with the minimum possible averaged coordination number $(\text{cn})_{\text{av}} = 2.5$, which is hardly probable. Therefore, the variant of existence of Ta^+ bronzes **I** and **II** seems to be more probable.

We revealed no qualitative differences between **I** and **II**. At the same time, their optical properties are obviously different—metal-like crystals **I** and smoke-brown semitransparent crystals **II**. We assume that these differences should be associated with the presence in the channels of unreduced Ta^{5+} ions—there are no such ions in completely reduced bronze **II**, but they are present in partly reduced bronze **II**. With due regard for this fact, the most probable composition of **I** is $[\text{K}_6\text{Ta}_6^{5+}\text{O}_{15}\text{F}_6\{\text{Ta}_{0.34}^+\}][\text{Ta}_{0.49}^+\text{F}_1\{\text{Ta}_{0.17}^+\}] = \text{K}_6\text{Ta}_6^{5+}\text{Ta}^+\text{O}_{15}\text{F}_7 = \text{K}_6\text{Ta}_7\text{O}_{15}\text{F}_7$. Taking into account that the absence of oxygen anions in the structure channels is favorable, it is most likely that bronze **II** has the composition



Effect analogous to the effect of high pressure. We repeatedly noted [2, 4, 8, 9] that all the compounds synthesized by electrodeposition at the cathode show characteristics analogous to the effect of high pressure.

The present case is no exception. The densities of bronzes **I** and **II** are $d_X = 5.46$ and 5.38 g/cm³, respectively, i.e., are much higher than the density of Ta^{5+} compound **III**, $d_X = 5.06$ g/cm³. Moreover, the anomalously short K– Ta_{int} distances (for Ta_{int} in the $M(3)$ position) are equal to ~ 2 Å, which confirms the analogy with high pressure.

CONCLUSIONS

The structures of three crystals of the (K, Ta, O, F) compounds having the same structure type of hexagonal bronzes have been studied by single crystal X-ray diffraction methods. The crystals studied possess different optical characteristics (color and degree of transparency) because of different degree of reduction of $\text{Ta}^{(5-\delta)+}$ ions. Comparison of the data obtained with the data published earlier for analogous structures of two other crystals allowed us to characterize the structure type of the crystals and establish their specific structural characteristics during partial reduction of tantalum ions.

The structure of hexagonal tantalum bronzes (sp. gr. $P6/m$, $a \sim 13.13$ Å and $c \sim 3.86$ Å) is characteristic of compounds with a variable composition $\text{K}_6\text{Ta}_{6+z}\text{O}_{15}\text{F}_6(\text{F}, \text{O})_y$, where $Z \leq 1$ and $y \leq 3$, which contains both tantalum oxidized to the highest degree (Ta^{5+} -containing compounds) and tantalum in two different degrees of oxidation Ta^{5+} and $\text{Ta}^{(5-\delta)+}$ ($\text{Ta}^{(5-\delta)+}$ bronzes) with δ taking the values 1, 2, 3, 4, or 5.

The Ta^{5+} -containing compounds form colorless transparent crystals. Crystals of bronzes have visually different optical characteristics. Their color varies from light to dark brown, the crystals vary from transparent to semitransparent, and the luster changes from glassy to mat finish. Against the background of this continuous spectrum of crystal characteristics, we also observed crystals of qualitatively different dark gray metal-like bronzes.

The structure of all the representatives of this structure type is built by two main structural units— $[\text{K}_6\text{Ta}_6^{5+}\text{O}_{15}\text{F}_6]$ framework with a stable structure and composition and $[\text{Ta}_x(\text{F}, \text{O})_y]$ channels of variable composition and structure with Ta cations located along their hexagonal axes ($x \leq Z$). The channel atoms are highly mobile but form no sublattice with the symmetry and parameters different from the symmetry and parameters of the framework.

Unlike Ta^{5+} -containing compounds, the bronzes contain interstitial defects—reduced tantalum cations, $z\text{Ta}_{\text{int}}^{(5-\delta)+}$, ($z + x + Z$). All or only some reduced cations in the channel are in the same reduced state $\text{Ta}^{(5-\delta)+}$. Therefore, one should also distinguish between completely and partly reduced bronzes. Presumably, completely reduced bronzes would have metallic properties.

Unlike Ta⁵⁺-containing compounds, the chemical composition of the bronzes contain interstitial defects—reduced tantalum cations, $z\text{Ta}_{\text{int}}^{(5-\delta)+}$, ($z + x + Z$). Therefore, one should also distinguish between the completely and partly reduced bronzes. Ta⁵⁺-containing compounds is $\text{K}_6\text{Ta}_{6+x}\text{O}_{15}\text{F}_6(\text{F}, \text{O})_y = [\text{K}_6\text{Ta}_6\text{O}_{15}\text{F}_6][\text{Ta}_x(\text{F}, \text{O})_y]$, where $y \leq 3$ and $x \leq 1$. In the square brackets, the compositions of the framework and the channel are indicated. The most probable compositions are $\text{K}_6\text{Ta}_{6+x}\text{O}_{15}\text{F}_{6+5x} = [\text{K}_6\text{Ta}_6\text{O}_{15}\text{F}_6][\text{Ta}_x\text{F}_{5x}]$ with $0 < x \leq 0.6$. Both structural units in Ta⁵⁺ compounds have no electrostatic charge, which explains their relatively high mobility. We studied the structures of colorless transparent crystals of the Ta⁵⁺ compound of the composition $[\text{K}_6\text{Ta}_{6+x}\text{O}_{15}\text{F}_6][\text{Ta}_{0.27}\text{F}_{1.4}] = \text{K}_6\text{Ta}_{6.27}\text{O}_{15}\text{F}_{7.4}$.

With due regard for the specific features of the formation of compounds during reduction at the cathode in the electrolysis of the salt melt, the composition of Ta^{(5-δ)+} bronzes can be written as $\text{K}_6\text{Ta}_{6+x'}\text{Ta}_{Z-x'}^{(5-\delta)+}\text{O}_{15+y(\text{O})}\text{F}_{6+y-y(\text{O})}$ with $\delta = 1, 2, 3, 4$, or 5. Here, $y \leq 3$ is the total variable number of (F, O) anions, including $y(\text{O}) \leq 2.5$ oxygen ions; $Z \leq 1$ is the total variable number of Ta cations including $x' = (y + y(\text{O}) - (5 - \delta)Z)/\delta$ unreduced Ta⁵⁺ cations, where $0 \leq x' < 1$. We also studied the structure of a metal-like crystal of completely reduced Ta⁺ bronze of the composition $[\text{K}_6\text{Ta}_6^{5+}\text{O}_{15}\text{F}_6\{\text{Ta}_{0.34}^+\}][\text{Ta}_{0.49}^+\text{F}_1\{\text{Ta}_{0.17}^+\}] = \text{K}_6\text{Ta}_6^{5+}\text{Ta}^+\text{O}_{15}\text{F}_7 = \text{K}_6\text{Ta}_7\text{O}_{15}\text{F}_7$ and a brown semitransparent crystal of partly reduced Ta⁺ bronze of the composition $\text{K}_6\text{Ta}_6^{5+}\text{O}_{15}\text{F}_6\{\text{Ta}_{0.12}^+\}[\text{Ta}_{0.325}^{5+}\text{Ta}_{0.191}^+\text{F}_{2.18}\{\text{Ta}_{0.24}^+\}] = \text{K}_6\text{Ta}_{6.33}^{5+}\text{Ta}_{0.55}^+\text{O}_{15}\text{F}_{8.2} = \text{K}_6\text{Ta}_{6.88}\text{O}_{15}\text{F}_{8.2}$. Curly brackets show Ta_{int} atoms playing the role of interstitial defects.

Analysis of the structural data obtained for one Ta⁵⁺-containing compound and two bronzes formed during the same electrochemical experiment allowed us to suggest the scheme of crystal reduction on the cathode in electrolysis of the salt melt. According to this scheme, the most probable composition of the Ta^{(5-δ)+}

bronzes is $\text{K}_6\text{Ta}_{6+x'}\text{Ta}_{Z-x'}^{(5-\delta)+}\text{O}_{15}\text{F}_{6+y}$, where $Z \leq y/(5 - \delta)$ if $\delta \neq 5$ and $x' = (y - (5 - \delta)Z)/\delta$.

In comparison with Ta⁵⁺-containing compounds obtained by reduction at the cathode, bronzes are characterized by higher density and shorter cation–cation distances. This confirms our earlier assumption that, in electrolysis, a behavior analogous to the high-pressure effect should be observed.

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REFERENCES

1. *Oxide Bronzes*, Ed. by V. I. Spitsyn (Nauka, Moscow, 1982).
2. A. V. Arakcheeva, G. Chapuis, V. Grinevitch, and V. Shamray, *Acta Crystallogr., Sect. B: Struct. Sci.* **57**, 157 (2001).
3. E. A. Zhurova, V. E. Zavodnik, and V. G. Tsirel'son, *Kristallografiya* **40** (5), 816 (1995) [*Crystallogr. Rep.* **40**, 753 (1995)].
4. A. V. Arakcheeva, V. V. Grinevich, A. V. Mitin, *et al.*, *Kristallografiya* **46** (2), 221 (2001) [*Crystallogr. Rep.* **46**, 182 (2001)].
5. M. Vlasse, *Mater. Res. Bull.* **14**, 101 (1979).
6. V. Petricek and M. Dusek, *Jana 2000. Structure Determination Software Programs* (Inst. of Physics, Praha, 2000).
7. I. D. Brown, *J. Appl. Crystallogr.* **29**, 479 (1996).
8. A. V. Arakcheeva, G. Chapuis, and V. Grinevitch, *Acta Crystallogr., Sect. B: Struct. Sci.* **58**, 1 (2002).
9. A. V. Arakcheeva, V. V. Grinevich, G. Chapuis, and V. F. Shamraï, *Kristallografiya* **47** (2), 272 (2002) [*Crystallogr. Rep.* **47**, 237 (2002)].

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