

Formation of nano-sized oxides in the K-Ta-O system by chemical reaction of Ta metal with KNO_3 -KOH melts

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The reaction of Ta metal with potassium nitrate melts at 600°C has been studied. It was established that the composition of the reaction product could be varied by an appropriate choice of the base-acid properties of the melt, which were regulated by additions of potassium hydroxide. Pure potassium metatantalate KTaO_3 is formed when the KOH/KNO_3 molar ratio is about 1.2 or slightly higher. A mixture of the metatantalate with tetra- and ditantalate ($\text{K}_2\text{Ta}_4\text{O}_{11}$ and $\text{K}_2\text{Ta}_2\text{O}_6$) is formed at lower molar ratios. The content of tetratantalate increases as the concentration of KOH in the melt decreases and it becomes the main reaction product in pure nitrate melt. Pure metatantalate was obtained in the form of powders with grain sizes of about 80 nm. This product possessed ferroelectric properties with a dielectric constant of 250-300. Such nano-powders exhibit the properties of a semiconductor, which is not common for large-crystal materials. The conductivity is $10^{-5} \text{ S cm}^{-1}$ at room temperature and increases exponentially with increasing temperature.

Potassium tantalates / Nitrate melts / Nano-sized oxides / Metatantalate / Ferroelectricity

Introduction

Several potassium tantalates(V) are known with different $\text{K}_2\text{O}/\text{Ta}_2\text{O}_5$ ratios from polytantalates $\text{K}_2\text{O}\cdot n\text{Ta}_2\text{O}_5$ ($n \geq 2$) to orthotantalate K_3TaO_4 [1,2]. Among them, metatantalate KTaO_3 with perovskite structure is possibly the most practically important one in view of its ferroelectric properties [3].

Commonly, ceramic methods are used for the synthesis of crystalline KTaO_3 . They are based on the calcination of a mixture of Ta_2O_5 with potassium hydroxide or carbonate at 1200-2000°C. According to the phase diagram of the system $\text{K}_2\text{O}-\text{Ta}_2\text{O}_5$ [4], metatantalate melts incongruently at 1370°C. Hence, it is not surprising that the ceramic method does not allow producing high-purity monophase crystals of metatantalate. Besides, this method is energy consuming and technically complicated, requiring high-temperature corrosion resistant equipment.

Sol-gel synthesis is under investigation as an alternative to the ceramic one. Tantalum and potassium alcoholates are most often used as

precursors in this method [5-7]. Sol-gel synthesis is commonly used for the preparation of thin films of potassium tantalate or its solid solutions. For the same purpose, laser spray deposition has been proposed. In particular, it has been used to prepare highly oriented films of metatantalate on silicon single crystals [8].

Recently, the method of preparation of various metal oxides, both simple and complex ones, by oxidation of metals or their compounds in molten nitrate media has received considerable attention [9-11]. The main advantage of this method is the by far lower formation temperatures of the oxides (300-500°C), which simplifies the process and decreases the energy consumption. In addition, the method enables preparation of nanoscale oxide materials, which are now a subject of worldwide investigation because of a number of unique properties distinguishing them from the common large-crystal materials [12,13]. Finally, the method makes it possible to vary the composition of the product, changing the basicity by means of additives to the melt.

In the present work, we have studied the formation of different tantalates by oxidation of tantalum metal

powder in a potassium nitrate melt, the basicity of which was varied by potassium hydroxide additives.

Experimental

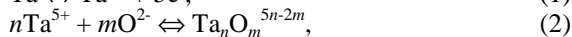
Tantalum powder (assay 99.9%, particle size 5-10 μm) and chemical grade potassium nitrate and hydroxide were used. The oxidation process was carried out in air at 500-600°C in alumina crucibles placed in an electric furnace. At the end of the reaction (1-1.5 hours), the melt was cooled down to room temperature and rinsed with distilled water. A milk-white suspension was formed, which was centrifuged to separate the fine powder of the product. The powder was washed, first with water, then with ethanol, and dried in air at 100-110°C.

The phase composition of the product was investigated by XRD with a DRON-3M diffractometer and $\text{CuK}\alpha$ radiation. For measuring the electric properties, the powder was pressed into cylindrical tablets of 4-7 mm length and 5 mm diameter. To produce the tablets, the powder was mixed with a 5% aqueous solution of polyvinyl alcohol up to the formation of a viscous mass, which was then pressed at 400 kg cm^{-2} , dried in air at room temperature and then at 700 °C.

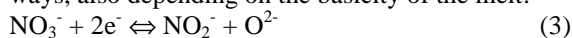
The dielectric constant of the samples was measured with a digital RCL-meter E7-8 at room temperature with 1 kHz working frequency. The electrical conductivity of the pressed tablets was determined in the temperature range 20-100°C with an AC bridge at frequencies from 0.1 to 10 kHz. Electron microscopy investigations were performed by the TEM method with a MET JEOL-2000 EX-II microscope operating at 200 kV.

Results and discussion

A general simplified scheme for the oxidation of tantalum metal can be conveniently represented as the combination of the 5-electron half-reaction of oxidation followed by the acid-base equilibrium of the formation of tantalates:



where the m/n ratio, depending on the acid-base properties of the molten media, can vary from 2.5 (Ta_2O_5 oxide) to 4 (K_3TaO_4 orthotantalate) via intermediate values $2.5 < m/n < 3$ for polytantalates and 3 for metatantalate. The electrons from Ta (reaction 1) are consumed in the half-reaction of the nitrate ion reduction, which can proceed in different ways, also depending on the basicity of the melt:



or



Hence, one can conclude that the acid-base properties of the media is a key factor determining the path of the

metal oxidation reaction and thus the possibility to produce the required product.

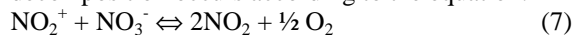
According to the Lux-Flood theory, in melts containing oxoanions, an acceptor of oxygen ions O^{2-} is an acid and its donor is a base [14,15]. The acid-base equilibrium (2) is a particular case of a general equation, which can be represented as:



The nitrate ion itself is considered as a base dissociating in accordance with the reaction [16]:



Introducing some acid species (e.g. metal cations) into the melt shifts the equilibrium (6) to the right, very reactive cations NO_2^+ accumulate in the melt and decomposition occurs according to the equation:



Since the quantitative characteristics of the acid-base equilibria in molten nitrates are not known, we cannot envisage beforehand the required composition (basicity) of the reaction mixture, which is necessary to form, for instance, pure KTaO_3 . It seems probable that the content of O^{2-} in pure molten potassium nitrate should not be enough to form this phase. The experiment confirms this assumption. The XRD pattern of the product obtained by oxidation of Ta powder in pure molten KNO_3 , with its molar ratio to Ta being equal to 5, at 650°C (Fig. 1, pattern 1) shows the tetratantalate $\text{K}_2\text{Ta}_4\text{O}_{11}$ (JCPDS 12-0092) as the main phase with small admixtures of $\delta\text{-Ta}_2\text{O}_5$ (JCPDS 18-1304), ditantalate $\text{K}_2\text{Ta}_2\text{O}_6$ (JCPDS 21-0685), and metatantalate KTaO_3 (JCPDS 2-0822).

As follows from the above, it is necessary to increase the basicity of the melt by adding donors of oxygen ions to obtain the required phase of metatantalate. The most convenient substance for this purpose is potassium hydroxide. According to the Lux-Flood concept, its basicity is provided by the equilibrium:



That is why we have studied the oxidation of Ta in $\text{KNO}_3\text{-KOH}$ melts with different content of potassium hydroxide. The ratio $\text{KNO}_3/\text{Ta} = 5$ was fixed and the KOH/Ta ratio was varied. Fig. 1 (patterns 2-4) and Fig. 2 show the results of this study. One can see that the increase of the basicity (KOH to Ti ratio with fixed amount of KNO_3) results in the gradual increase of the content of metatantalate in the samples. Finally, it becomes the only product of the Ta oxidation at $\text{KOH}/\text{Ta} = 1.2$. In that case, the overall reaction for the synthesis of KTaO_3 can be written as follows:



As follows from (9), the experimental composition that we have found for the synthesis of pure metatantalate corresponds to a 20% excess of KOH ($\text{KOH}/\text{Ta} = 1.2$) and 100% excess of KNO_3 ($\text{KNO}_3/\text{Ta} = 5$).

Pure cubic phase of KTaO_3 with cell parameter $a = 3.988 \text{ \AA}$ was obtained at these conditions (Fig. 1, pattern 4).

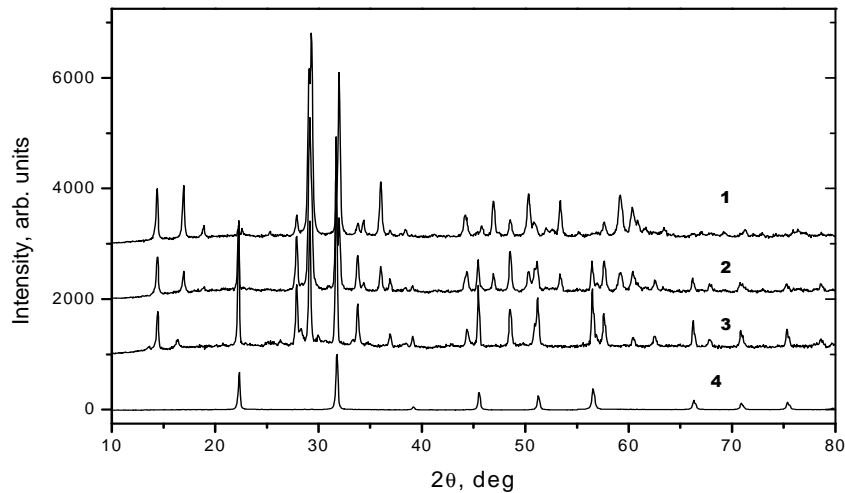


Fig. 1 XRD patterns of samples obtained by oxidation of Ta powder at 650 °C in molten KNO₃ for the molar ratios KNO₃/Ta = 5 and KOH/Ta = 0 (pattern 1), 0.3 (2), 1 (3) or 1.2 (4).

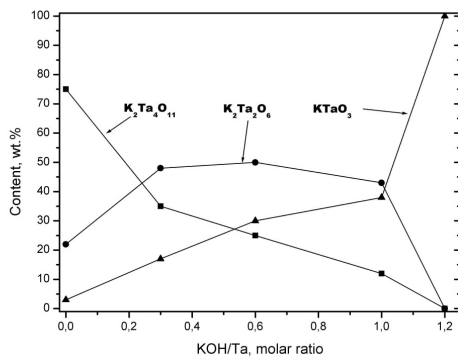


Fig. 2 Approximate phase compositions of samples obtained by oxidation of Ta powder at 650 °C for a fixed molar ratio KNO₃/Ta = 5, varying the KOH/Ta ratio. The contents were estimated from the relative intensities of appropriate XRD peaks.

The sizes of the crystals were estimated from XRD data using the Debye-Scherrer equation:

$$d = \frac{0.9\lambda}{B \cos \theta} \quad (10)$$

where $\lambda = 0.1542$ nm is the wavelength of the X-ray radiation, B is the half-width of the diffraction maximum in radians, θ is the angle corresponding to the position of the diffraction maximum. The average crystal size for the sample of Fig. 2 is equal to 90-95 nm, which agrees with the data of the TEM investigation (Fig. 3). Such a product should be related to the class of nanomaterials. However, it is known that the special features of nanoscale materials become most pronounced for crystal sizes of about 10-50 nm [13]. That is why we have studied the possibility to decrease the size of the crystals by

means of dilution of the melt, i.e. by increasing the amount of liquid phase in the reaction mixture with respect to the solid Ta powder, keeping the KOH to Ta ratio fixed. A set of experiments was carried out where the molar compositions of the reaction mixtures were Ta/KOH/KNO₃ = 1/1.2/ m ($m = 5, 10, 15, 10, 25$). The obtained samples were investigated by XRD, the lattice constants and average crystal sizes were determined and dielectric constants measured. The results are presented in Fig. 3 and Table 1.

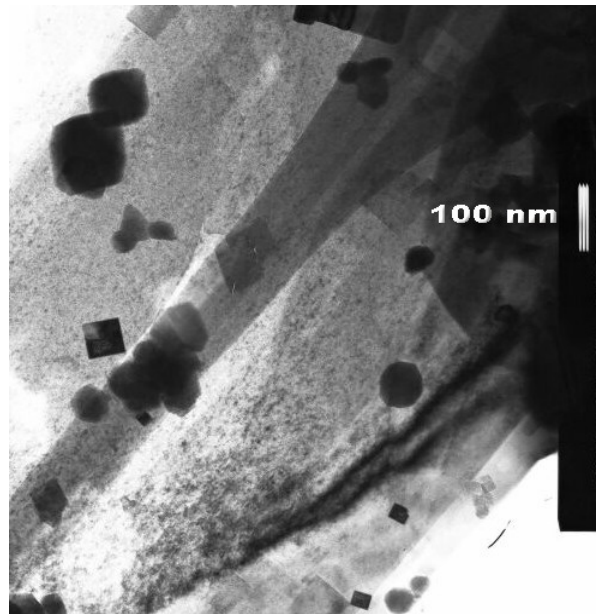
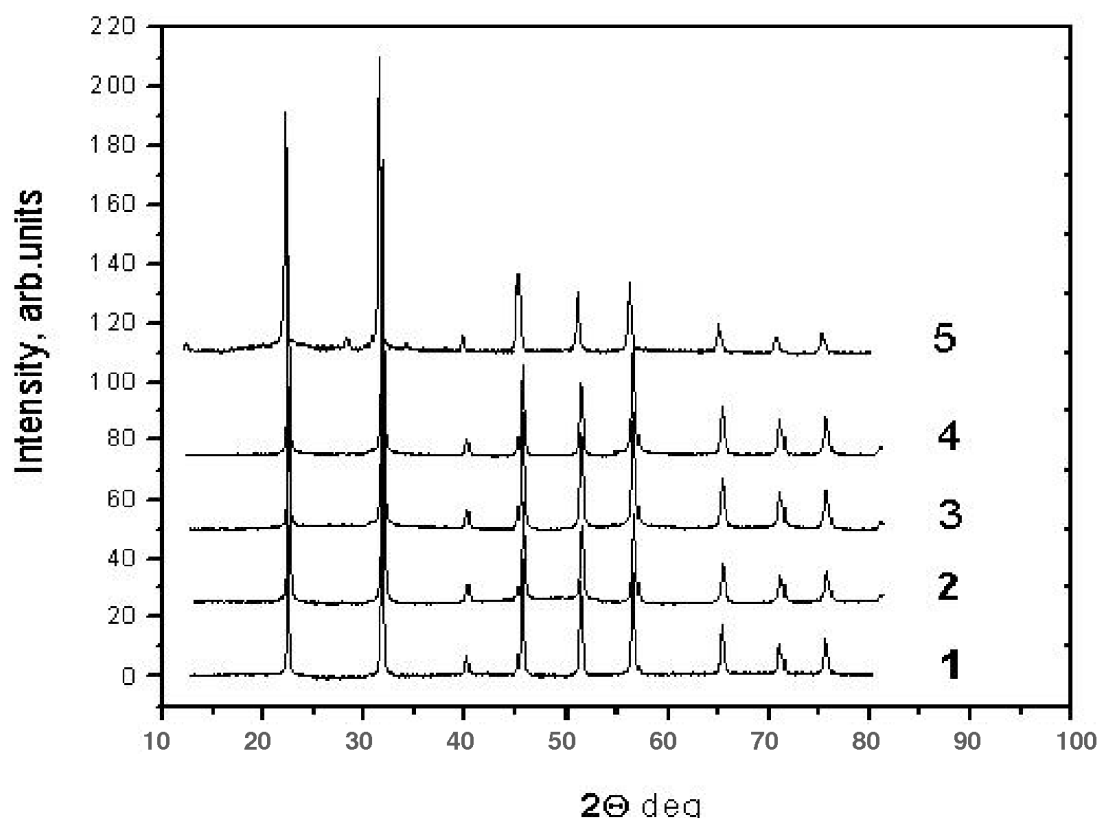


Fig. 3 TEM image of the powder of potassium metatantalate. Well formed cubic crystals with dimensions not exceeding 100 nm are clearly seen.

Table 1 Some properties of metatantalate samples prepared by oxidation of Ta powder at 650°C with different content of potassium nitrate and constant ratio KOH/Ta = 1.2 in the reaction mixtures.

Sample #	KNO ₃ :Ta molar ratio	Lattice parameter <i>a</i> , Å	Average crystal dimension ^a <i>D</i> , nm	Dielectric constant ^b ϵ
1	5	3.9886	96	262
2	10	3.9829	80	243
3	15	3.9857	85	245
4	20	3.9864	85	293
5 ^c	25	3.9889	85	225

^a calculated by the Debye-Scherrer equation (10)^b average from two independently measured values^c this sample contains small admixtures of polytantalates**Fig. 4** XRD patterns of samples obtained by oxidation of Ta powder in molten KNO₃ at 650°C for the molar ratios KOH/Ta = 1.2 and KNO₃/Ta = 5 (pattern 1), 10 (2), 15 (3), 20 (4), or 25 (5).

As follows from the data of **Table 1**, an increase of the relative amount of the nitrate results first in a slight decrease of the average crystal size, and then, for KNO₃/Ta > 10, causes practically no effect. The basicity of the melt becomes insufficient at very high dilutions (sample 5) and the product contains small admixtures of polytantalates. That is the possible reason for the somewhat lower dielectric constant of this sample. Thus, an increase of the nitrate content beyond KNO₃/Ta = 10 is not recommended since it increases the consumption of chemical with no essential effect on the properties of the product.

Though the results confirmed the ferroelectric properties of the product, the reproducibility of the

independent determinations of the dielectric constant was rather poor – the values for different tablets from the same material varied in the range of 40-50 units. The insufficient quality of the pressed pellets could be one of the reasons – we failed to attain a porosity less than 50%. However, the main reason is the electric conductivity of this material, which was found to be about 10⁻⁵ S cm⁻¹ at room temperature, increasing exponentially with increasing temperature (**Fig. 5**). Such a temperature dependence of the conductivity points to semiconductor properties with a width of the forbidden zone of about 0.3 eV, as can be estimated from the experimental value of the activation energy $E_A = 28.9 \pm 0.1$ kJ. To our knowledge, such properties

are not common for large crystals of KTaO_3 prepared by ceramic technique. Probably, it is the nanosize of the crystals that is responsible for such behavior.

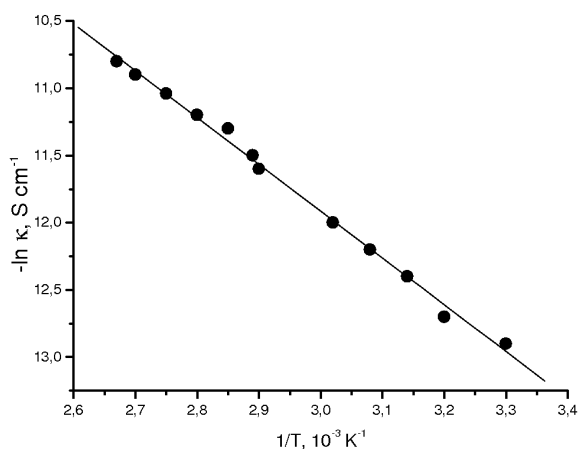


Fig. 5 Temperature dependence of the specific conductivity (sample #3 of Table 1) in form of an Arrhenius plot.

Conclusions

Pure potassium metatantalate can be prepared by oxidation of tantalum metal powder in potassium nitrate melt with additions of potassium hydroxide. The synthesis temperature is 600-650 °C, which is more than twice lower than required by common ceramic methods.

The recommended composition of the chemicals is rendered by the molar relation $\text{Ta/KOH/KNO}_3 \approx 1/(1.2-1.3)/(5-10)$. Perovskite-structured KTaO_3 without any impurities of poly- or orthotantalates is formed under these conditions. Amounts of polytantalates are formed at lower contents of KOH in the reaction mixture.

The metatantalate is a ferroelectric with a dielectric constant higher than 250. The crystal size of the product was about 80-90nm, which permits to relate it to the type of nanoscale materials. This material behaves as a semiconductor with noticeable conductivity ($10^{-6}-10^{-5} \text{ S cm}^{-1}$), which is not observed for the large-crystal material.

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