

## Electrometric Studies of the Formation of Niobates as a Function of pH

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A natureza precisa dos poliânions formados pela ação dos ácidos (HCl, HNO<sub>3</sub>, CH<sub>3</sub>COOH) sobre soluções de orthoniobato de potássio foi estudada por meio de titulações de pH e condutométricas. As inflexões e degraus nas curvas de titulações indicaram a formação de hexaniobato Nb<sub>6</sub>O<sub>19</sub><sup>8-</sup>, metaniobato NbO<sub>3</sub><sup>-</sup> e o óxido de nióbio Nb<sub>2</sub>O<sub>5</sub>.aq ao redor do pH 10,8, 7,6 e 3,8, correspondendo às razões 3Nb:5H, 3Nb:6H e 3Nb:9H, respectivamente. Titulações semelhantes de pH e condutométricas entre Zn<sup>2+</sup> e NbO<sub>4</sub><sup>3-</sup>, Nb<sub>6</sub>O<sub>19</sub><sup>8-</sup> e NbO<sub>3</sub><sup>-</sup> fornecem evidências incontestáveis sobre a formação de ortoniobato 3ZnO.Nb<sub>2</sub>O<sub>5</sub> e hexaniobato 4ZnO.3Nb<sub>2</sub>O<sub>5</sub> de zinco nas vizinhanças de pH 8,5 e 7,6, respectivamente. A precipitação de ortoniobato de zinco é praticamente quantitativa e estas titulações oferecem um método simples de determinação de ânions niobato. Estudos analíticos também foram realizados sobre precipitados de niobato de zinco, confirmando os resultados pelas técnicas eletrométricas.

The precise nature of the polyanions formed by the action of acids (HCl, HNO<sub>3</sub>, CH<sub>3</sub>COOH) on potassium orthoniobate solutions has been studied by pH and conductometric measurements involving glass electrode and conductometric titrations. The inflections and breaks in the titration curves indicate the formation of hexaniobate Nb<sub>6</sub>O<sub>19</sub><sup>8-</sup>, metaniobate NbO<sub>3</sub><sup>-</sup> and the niobium oxide Nb<sub>2</sub>O<sub>5</sub>.aq around pH 10.8, 7.6 and 3.8, corresponding to the ratios 3Nb:5H, 3Nb:6H and 3Nb:9H, respectively. Similar pH and conductometric titrations between Zn<sup>2+</sup> and NbO<sub>4</sub><sup>3-</sup>, Nb<sub>6</sub>O<sub>19</sub><sup>8-</sup> and NbO<sub>3</sub><sup>-</sup> provide definite evidence for the formation of orthoniobate 3ZnO.Nb<sub>2</sub>O<sub>5</sub> and hexaniobate 4ZnO.3Nb<sub>2</sub>O<sub>5</sub> of zinc in the vicinity of pH 8.5 and 7.6, respectively. The precipitation of the orthoniobate of zinc is almost quantitative and these titrations offer a simple means for the determination of niobate anions. The analytical investigations of the precipitates formed have also been carried out, which substantiate the results of the electrometric study.

**Keywords:** niobate anions, zinc niobates, electrometric techniques

### Introduction

Recently, a new interest in the chemistry of niobium has developed. This has arisen in part from the need of modern high temperature technology for materials which have strength at elevated temperatures. Niobium has its potentialities in atomic energy fields, where its high melting point, ductility, malleability, and low thermal-neutron capture cross-section make it very attractive as a construction material. There has also been a rapid increase in recent years in the use of niobium in the steel industry. Small amounts of niobium markedly increase the yield strength of mild steel plates and prevent weld decay and intergranular corrosion in stainless steels<sup>1</sup>. In addition to its continued use in the production of chrome and stainless steel, it is now

being used as a component for nonferrous superalloys, generally nickel-based<sup>2,3</sup>, which have been developed for the manufacture of jet engines, turbines, and missiles. It has also been found that certain niobium alloys, especially with tin and zirconium, become superconducting at easily available temperatures, and retain their superconductivity in magnetic fields<sup>4,5</sup>.

Some work has appeared on the electrodeposition of niobium alloys using niobate solutions in baths<sup>6,7</sup>. The literature surveyed clearly reflects the usefulness of niobium alloys in imparting specific properties, but almost no electrolytic bath has been developed until now which can deposit an alloy of good quality of some commercial value. Adequate control of the baths and the complicated chemistry of niobates seem to be the main sources of the problem.

Niobates have a strong tendency to form condensed complex ions in solution and from these polyniobates they crystallize depending upon the pH. It has been reported<sup>8</sup> that sodium ortho-niobate,  $\text{Na}_3\text{NbO}_4$ , dissolves in water giving a strongly alkaline solution due to its hydrolysis to the form  $\text{Nb}_6\text{O}_{19}^{8-}$  which upon decreasing the pH may successively change to  $\text{H}\text{Nb}_6\text{O}_9^{7-}$  and  $(\text{Nb}_6\text{O}_{18}^{6-})_n$ . A value of about 3 for  $n$ , has been suggested but Conard and Land<sup>9</sup> concluded that the value of  $n$  should be about 6. A large number of niobates with conflicting reports have been described in which the ratio of alkali metal to acid ( $\text{M}_2\text{O}/\text{Nb}_2\text{O}_5$ ) is given variously as 5/1, 4/1, 3/1, 2/1, 16/5, 3/2, 4/3, 4/5, 1/1, 6/7, 3/4, 2/3, 1/2, 1/3, and 1/4. There is no doubt, however, that the study of niobates is complicated by the fact that many of the hydrated salts do not exist in the anhydrous state, nor do they form congruently saturated solutions, while in both anhydrous and hydrated systems, metastability and slowness to attain equilibrium contribute to the variability of composition.

Because of the complexity of the equilibria between these polyanions, or due to experimental difficulties associated with the analytical work, the conclusions of earlier researchers seem to be overstrained and hence further verification and investigation is desirable. With the intention of studying in detail the chemistry of the decomposition of alkali metal niobates upon acidification, establishing the stoichiometry of intermediate species, and examining the suitable conditions for their stability and existence, it was considered worthwhile to make a careful and precise study of the acid-niobate system by electrometric techniques, which have provided more conclusive evidence of the condensation processes of tungstates<sup>11</sup>, antimonates<sup>12</sup>, vanadates<sup>13</sup> and thiotungstates<sup>14</sup>. After establishing for suitable conditions for the stability of different niobate polyanions, the investigations of the formation of zinc niobates as a function of pH were also carried out as no references could be found in the literature.

## Experimental

$\text{NbCl}_5$ ,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{KOH}$ ,  $\text{HNO}_3$ , hydrochloric acid and acetic acid of extra-pure grade were used, and their solutions were prepared in carbonate-free conductivity water. The solution of potassium orthoniobate was prepared by digesting  $\text{NbCl}_5$  in  $\text{KOH}$  solution of the required strength. The concentration of  $\text{K}_3\text{NbO}_4$  solution was further verified by determining niobium as pentoxide<sup>10b</sup>.

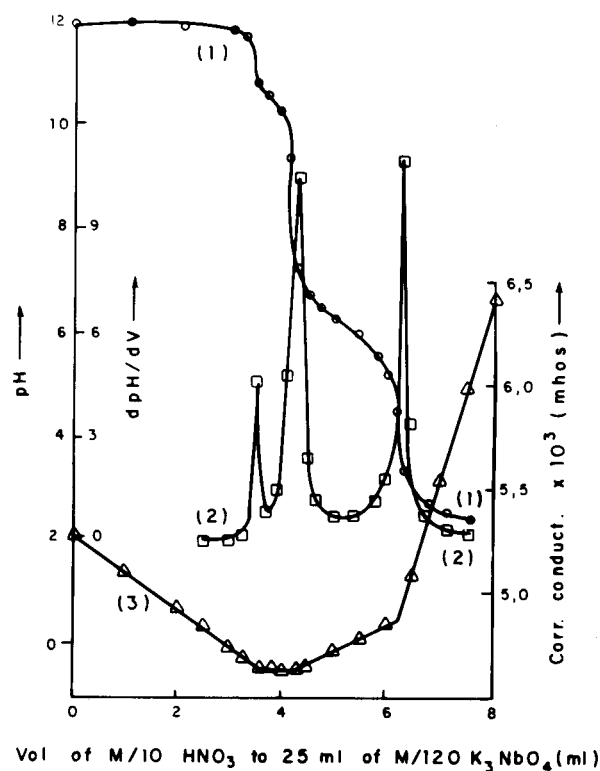
The pH and conductometric measurements were carried out in the usual manner<sup>11</sup>. A series of pH and conductometric titrations was carried out between potassium orthoniobate and  $\text{HNO}_3$ ,  $\text{HCl}$ , and  $\text{CH}_3\text{COOH}$  separately using the same concentrations of reactants in each titration. All observations were made at the state of chemical equilibrium. The curves were plotted between pH and corrected conductance and the volume of acid used. As the inflections

in the pH curves were not strongly defined, differential graphs in  $\text{dpH}/\text{dV}$  were drawn and the end-points were marked by pronounced maxima. The results were further confirmed by zero values in  $\text{d}^2\text{pH}/\text{dV}^2$  graphs. Figure 1 of the titrations with only one acid ( $\text{HNO}_3$ ) at only one dilution is given for the sake of brevity. The results have been summarized in Table 1. Job's method of continuous variation, using electrical conductance measurements was also employed for determining the stoichiometry of niobate anions formed by the interaction of an acid ( $\text{HNO}_3$ ,  $\text{CH}_3\text{COOH}$ ) and the ortho-niobate. The difference in specific conductivities (the sum of the conductivity of constitu-

**Table 1.** Summary of the results of the electrometric titrations. Volume of potassium niobate solution taken in the titration cell = 25 ml.

Molarity of solutions	Equivalence points (ml) for the formation of					
	Hexaniobate			Metaniobate		
$\text{HNO}_3$ $\text{K}_3\text{NbO}_4$	Calc.	A*	B*	Calc.	A	B
M/5 M/75	2.78	2.78	2.80	3.33	3.32	3.32
M/10 M/120	3.47	3.46	3.48	4.17	4.18	4.18
M/20 M/150	3.33	3.32	3.34	4.00	4.00	4.04
M/40 M/550	3.03	3.04	3.04	3.64	3.64	3.62

\* A and B represent the end-points observed from pH and conductometric titrations respectively.



**Figure 1.** pH and conductometric titrations of  $\text{HNO}_3$  with  $\text{K}_3\text{NbO}_4$ . 1: pH vs. volume of  $\text{HNO}_3$  added; 2:  $\text{dpH}/\text{dV}$  vs. volume of  $\text{HNO}_3$ ; 3: Corrected conductance vs. volume of  $\text{HNO}_3$ .

ent solutions minus the observed specific conductivity of the mixtures) were plotted against the composition of the mixtures. From the maxima obtained in such plots, the stoichiometry of the compound formed was established.

Electrometric and analytical investigations were performed on the formation of different niobates of zinc. Using different concentrations of zinc sulfate and the niobate anions ( $\text{NbO}_4^{3-}$ ,  $\text{Nb}_6\text{O}_{18}^{6-}$  and  $\text{NbO}_3^-$ ) a series of pH and conductometric titrations was carried out both by direct and reverse methods (*i.e.* when zinc sulfate solution from the microburette was added to alkali niobate solution in the titration cell, and vice-versa). Identical strengths of solutions were employed in both of the techniques for the sake of comparing the results.

The titrations were also carried out in the presence of 20% ethanol. The results are summarized in Table 2. The precipitates obtained at the end-points of the titrations were also analyzed by classical methods. Niobium<sup>15</sup> was determined as oxide and zinc<sup>16</sup> as pyrophosphate. The results are presented in Table 3. The analytical results were also confirmed by atomic absorption spectroscopy.

## Results and Discussion

Potassium orthoniobate solution was prepared by digesting  $\text{NbCl}_5$  in a  $\text{KOH}$  solution in 1:8 molar ratio.



**Table 2.** Summary of results of electrometric titrations on formation of zinc niobates. Volume of titre solution taken in the cell = 25 ml.

Molarity of Solutions		Equivalence points (ml)			Formula supported	
		Calc.	Observed from			
			pH	Conductance		
$\text{ZnSO}_4$	$\text{K}_3\text{NbO}_4$	Direct titration, Fig. 2, curve 1				
M/10	M/150	2.50	2.50	2.50	$3\text{ZnO} \cdot \text{Nb}_2\text{O}_5$	
M/20	M/375	2.00	2.00	1.98		
M/40	M/700	2.14	2.15	2.15		
Reverse titrations, Fig. 2, curve 2						
M/400	M/50	2.08	2.08	2.10	$3\text{ZnO} \cdot \text{Nb}_2\text{O}_5$	
M/550	M/70	2.12	2.12	2.12		
M/850	M/100	1.98	1.98	1.98		
$\text{ZnSO}_4$	$\text{K}_8\text{Nb}_6\text{O}_{19}$	Direct titrations, Fig. 2, curve 3				
M/10	M/500	2.00	2.00	2.00	$4\text{ZnO} \cdot 3\text{Nb}_2\text{O}_5$	
M/20	M/1100	1.82	1.82	1.84		
M/40	M/1750	2.29	2.30	2.30		
Reverse titrations, Fig. 2, curve 4						
M/550	M/200	2.27	2.26	2.28	$4\text{ZnO} \cdot 3\text{Nb}_2\text{O}_5$	
M/900	M/350	2.43	2.42	2.42		
M/1250	M/500	2.50	2.50	2.48		

**Table 3.** Summary of analytical results of the precipitates of zinc niobates.

Proposed formula of the compound	Mode of synthesis	Analysis %: Found (Calculated)	
		Zn	Nb
Analysis of the orthoniobate precipitates			
$3\text{ZnO} \cdot \text{Nb}_2\text{O}_5$	Direct*	35.10 (35.15)	33.33 (33.30)
	Reverse*	35.18	33.26
Analysis of the hexaniobate precipitates			
$4\text{ZnO} \cdot 3\text{Nb}_2\text{O}_5$	Direct	22.99 (23.03)	47.02 (46.97)
	Reverse	23.06	46.95

\* Direct - Zinc sulfate solution added to potassium orthoniobate solution. Reverse - Potassium orthoniobate solution added to zinc sulfate solution.

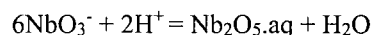
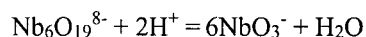
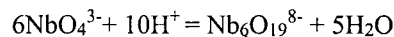
### Niobate anions

Figure 1, curve 1, represents the changes occurring in  $H^+$  concentration upon the addition of  $HNO_3$  to alkali orthoniobate solution. It is noted that the addition of about 1.5 moles of acid per mole of orthoniobate does not cause any appreciable change in the pH of the system. In turn, a buffer region from pH 12.0 to 11.6 is established showing strong affinity for the hydrogen ions in this region. Subsequently, the addition of  $HNO_3$  beyond 1.6 moles of  $HNO_3$  per mole of niobate causes a rapid decrease in the pH, indicating an inflection at the molar ratio  $K_3NbO_4:HNO_3$  as 3:5, corresponding to the formation of hexaniobate anions  $Nb_6O_{18}^{6-}$ , as also evidenced by Nelson and Tobias<sup>17,18</sup> by their light scattering and ultracentrifugation studies. Further addition of acid yields two more prominent inflections in the pH values corresponding to the additions of 2 and 3 moles of  $HNO_3$  per mole of  $K_3NbO_4$ , suggesting the formation of metaniobate anions  $NbO_3^-$  and  $Nb_2O_5$ , respectively. The formation of similar metaniobates has also been reported in the literature<sup>19,20</sup>. These three inflections (curve 1) in the pH titration curves and maxima in  $dpH/dV$  (curve 2) indicate that the addition of  $HNO_3$  to  $K_3NbO_4$  solution successively forms hexaniobate, metaniobate and niobium pentoxide in the vicinity of pH 10.8, 7.6 and 3.8, respectively.

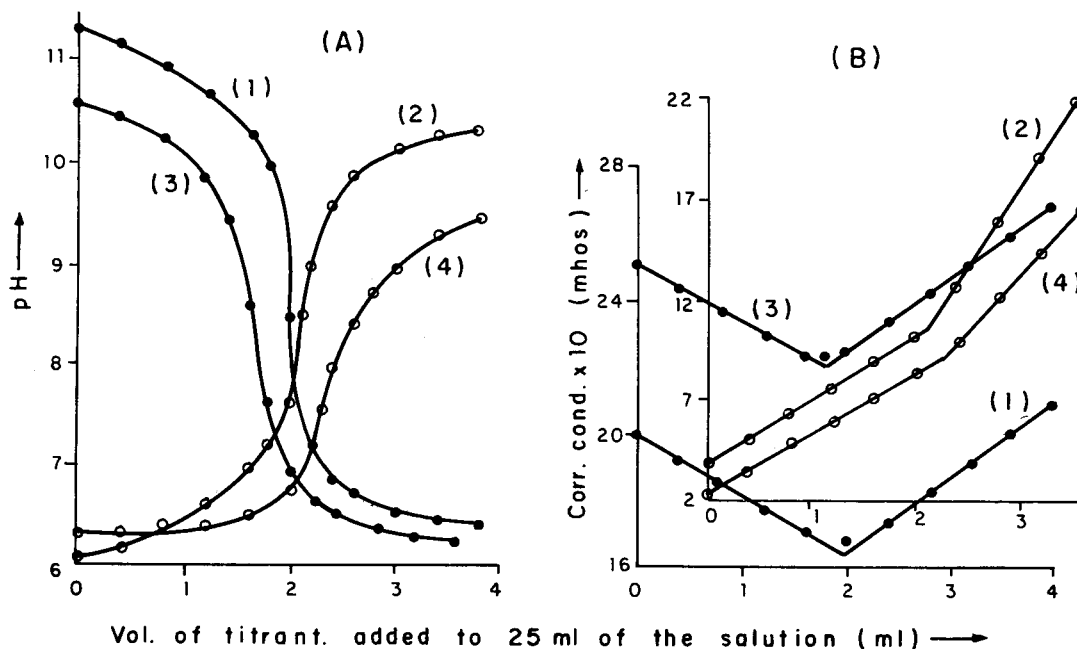
Conductometric titrations between  $HNO_3$  and  $K_3NbO_4$  were also carried out using the same concentrations of the reactants as in the pH titrations, for the sake of comparing results. The observed breaks (Fig. 1, curve 3) confirm the results obtained by the pH study for the formation of

hexaniobate and metaniobate before the final degradation to niobium pentoxide. The titration curves show a rapid diminution in conductance values which occurred during the reaction up to the equivalence point, corresponding to the formation of hexaniobate, revealing that the salt must be considerably hydrolyzed. This is in agreement with the glass electrode titration curves of orthoniobate which show high pH values during the addition of first five moles of acid for three moles of potassium orthoniobate. From these observations it is inferred that orthoniobate is not very stable, and hydrolyzes giving hydroxyl and  $Nb_6O_{18}^{6-}$  ions. This confirms the observations of Jander and Ertel<sup>8</sup>. Job's method of continuous variation using electrical conductance measurements was also employed for determining the stoichiometry, which confirmed the formation of metaniobate anions.

The step-by-step changes in the orthoniobate upon acidification can be represented by the following equations:



The results of the careful pH and conductometric study on the acid-niobate system provide definite evidence for the formation of hexa- $Nb_6O_{19}^{8-}$  and meta- $NbO_3^-$  niobate anion in the neighborhood of pH 10.8 and 7.6, respectively. The observations of Lehné and coworkers<sup>21</sup> for the formation of  $Nb_5O_{16}^{2-}$ , and of Jander and Ertel<sup>8</sup> for  $HNb_6O_{19}^{7-}$  could not be confirmed by this study.



**Figure 2.** (A) pH and (B) conductometric titrations of zinc sulfate with potassium niobates. 1: M/20  $ZnSO_4$  added to M/375  $K_3NbO_4$ ; 2: M/50  $K_3NbO_4$  added to M/400  $ZnSO_4$ ; 3: M/20  $ZnSO_4$  added to M/1100  $K_8Nb_6O_{19}$ ; 4: M/200  $K_8Nb_6O_{19}$  added to M/550  $ZnSO_4$ .

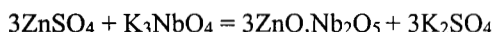
### Zinc niobates

The electrometric and analytical investigations of the formation of zinc niobates have been carried out by the interaction of zinc sulfate with different potassium niobates. Potassium hexaniobate (pH 10.8) and metaniobate (pH 7.6) solutions were prepared by the action of potassium orthoniobate solutions with HNO<sub>3</sub> in the molar ratios 3Nb:5H and 3Nb:6H, respectively.



### Orthoniobate titrations

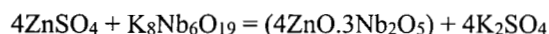
Figure 2A (curves 1 and 2) illustrates the changes occurring in H<sup>+</sup> concentration when zinc sulfate solution is treated with K<sub>3</sub>NbO<sub>4</sub> solution. In direct titrations (curve 1), when zinc sulfate solution (pH 6.1) was added from the microburette to the K<sub>3</sub>NbO<sub>4</sub> solution (pH 11.8) a sharp fall in pH was noted with an inflection at a 3:2 molar ratio of Zn<sup>2+</sup>:NbO<sub>4</sub><sup>3-</sup>, corresponding to the stoichiometry for the formation of zinc orthoniobate 3ZnO.Nb<sub>2</sub>O<sub>5</sub>, in the vicinity of pH 8.5. In the case of reverse titrations (curve 2) when basic K<sub>3</sub>NbO<sub>4</sub> solution was used as a titrant, the pH first increased slowly, but at the equivalence point a marked upward jump in pH confirmed the formation of the same compound according to the following equation:



Employing similar concentrations of the reactants, both direct (Fig. 2B, curve 1) and reverse (Fig. 2B, curve 2) conductometric titrations between ZnSO<sub>4</sub> and K<sub>3</sub>NbO<sub>4</sub> were carried out. Well-defined breaks were obtained at a 3:2 molar ratio of Zn<sup>2+</sup>:NbO<sub>4</sub><sup>3-</sup>, which confirm the formation of the identical compound, zinc orthoniobate 3ZnO.Nb<sub>2</sub>O<sub>5</sub>. In direct titrations (curve 1), when zinc sulfate solution was added from the microburette to the orthoniobate solution in the titration cell, a gradual decrease in conductance values was observed (due to the removal of NbO<sub>4</sub><sup>3-</sup> ions in the form of precipitate) until the stoichiometric end-point, after which the conductance increased with the increase in ionic concentration. In the case of the reverse titrations (curve 2), as the zinc ions are removed in the form of precipitate and more mobile potassium ions are introduced in the solution, the conductance value starts increasing from the very beginning.

### Hexaniobate titrations

The pH (Fig. 2A, curves 3 and 4) and conductometric (Fig. 2B, curves 3 and 4) titrations provide well-defined inflections at the molar ratio of Zn<sup>2+</sup>:Nb<sub>6</sub>O<sub>19</sub><sup>8-</sup> as 4:1, corresponding to the stoichiometry for the formation of the hexaniobate of zinc 4ZnO.3Nb<sub>2</sub>O<sub>5</sub> in the neighborhood of pH 7.6. The reaction can be represented as follows:



The reaction between zinc sulfate and potassium metaniobate was also studied by pH and conductometric titrations, but the curves did not exhibit sharp breaks and inflections. This may be ascribed to a small difference in pH values of the reactants and the presence of KNO<sub>3</sub> in appreciable amounts, preventing the occurrence of breaks in the conductometric titration curves.

It is noted that after each addition of the titrant it takes a little time for the pH and conductance values to become steady. The presence of ethanol (20%) increases the magnitude of the jump in pH curves as it decreases the solubility of the precipitates formed and minimizes hydrolysis and adsorption. The precipitation of zinc orthoniobate is almost quantitative and, the pH titrations offer a simple means for the determination of the niobate anions.

The precipitates obtained at the end-points of the titrations of zinc sulfate with potassium niobates were analyzed by standard gravimetric methods. Niobium was determined as pentoxide, zinc as pyrophosphate, and oxygen was calculated from the difference in the percentage. From the proportions of zinc, niobium and oxygen in the compounds thus obtained, their compositions were established, which were found to be the same as obtained by the electrometric study (see Table 3). The analytical results obtained were also confirmed by atomic absorption spectroscopy.

The above electrometric and analytical studies confirm the formation of ortho-3ZnO.Nb<sub>2</sub>O<sub>5</sub> and hexa-4ZnO.3Nb<sub>2</sub>O<sub>5</sub> niobates of zinc in the vicinity of pH 8.5 and 7.6, respectively<sup>22</sup>. As the structure of these compounds is not known they are represented as double oxides, in the manner usually adopted for such compounds<sup>23,24</sup>.

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### References

1. B.B. Argent, *Sci. Progr. London* **52**, 608 (1964)
2. C.C. Koch, O.B. Cavin, C.G. McKamey and J.O. Scarbrough, *Appl. Phys. Lett.* **43**, 1017 (1983).
3. T. Nasu *et al.*, *J. Noncryst. Solids* **117/118**, 725 (1990).
4. J.E. Kunzler, E. Buehler, F.S.L. Hsu and J.H. Wernick, *Phys. Rev. Letters* **6**, 89 (1961).
5. D.L. Martin, M.G. Benz, C.A. Bruch and C.H. Rosner, *Cryogenics* **3**, 144 (1963).
6. J. Bost, German Offen. 2,064,586 (1971); *Chem. Abstr.* **75**, 70757 (1971).
7. D.H. Baker and J.D. Ramsdell, *J. Electrochem. Soc.* **107**, 985 (1960).
8. G. Jander and D. Ertel, *J. Inorg. Nucl. Chem.* **14**, (a) 71, (b) 77, (c) 85 (1960).
9. R.W. Conard and J.E. Land, *J. Less-Common Metals* **7**, 180 (1964).

10. F. Fairbrother, *The Chemistry of Niobium and Tantalum* (Elsevier Publishing Co., Amsterdam, 1967), pp. (a) 36, (b) 222.
11. S. Prasad, *Quím. Nova* **17**(1), 31 (1994).
12. S. Prasad, *Bull. Electrochem.* **6**(1), 163 (1990).
13. S. Prasad, *An. Acad. Brasil. Ciênc.* **53**(3), 471 (1981).
14. S. Prasad, *Can. J. Chem.* **59**(3), 563 (1981).
15. R.N. Moshier, *Analytical Chemistry of Niobium and Tantalum* (The Macmillan Co., New York, 1964), p. 27.
16. A.I. Vogel, *A Textbook of Quantitative Inorganic Analysis*, (Longmans, London, Third Edition, 1962), p. 532.
17. W.H. Nelson and R.S. Tobias, *Can. J. Chem.* **42**, 731 (1964).
18. W.H. Nelson and R.S. Tobias, *Inorg. Chem.* **2**, 985 (1963).
19. A. Reisman and F. Holtzberg, *J. Amer. Chem. Soc.* **77**, 2115 (1955).
20. G. Brauer and H. Waltz, *Z. anorg. und. allgem. Chem.* **319**, 236 (1963).
21. M. Lehné and H. Goetz, *Bull. Soc. Chim. France*, 334 (1961); J. Leicht, M. Lehné and R. Rohmer, *ibid.* 213 (1963).
22. S. Prasad, XI Congresso Ibero-Americano de Eletroquímica (Águas de Lindóia - SP, 1994), p. 500.
23. A. Standen, Ex. Ed., *Kirk-Othmer Encyclopedia of Chemical Technology* (Interscience Publishers, New York, Second Edition, 1967), vol. 13, p. 782.
24. G. Brauer, Ed., *Handbook of Preparative Inorganic Chemistry* (Academic Press, New York, Second Edition, 1965), vol. 2, p. 1705.