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Niobates and Tantalates of Tervalent Elements

A.M.Sych and A.M.Golub

The types of compounds in the A_2O_3–B_2O_5 systems, where A = the *p*-, *d*-, and *f*-elements of Group III, the *p*-elements of Group V, and the *d*-elements of the fourth period in the tervalent state and B = Nb or Ta, are considered. An analysis of the methods of making the niobates and tantalates is given, their structure is described, and their physicochemical and electrophysical properties are reviewed. Special attention has been paid to the description of the rare-earth element metaniobates, which exhibit the properties of electrets, and of the compounds of composition ABO_4 (A = Sb, Bi; and B = Nb, Ta), which belong to a new group of ferroelectrics. Bibliography of 147 references.

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I. INTRODUCTION

Niobates and tantalates of various metals are widely used in contemporary technology. They are usually used as the pure compounds or as components of solid solutions, which exhibit ferro-, piezo-, and pyro-electric, electro-optical, and other properties[1-3]. Materials based on them are employed in the production of ceramic generators of ultrasound, sound pickups, piezoelectric microphones and telephones, strain gauges, hydroacoustic collectors (receivers) of energy, laser crystals, etc.[3]

The development of the newest technology and the consequent requirement for new materials has aroused exceptional interest in the niobates and tantalates of tervalent metals. The successful combination of various physical properties with chemical inertness, high resistance to heat and moisture, and mechanical strength puts the niobates and tantalates of the tervalent metals among the most important materials of the new technology. Thus the rare-earth element (r.e.e.) orthoniobates of composition $RNbO_4$, activated with Nd^{3+} ions, serve as materials for lasers[4]. Antimony and bismuth orthoniobates and orthotantalates of composition ABO_4 have ferroelectric properties, which are successfully combined with high pyro- and piezo-sensitivity[5]. The metaniobates $R(NbO_3)_3$ can be used as ceramic electrets[6,7]. The niobates and tantalates of composition RBO_4 (where R = Y, La, or Nd) with fergusonite structure are antiferroelectrics with a high Curie temperature[8,9].

The number of papers dealing with the preparation and investigation of the properties of niobates and tantalates began to increase sharply after 1960. However, the results obtained have not yet been systematically examined, although there have been monographs[1,2] which deal with a limited set of problems on the preparation and certain properties of the niobates and tantalates of tervalent elements.

The present paper systematically examines the results on the methods of preparation, crystal-chemistry, and certain physicochemical and electrophysical properties of the niobates and tantalates of tervalent elements. Of the many types of compound among the niobates and tantalates we will consider only the simple compounds of the A_2O_3–B_2O_5 binary systems, where B is Nb or Ta, and will not deal in detail with mixed niobates and tantalates, that is, the compounds formed in the M_2O–A_2O_3–B_2O_5 systems and also the so-called aquoniobates and aquotantalates formed in the A_2O_3–B_2O_5–H_2O system. Special attention is paid to the most important inorganic materials of contemporary technology, the r.e.e., Sb, and Bi niobates and tantalates.

The niobates and tantalates of tervalent metals can be regarded as salts of hypothetical niobic and tantalic acids, namely, the ortho-salts ABO_4 as derivatives of the ortho-acids H_3BO_4 ($3H_2O.B_2O_5$), the meta-salts $A(BO_3)_3$ as derivatives of the meta-acids HBO_3 ($H_2O.B_2O_5$), and finally, many polyniobates and polytantalates $A_nB_mO_{2.5m+1.5n}$ (for example, ANb_5O_{14}, $ANb_{11}O_{29}$, $A_2Nb_{12}O_{33}$, $A_2Ta_{12}O_{33}$) as salts of the acids $nH_2O.mB_2O_5$.

Depending on the chemical nature of element A, it is desirable to consider the niobates and tantalates by dividing them into the following classes: (a) the niobates and tantalates of the Group III *p*-elements (Al, Ga, In, Tl); (b) the niobates and tantalates of the Group III *d*- and *f*-elements (r.e.e.); (c) the niobates and tantalates of the Group V *p*-elements (Sb and Bi); (d) the niobates and tantalates of the fourth period *d*-elements (Ti, V, Cr, and Fe).

II. TYPES OF COMPOUND

1. ALUMINIUM, GALLIUM, INDIUM, AND THALLIUM NIOBATES AND TANTALATES

Table 1 shows the niobates and tantalates of the metals of the aluminium subgroup known at present. The orthoniobates and orthotantalates of composition ABO_4 (known for all the elements except thallium) are characteristic. Aluminium orthotantalate $AlTaO_4$ is encountered in nature as the mineral simpsonite[28]. The existence of metaniobates and metatantalates of composition $A(BO_3)_3$ has been established reliably only for thallium[26,27]. There are reports of the preparation of the aquometaniobates $Al(NbO_3)_3.nH_2O$[20,29,30] and $In(NbO_3)_3.nH_2O$.[25]

The compounds in the Al_2O_3–Nb_2O_5 system (Fig. 1) have been studied most completely; apart from $AlNbO_4$, the existence of the polyniobates $AlNb_{11}O_{29}$ and $AlNb_{49}O_{124}$ has been found[12,21]. There have also been reports of the existence in this system of the compounds $AlNb_9O_{24}$,[14] $AlNb_{25}O_{64}$,[14] and $AlNb_{29}O_{74}$.[16]

Table 1. Niobates and tantalates of the *p*-elements of Group III and methods of making them.

B	Al		Ga		In		Tl	
	composition	method of preparation*	composition	method of preparation*	composition	method of preparation*	method	method of preparation*
Nb	$AlNbO_4$ [10–13]	T[10–13,18], CO[20]	$GaNbO_4$ [13,21,22]	T[19,21,22]	$InNbO_4$ [13,22,24]	T[13,22,24], CO[25]	—	—
	$AlNb_9O_{24}$ [14]	T[14]	$GaNb_5O_{14}$ [22]	T[22]			$TlNb_3O_{19}$ [26]	T[26]
	$AlNb_{11}O_{29}$ [11–17]	T[11–17]	$GaNb_{11}O_{29}$ [21]	T[21]			$Tl_4Nb_6O_{21}$ [26]	T[26]
	$AlNb_{25}O_{64}$ [14]	T[14]	—	—				
	$AlNb_{29}O_{74}$ [16]	T[16]	$GaNb_{29}O_{74}$ [16]	T[16]				
	$AlNb_{49}O_{124}$ [13,17]	T[13,17]	$GaNb_{49}O_{124}$ [21]	T[21]				
Ta	$AlTaO_4$ [11,13]	T[11,19,19]	$GaTaO_4$ [13,23]	T[19,19,23]	$InTaO_4$ [13,24]	T[13,24]	—	—
							$TlTa_3O_9$ [27]	CO[27]
							$Tl_4Ta_6O_{21}$ [27]	CO[27]

T = solid-phase preparation by heating mixture of oxides; CO = coprecipitation of the components from solutions.

Note. In this table and in subsequent tables all superscripts are reference numbers.

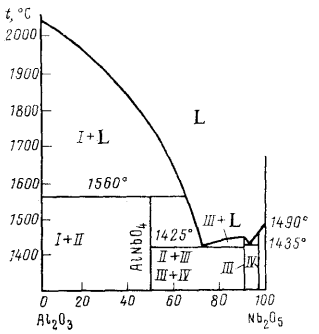


Figure 1. Equilibrium diagram of the Al_2O_3–Nb_2O_5 system[12]: *I* = Al_2O_3; *II* = $AlNbO_4$; *III* = $AlNb_{11}O_{29}$; *IV* = Nb_2O_5.

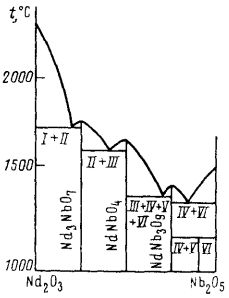


Figure 2. Equilibrium diagram of the Nd_2O_3–Nb_2O_5 system[59]. *I* = Nd_2O_3; *II* = Nd_3NbO_7; *III* = $NdNbO_4$; *IV* = $NdNb_3O_9$; *V* = $Nd_2Nb_{12}O_{33}$; *VI* = Nb_2O_5.

2. R.E.E. NIOBATES AND TANTALATES

In considering the niobates and tantalates of the Group III *d*- and *f*-elements it is desirable to isolate into separate groups Sc and Y compounds, compounds of the cerium-subgroup lanthanides (La, Ce, Pr, Nd, Sm, and Eu), and those of the yttrium-subgroup lanthanides (Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu). The many types of niobates and tantalates of these subgroups of metals are shown in Table 2, from which it is clear that compounds ABO_4 are known for all the r.e.e. Compounds of this composition are widely encountered in nature as the minerals fergusonite[83] ($YNbO_4$) and formanite ($YTaO_4$).

The compounds A_3NbO_7 and A_3TaO_7 are also known for all the r.e.e. However, the niobates A_3NbO_7 of the yttrium-subgroup elements have been obtained only for Gd,[38] Dy,[38] and Ho,[78] whereas tantalates of analogous composition are known for all the elements. The metaniobates RNb_3O_9 have been described only for the lanthanides of the cerium subgroup. The elements with ionic radius < 0.80 Å apparently cannot form compounds of this type. However, metatitanates RTa_3O_9 have been obtained for almost all the r.e.e. Since the r.e.e. metaniobates and metatantalates have the structure of perovskite ABO_3, their formula is best represented as $Ln_{1/3}NbO_3$ and $R_{1/3}TaO_3$.

The formation of pentaniobates of composition $LnNb_5O_{14}$ has been shown for La, Ce, Pr, Nd, and Eu[56–58] but such compounds are not formed for the other elements. There is no information about r.e.e. pentatantalates. Dodecaniobates $Ln_2Nb_{12}O_{33}$ (Ln = La, Ce, Pr, and Nd)[45,59] and dodecatantalates $Ln_2Ta_{12}O_{33}$ (Ln = La, Nd)[37,61] have been described only for the elements of the cerium subgroup.

For tantalum, the compounds $LnTa_7O_{19}$ are also known[38,41], being formed throughout the entire series of lanthanides except for Yb and Lu.[41] The equilibrium diagrams in the Ln_2O_3–Nb_2O_5 and Ln_2O_3–Ta_2O_5 systems have not been studied systematically. As an example, Fig. 2 gives the equilibrium diagram of the Nb_2O_5–Nd_2O_3 system as an example. The existence of the compounds Nd_3NbO_7, $NdNbO_4$, $NdNb_3O_9$, and $Nd_2Nb_{12}O_{33}$ has been observed.

Table 2. Rare-earth element niobates and tantalates and methods for making them.

B	Sc, Y		La—Eu		Gd—Lu	
	composition	method of preparation*	composition	method of preparation*	composition	method of preparation*
Nb	$ANbO_4$ [13,31—37]	T[13,31—35], CO[36,42,43], Kp[37,44]	$LnNbO_4$ [13,30,45—53]	T[13,31,45—53], CO[6,51,67,68,73,74], Ч[69], Kp[44]	$LnNbO_4$ [21,31,53,77—79]	T[13,31,53,71,72], CO[68,77]
	A_3NbO_7 [38]	T[38]	Ln_3NbO_7 [31,38,48—50,54]	T[31,38,48,49], CO[54]	Ln_3NbO_7 [38,78]	T[38,78]
	—	—	$LnNb_9O_9$ [40,48—50,55]	T[48,49,53,55], CO[6,51,70]	—	—
	—	—	$LnNb_5O_{14}$ [50,56—58]	T[57]	—	—
	—	—	$Ln_2Nb_{12}O_{33}$ [49,59]	T[49,59], CO[59]	—	—
Ta	$ATaO_4$ [13,31,34,35,39]	T[13,31,34,35,39]	$LnTaO_4$ [13,31,53,60—66]	T[13,31,49,53,60—63], CO[65,66]	$LnTaO_4$ [13,62,63,80—82]	T[13,62,80—82], CO[63]
	A_3TaO_7 [38]	T[38]	Ln_3TaO_7 [31,38,44,61,63]	T[31,38,49,61,63]	Ln_3TaO_7 [38,63]	T[38,63]
	ATa_3O_9 [40]	T[40]	$LnTa_3O_9$ [40,55,61,63,66]	T[41,40,55,61,63]	$LnTa_3O_9$ [40,55,63]	T[40,55,63]
	—	—	$Ln_2Ta_{12}O_{33}$ [49,61]	T[49,61]	—	—
	ATa_7O_{19} [41]	T[41], CO[41]	$LnTa_7O_{19}$ [41,57]	T[41,57], CO[41]	$LnTa_7O_{19}$ [41]	T[41], CO[41]

*T = solid-phase preparation by heating mixtures of oxides; CO = coprecipitation of the components from solutions; Kp = crystallisation from solution in a melt; Ch = preparation of single crystals after Czochralski.

Even a simple list of the types of compounds of the elements of subgroup IIIa shows that (unlike the niobates) the tantalates exist in a large number of varieties. This is especially noticeable for Sc, Y, and the yttrium subgroup of lanthanides.

3. ANTIMONY AND BISMUTH NIOBATES AND TANTALATES

The minerals stibiocolumbite $SbNbO_4$, stibiotantalite $SbTaO_4$, and bismutotantalite $BiTaO_4$,[83] are encountered in nature, and these compounds have been prepared under laboratory conditions only comparatively recently[13,84-93], evidently owing to the volatility of the oxides Sb_2O_3 and Bi_2O_3 above 650–700°C.

Table 3. Antimony and bismuth niobates and tantalates and methods for making them.

B	Sb		Bi	
	composition	method of preparation	composition	method of preparation
Nb	$SbNbO_4$ [13,84—87]; $SbNb_3O_9$ [90]	T[13,84,85], H[86,95—97], CO[87]; T[90]	$BiNbO_4$ [84,88,89]	T[84,88,89], H[98], CO[98]
			—	—
			$Bi_3Nb_3O_{15}$ [89]	T[89]
			$Bi_8Nb_{18}O_{63}$ [89]	T[89]
			$BiNb_5O_{14}$ [89]	T[89]
			$Bi_3Nb_{17}O_{47}$ [92]	T[89]
Ta	$SbTaO$ [84—86,91]	T[84—86], H[96], CO[147]	$BiTaO_4$ [84,88]	T[84,88], H[98], CO[147]

*T = solid-phase preparation by heating mixtures of oxides; CO = coprecipitation of the components from solutions; H = hydrothermal preparation.

Special interest in the Sb and Bi niobates and tantalates was aroused recently owing to the observation of ferroelectric properties in the mineral stibiotantalite[5] and the synthetic ABO_4 (where A = Sb or Bi, B = Nb or Ta)[94]. Table 3 gives the types of antimony and bismuth compounds. The most characteristic compounds are the orthoniobates and orthotantalates ABO_4. For antimony, the compound $SbNb_3O_9$ is also known[90].

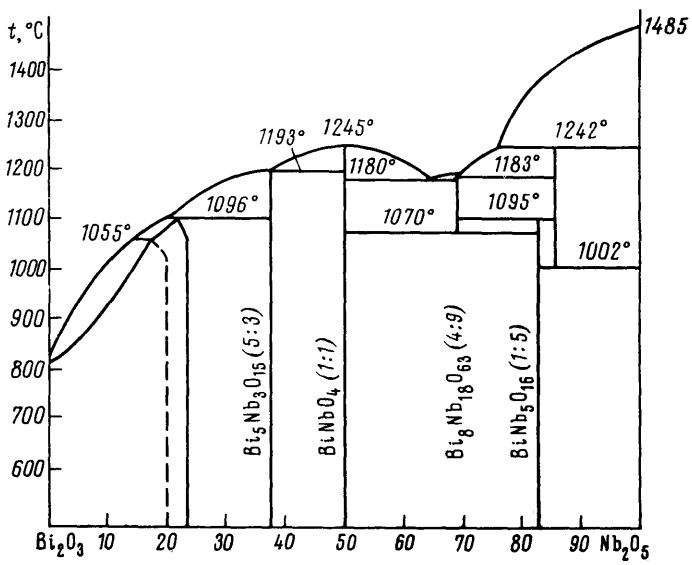


Figure 3. Equilibrium diagram of the Bi_2O_3–Nb_2O_5 system[89].

Fig. 3 gives the equilibrium diagram of the Bi_2O_3–Nb_2O_5 system. Formation of the compounds $BiNbO_4$, $Bi_5Nb_3O_{15}$, $Bi_8Nb_{18}O_{63}$, and $BiNb_5O_{14}$ has been reported[89].

Nothing has been published on the existence of Sb and Bi tantalates of a composition other than ABO_4.

4. NIOBATES AND TANTALATES OF THE *d*-METALS OF GROUPS IV–VIII

Of all the *d*-elements of periods IV and V which can exist in the tervalent state, only Ti, V, Cr, Mn, Fe, and Rh are known to have niobates and tantalates. Table 4 shows that in addition to the compounds of type ABO_4 several polyniobates have also been described[17,103].

Information is also available about the existence of the orthoniobates $TiNbO_4$,[13] $VNbO_4$,[13] $MnNbO_4$,[81] $RhNbO_4$,[13,18] and the orthotantalates $TiTaO_4$,[13] $VTaO_4$,[13] and $RhTaO_4$.[13,18] The possibility of the formation of iron hexatantalate $Fe_8(Ta_6O_{19})_3.44H_2O$ has also been suggested[105].

Table 4. Chromium and iron niobates and tantalates and methods for making them.

B	Cr		Fe	
	composition	method of preparation*	composition	method of preparation
Nb	$CrNbO_4$ [13,99–102]	T[13,19,99–101], TRG[102]	$FeNbO_4$ [100–104]	T[19,100,103,104], TRG[102]
	—	—	$FeNb_9O_{24}$ [103]	T[103]
	$CrNb_{11}O_{29}$ [17]	T[17]	$FeNb_{11}O_{29}$ [17]	T[17]
	—	—	$Fe_2Nb_{50}O_{93}$ [103]	T[103]
	$CrNb_{49}O_{129}$ [17]	T[17]	$FeNb_{49}O_{124}$ [17,103]	T[17,103]
Ta	$CrTaO_4$ [13,99]	T[13,19,99]	$FeTaO_4$ [18]	T[18,19]

*T = solid-phase preparation by heating mixtures of oxides; TRG = transport reactions from the gas phase with formation of single crystals.

III. PREPARATION OF NIOBATES AND TANTALATES OF TERVALENT ELEMENTS

Almost all the methods of making inorganic materials are used for obtaining niobates and tantalates of tervalent elements but the following are those used most widely: (1) solid-phase synthesis (T); (2) coprecipitation of the components from solutions followed by heating of the precipitate (CO); (3) hydrothermal synthesis (H). Tables 1–4 give information about the use of the various methods for making the niobates and tantalates.

1. SOLID-PHASE SYNTHESIS

Solid-phase synthesis (in other words, the ceramic method) which consists in the high-temperature heating of a mechanical mixture of the components, has been widely used for every niobate and tantalate of a tervalent element (Tables 1–4).

The starting materials in the solid-phase synthesis of niobates and tantalates are usually mixtures of the corresponding oxides. Much more rarely, a mixture of the oxides Nb_2O_5 (Ta_2O_5) with the carbonates, oxalates, nitrates, or other thermally unstable salts of the tervalent metal is used. Since the mechanism of solid-phase reactions depends mainly on the phase composition of the initial mixture, the latter also determines the temperature at which the mixture is heated.

We give below some examples of solid-phase synthesis. Thus for the preparation of R_3NbO_7, where R = La, Nd, Sm, Gd, Dy, Sc, and Y the oxides R_2O_3 and Nb_2O_5 are mixed in the necessary ratio and heated as tablets for 2 h at 1000°C. Then the mixture was pressed again and heated for 2 h at 1400°C. The tablets were then homogenised by being heated rapidly to 1800°C.[38] The r.e.e. and also V, Cr, Fe, and Rh orthoniobates were made analogously at 1250°C and the orthotantalates of the same elements at 1350°C.[13] The La, Ce, Pr, and Nd metaniobates and also the La, Ce, Pr, Nd, Sm, Gd, Dy, and Y metatantalates are obtained by heating mixtures of the oxides to 1450–1500°C.[40] Afonskii and Neiman[61] obtained the tantalates $LaTaO_4$, La_3TaO_7, $LaTa_3O_9$, and $La_2Ta_{12}O_{33}$ at lower temperatures (1300–1500°C).

A comparison of the results shows that different investigators give different temperatures for the preparation of the same compound. This is because the solid-phase reaction can be carried out over some range of temperatures higher than the temperature for the start of interaction between the initial oxides. Actually, in an investigation[72] of the interaction of a mixture of the oxides La_2O_3 and Nb_2O_5 the effect due to the formation of lanthanum orthoniobate $LaNbO_4$ is observed at 1190°C. $LaNbO_4$ has been prepared by various investigators at 1250–1300°C[52] and even 1600°C.[71] It seems that the reaction temperature depends on the duration of the sintering, which determines the completeness of the interaction of the initial substances. The tervalent metal tantalates are almost always prepared at higher temperatures than the niobates.

When one of the oxides in the solid-phase synthesis is volatile (for example, Sb_2O_3 and Bi_2O_3), then the niobates and tantalates are prepared in a closed volume. For example, to make antimony orthoniobate the mixture of oxides was first heated at 820°C for 2 h. After this, the material was sealed in a platinum tube and heated at 905°C for 16 h, then at 1000°C for 1 h, and at 1103°C for 14 h.[84]

The mechanism of the solid-phase processes has been studied repeatedly. The simplest compounds ABO_4 are evidently formed in a single stage[50,60]. The compounds Ln_3NbO_7 are formed in stages. The example of Eu_3NbO_7 showed[50] that initially (in the temperature range up to 1100°C) $EuNbO_4$ is formed and then further addition of Eu_2O_3 is observed at 1300°C.

The mechanism of formation of cerium metaniobate $CeNb_3O_9$ can, according to Godina and coworkers[51], be represented by the following processes:

$$Ce_2O_3 \cdot n\,H_2O + Nb_2O_5 \cdot n\,H_2O \xrightarrow{850^\circ} CeNbO_4\ (\text{cub.}) + Nb_2O_5\ (T\text{-form}),$$
$$CeNbO_4 + Nb_2O_5 \xrightarrow{1000-1100^\circ} CeNb_3O_9.$$

Kiparisov and coworkers[50] think that the formation of europium metaniobate $EuNb_3O_9$ takes place by the reaction:

$$EuNb_5O_{14} \xrightarrow{1500^\circ} EuNb_3O_9 + Nb_2O_5.$$

The scheme of formation of dodecaniobates (for example, $Ce_2Nb_{12}O_{33}$) postulates the formation of the intermediate phases $CeNbO_4$ and $CeNb_3O_9$.[51]

The kinetics of interaction of Sc_2O_3 and Y_2O_3 with Nb_2O_5 have been studied[32,35], also those of Y_2O_3, Sm_2O_3, Eu_2O_3, and Gd_2O_3 with Ta_2O_5.[35,62] The activation energy is 48.3 kcal mole^{-1} for the formation of $ScNbO_4$,[32] 56.8 kcal mole^{-1} for $YNbO_4$,[35] and 42.3 kcal mole^{-1} for $YTaO_4$.[35]

As noted above, the solid-phase synthesis can be carried out over a rather wide range of temperatures, which allows the various polymorphic configurations of the niobates and tantalates to be investigated[53,71]. However, the ceramic method has significant drawbacks, which reduce the effectiveness and make it unpromising in practice. These drawbacks are: (a) the heterogeneity of the product; (b) the purity of the product being inadequate; (c) the low stoichiometry of the components; (d) the comparatively high synthesis temperatures. The duration of the process is also characteristic of this method, several days sometimes being required for homogeneity to be attained and the reaction to be complete; higher synthesis temperatures lead to the high energy capacity of the method.

2. COPRECIPITATION OF THE COMPONENTS FROM SOLUTIONS

The precipitation of the components from solutions can be brought about by mixing aqueous solutions of the niobates $KNbO_3$, K_3NbO_4, and $K_8Nb_6O_{19}$ or tantalates $K_8Ta_6O_{19}$ with solutions of tervalent metal salts. In addition, a version of the preparation in which hydroxides are precipitated by the action of ammonia on a mixture of a solution of $NbCl_5$ ($TaCl_5$) and a salt of the metal, the compound of which is being made. $(NH_4)_2CO_3$ can also be used as precipitant. In both instances the precipitate was heated to the crystallisation temperature of the corresponding niobate or tantalate.

Soluble orthoniobates were used as starting materials for obtaining the orthoniobates $AlNbO_4$,[20] $InNbO_4$,[25] $YNbO_4$,[42] and $ScNbO_4$.[43] Aluminium[20,29,30] and indium[25] aquometaniobates have been made by this method.

The mechanism of the precipitation of Al, In, Y, and Sc ortho- and meta-niobates when aqueous solutions of the corresponding potassium niobates and salts of the metals being precipitated are mixed has been studied[20,25,42,43]. Orthoniobates of these metals are precipitated on reaching the ratio A : Nb = 1 : 1, which corresponds to pH 6–7. Metaniobates are precipitated when the ratio in the solution is A : Nb = 1 : 3.

Clearly, this version of the coprecipitation method requires the preliminary preparation of water-soluble niobates and tantalates, which somewhat reduces its effectiveness. A second version of the preparation, which uses the coprecipitation of the components in the form of hydroxides is evidently more effective, since it can be used for making the niobates and tantalates of any composition and it employs readily available reagents.

R.e.e. orthoniobates[36] and the tantalates $Tl_4Ta_6O_{21}$ and $TlTa_3O_9$[27] were obtained by using aqueous solutions. Since aqueous solutions of niobium and tantalum are unstable, a method using precipitation of the components from non-aqueous solutions is receiving greater attention. Thus, in making lanthanide orthoniobates $LnNbO_4$ (La, Ce, Pr, Nd),[67,68] the metaniobates $LnNb_3O_9$ (La, Pr, Nd, Sm),[6,51] the niobates Ln_3NbO_7 (La, Pr, Nd)[54] and $Ln_2Nb_{12}O_{33}$ (La, Ce, Pr, Nd),[59] and also bismuth orthoniobate $BiNbO_4$,[93] coprecipitation of the niobium and tervalent element hydroxides was carried out from alcoholic solutions.

Despite the rather wide use of coprecipitation for making niobates and tantalates, the mechanism of the process itself has still been studied insufficiently. There appear to be two possibilities: one is linked with the high dispersion of the coprecipitated components, the other, with the formation of contact compounds between the solid phases being coprecipitated[106]. Whereas the heat treatment of the material formed in the first instance gives some reduction of the crystallisation temperature of the final products as compared with the ceramic method, in the second instance the formation of crystalline compounds takes place at an appreciably lower temperature than in the sintering of the oxides.

The mechanism of the formation of the compounds during coprecipitation has been studied for only certain examples[6,67,87,93]. Chemical interaction of the components has been observed in the coprecipitation of Nd and Nb from aqueous alcoholic solutions. The precipitate obtained contained up to 60% combined Nd. In this instance hydroxoniobates of the type

$$Ln[NbO_{3-x/2}(OH)_x]_3 \cdot nH_2O,$$

where $x = 0–6$, are probably formed. Analogous results were obtained in studies of the formation of Ce, Pr, Nd,[67] Sb,[87] and Bi[93] orthoniobates.

There have been considerably more papers on the chemical reaction of the coprecipitated hydroxides of niobium or tantalum and a tervalent element during heating. However, they relate mainly to the processes taking place with participation of r.e.e. hydroxides[51,54,59,65,73,74,77] and, as noted above, only two studies concern the reaction of coprecipitated niobium and antimony or bismuth hydroxides[87,93]. In all these investigations it was found that when coprecipitated hydroxides are heated niobates (or tantalates) are formed without the intermediate production of the free oxides[6,51,59,93]. Usually, the crystallisation temperature is 300–500 K below the synthesis temperature in ceramic technology. This reduction in the temperature of preparation of the compounds is a principal advantage of the method of coprecipitation of the components from solution.

The observed decrease in the temperature of formation of niobates and tantalates when the coprecipitation method is used is often explained by the Hedvall effect, that is, the increase in the activity of the components during the thermal decomposition (dehydration) of hydroxides or salts. However, on taking into account the fact of chemical interaction between the components even at the moment of precipitation, it is thought[6,93,106] that the formation of intermediate compounds of the hydroxoniobate type, which are converted into niobates at comparatively low temperatures can also be responsible for the reduction in the synthesis temperature. The absence of individual oxides during the heating of the coprecipitated components suggests the impossibility of relating the mechanism of formation of the niobates and tantalates to simple interaction of oxides of increased activity.

In conclusion, it must be mentioned that in addition to the decrease in the synthesis temperature the coprecipitation method allows products of high homogeneity to be obtained. The purity of the compounds prepared by this method is usually higher than the purity of the initial solutions. These advantages make the method irreplaceable in the need to obtain homogeneous, high-purity materials with well reproducible properties.

3. HYDROTHERMAL SYNTHESIS

Crystallisation from solution at elevated pressures and temperatures has been used as a method of preparation only for antimony[86,96] and bismuth[98] orthoniobates and orthotantalates of composition ABO_4. The crystallisation was carried out in batch autoclaves. The starting materials were Sb_2O_3, Bi_2O_3, Nb_2O_5, and Ta_2O_5. The main parameters of the crystallisation process are: temperature 500–650°C, temperature rise up the height of the autoclave 15–65 K, coefficient of filling 0.6–0.65. Sych and coworkers[87,93] started from polycrystalline $SbNbO_4$ and $BiNbO_4$ with the aim of increasing the yield of single crystals; the recrystallisation of $SbNbO_4$ and $BiNbO_4$ took place at 500–560°C and a temperature gradient of 1.0–2.5 K cm^{-1} up the height of the autoclave.

IV. CRYSTAL-CHEMISTRY OF NIOBATES AND TANTALATES OF TERVALENT ELEMENTS

The structures of tantalates and niobates of the same composition type are usually similar, but in certain instances they are not completely isostructural.

1. NIOBATES AND TANTALATES OF THE GROUP III *p*-ELEMENTS

Little is known about the crystal-chemistry of the aluminium, gallium, indium, and thallium niobates and tantalates. Only the $ANbO_4$ (A = Al, Ga, In), $InTaO_4$, and $ANb_{11}O_{29}$ have been investigated by X-ray diffraction. According to Pedersen[75], $AlNbO_4$ is monoclinic, space group $C2/m$. The number of formula units $AlNbO_4$ in the unit cell is $Z = 4$. The monoclinic lattice parameters are: $a = 12.13$, $b = 3.726$, $c = 6.46$ Å, $\beta = 107.2°$. However, Burdese and Lucco[76] state that $AlNbO_4$ is orthorhombic with $a = 6.17$, $b = 7.38$, $c = 8.4$ Å, $Z = 6$, $\rho_{expt} = 4.5$, $\rho_{X\text{-ray}} = 4.15$ g cm^{-3}.

Gallium orthoniobate $GaNbO_4$ is monoclinic[21,107] with $a = 15.22$, $b = 3.75$, $c = 8.07$ Å, $\beta = 141.5°$;[21] it does not undergo any polymorphic transformations up to the melting point (1480°C).[22]

The compounds $InNbO_4$ and $InTaO_4$ are isostructural and of the wolframite type[13,24], space group $P2/c$, $Z = 2$. The $InNbO_4$ monoclinic lattice parameters[13] are: $a = 4.843$, $b = 5.773$, $c = 5.140$ Å, $\beta = 91.140°$, $\rho_{expt} = 6.22$, $\rho_{X\text{-ray}} = 6.28$ g cm^{-3}.

The compounds $AlNb_{11}O_{29}$ and $GaNb_{11}O_{29}$ are monoclinic[15,16]. The lattice parameters of $GaNb_{11}O_{29}$ are[16]: $a = 15.35$, $b = 3.82$, $c = 20.91$ Å, $\beta = 113°26'$. Other investigators[16,21] have reported the existence also of an orthorhombic modification of $GaNb_{11}O_{29}$ with lattice parameters: $a = 28.67$, $b = 3.813$, $c = 20.58$ Å.

Table 5. Lattice parameters of the r.e.e. orthoniobates[13].

Compound	*a*, Å	*b*, Å	*c*, Å	β	*Z*	ρ_{expt}, g cm^{-3}	$\rho_{X\text{-ray}}$, g cm^{-3}
$LaNbO_4$	5.565	11.528	5.201	94°40′	4	5.82	5.909
$CeNbO_4$	5.539	11.415	5.165	94°33′	4	6.04	6.061
$PrNbO_4$	5.499	11.342	5.137	94°34′	4	6.10	6.170
$NdNbO_4$	5.468	11.282	5.144	94°32′	4	6.31	6.324
$SmNbO_4$	5.417	11.166	5.117	94°40′	4	6.61	6.616
$EuNbO_4$	5.393	11.133	5.113	94°35′	4	6.67	6.705
$GdNbO_4$	5.371	11.090	5.107	94°37′	4	6.80	6.882
$TbNbO_4$	5.349	11.036	5.085	94°33′	4	6.93	7.012
$DyNbO_4$	5.320	11.000	5.074	94°34′	4	7.12	7.168
$HoNbO_4$	5.298	10.957	5.068	94°29′	4	7.15	7.167
$ErNbO_4$	5.280	10.914	5.064	94°29′	4	7.30	7.400
$TmNbO_4$	5.262	10.876	5.049	94°31′	4	7.51	7.517
$YbNbO_4$	5.237	10.842	5.043	94°47′	4	7.56	7.677
$LuNbO_4$	5.293	10.043	5.065	94°32′	4	7.69	7.756
$YNbO_4$	5.293	10.943	5.065	94°32′	4	5.53	5.583
$ScNbO_4$	4.818	5.655	5.101	88°25′	2	4.76	4.817

2. NIOBATES AND TANTALATES OF THE GROUP III *d*- AND *f*-ELEMENTS

This section considers the structural features of the compounds RBO_4, $R_{1/3}BO_3$, R_3BO_7, and RB_5O_{14}. Information about the crystal-chemistry of the other niobates and tantalates is extremely limited or completely non-existent.

A. Orthoniobates and Orthotantalates of Composition ABO_4

The r.e.e. (with the exception of Sc) orthoniobates of composition $RNbO_4$ have a fergusonite structure at room temperature[13,50,53,108]. As Table 5 shows, as the ionic radius of the lanthanide in $LnNbO_4$ is reduced there is a regular decrease in the monoclinic lattice parameters, the parameters *a* and *c* falling linearly from La to Eu and from Gd to Lu, with a pronounced break at $EuNbO_4$ (Fig. 4). The lattice parameters of $YNbO_4$ do not fit into this regularity. It seems that the dimensions of the $RNbO_4$ unit cell are affected not only by the ionic radius of the cation but also by the fraction of the covalent bond A–O, which decreases appreciably on going from Sc to Y and La.

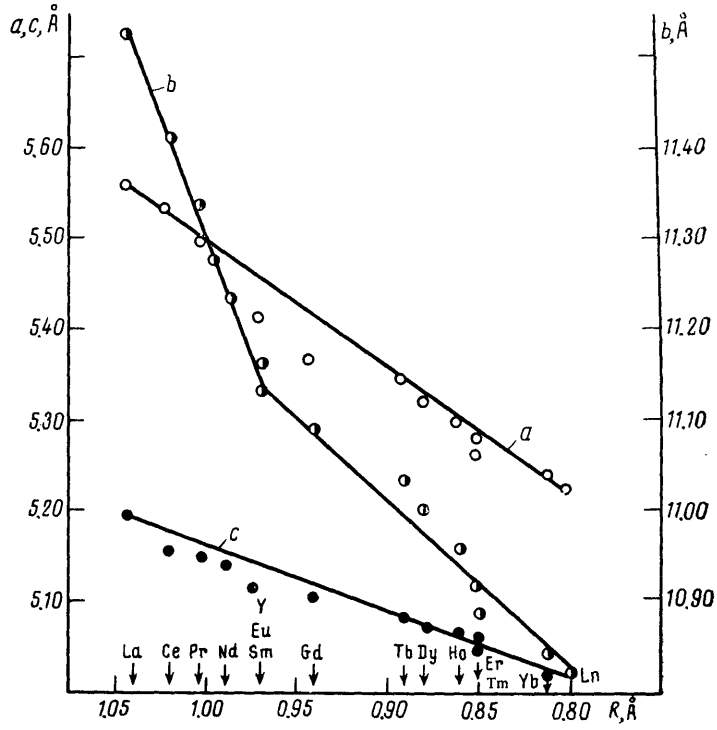


Figure 4. Variation of the lattice parameters of the r.e.e. orthoniobates[13] with the radius of the r.e.e. ion[116].

The orthotantalates $LnTaO_4$, where Ln = Nd–Lu, and $YTaO_4$ also crystallise in a monoclinic lattice of the fergusonite type[13,109,110] (Table 6). As for the orthoniobates, there is a linear increase in the size of the monoclinic cells of the $LnTaO_4$ as the ionic radius of the lanthanide is increased.

The ABO_4 crystal structure of fergusonite type is a distorted scheelite structure[45,111]. The Nb (or Ta) atoms are situated within several distorted tetrahedra of oxygen atoms. The r.e.e. atoms have coordination number 8 and are also surrounded by oxygen atoms[45,108,111]. All 16 oxygen atoms in the $LnNbO_4$ unit cell ($Z = 4$) occupy positions with general symmetry (C_1) and the Ln and Nb atoms are situated at points with site symmetry C_2.

It has been reported[112] that the X-ray diffraction pattern of $YTaO_4$ can be indexed in a basocentric monoclinic unit cell with $a = 6.978$, $b = 10.930$, $c = 5.323$ Å, $\beta = 133°50'$. Probable space group: $C2/c$ or Cc.

B. Isomorphism of the Compounds ABO_4 with Fergusonite Structure

When compounds of the $RNbO_4$ (R = Y, Ln) or $RTaO_4$ (R = Y, Nd–Lu) type are heated their monoclinic cell is converted into a tetragonal one (scheelite structure)[45,53]. The transformation is reversible, takes place in stages, has a "shear" nature[45], and is accompanied by a gradual change in the lattice parameters, which is accelerated close to the transformation temperature[109]. During such a transformation the parameters a and c of the monoclinic cell become equal to the parameter a of the tetragonal, and the parameter b of the monoclinic cell is changed to the parameter c of the tetragonal cell[53].

Table 6. Lattice parameters of the r.e.e. orthotantalates.

Compound	a, Å	b, Å	c, Å	β	Z	ρ_{expt}, g cm^{-3}	$\rho_{X\text{-ray}}$, g cm^{-3}
$LaTaO_4$ [13]	7.651	5.577	7.823	101°31′	—	—	—
$NdTaO_4$ [13]	5.514	11.237	5.114	95°42′	4	8.12	8.199
$SmTaO_4$ [13]	5.455	11.137	5.091	95°44′	4	8.47	8.548
$EuTaO_4$ [13]	5.428	11.103	5.087	95°44′	4	8.60	8.644
$GdTaO_4$ [13]	5.405	11.063	5.084	95°35′	4	8.76	8.830
$TbTaO_4$ [13]	5.382	11.022	5.068	95°40′	4	8.82	8.967
$DyTaO_4$ [13]	5.354	10.974	5.061	95°43′	4	8.97	9.147
$HoTaO_4$ [13]	5.329	10.935	5.056	95°32′	4	9.25	9.284
$ErTaO_4$ [13]	5.306	10.893	5.042	95°44′	4	9.27	9.443
$TmTaO_4$ [86]	5.053	10.82	5.243	95°11′	4	—	—
$YbTaO_4$ [82]	5.035	10.82	5.23	84°22′	4	—	—
$LuTaO_4$ [82]	5.03	10.78	5.25	84°22′	4	—	—
$YTaO_4$ [13]	5.239	10.893	5.056	95°31′	4	7.56	7.592
$ScTaO_4$ [13]	4.809	5.670	5.118	88°20′	4	6.84	6.802

The temperature of the transformation into the scheelite structure for the orthoniobates is 500–800°C. Usually the temperature for the appearance of the tetragonal phase increases with decrease in the atomic radius of the r.e.e., that is, in the order La–Lu. It is significantly higher for the tantalates than for the niobates[109]. A high-temperature form has not been observed for the Tm, Yb, and Lu tantalates[109].

During the growing of single crystals of the r.e.e. orthoniobates and orthotantalates the formation of a third polymorphic modification of the ABO_4 compounds was observed[113,114]. The monoclinic lattice parameters (example, $YTaO_4$)[114] are: $a = 5.292$; $b = 5.451$, $c = 5.110$ Å, $\beta = 96.44°$, $Z = 2$. In the structure of this modification of $YTaO_4$ the Ta atoms are at the centre of a distorted TaO_4 tetrahedron (Ta–O distance = 1.94–2.03 Å) and the Y atoms are at the centre of a distorted cube (Y–O distance = 2.25–2.42 Å).

C. The Orthotantalates $LnTaO_4$ (Ln = La, Ce, Pr)

The La, Ce, and Pr orthotantalates are not isostructural with the corresponding orthoniobates. $LaTaO_4$ is monoclinic, space group $P2_1/c$.[115] The Ta atoms are situated close to the centres of distorted octahedra, and the Ta–O distance varies within the limits 1.91–2.05 Å (mean distance 2.00 Å). The octahedra are linked at the vertices and form an infinite (in two-dimensions) corrugated layer. Each octahedron has four vertices in common with four neighbouring octahedra, the layers being separated from those similar in configuration to them by layers of La atoms, which have eightfold coordination, the eight La–O distances lying within the range 2.40–2.84 Å.[115] Fig. 5 shows a fragment of the $LaTaO_4$ structure.

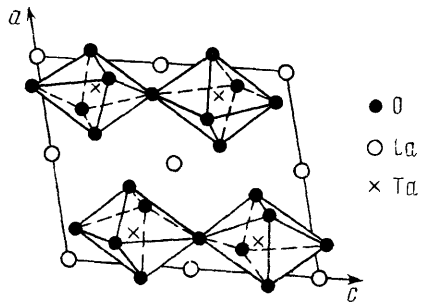


Figure 5. Fragment of the $LaTaO_4$ structure projected on [010].

Scandium orthoniobate and orthotantalate are monoclinic[53] (Tables 5 and 6). Their structure shows greater similarity with the wolframite structure[32,53] than with the fergusonite structure, which seems to be due to the appreciable difference between the size of the Sc^{3+} ion and those of the other r.e.e. ions.

D. R.e.e. Metaniobates and Metatantalates

All the r.e.e. metaniobates and metatantalates have a perovskite ABO_3 structure[40,55,110,117] and their formulae are usually written as $R_{1/3}BO_3$. Whereas the metatantalates $R_{1/3}TaO_3$ are known for almost all the r.e.e., metaniobates have been obtained only for La, Ce, Pr, Nd, and Eu.

The lanthanide metaniobates are orthorhombic; the La, Ce, Gd, Dy, Ho, Eu, and Y metatantalates are tetragonal; Pr, Nd, and Tb metatantalates are orthorhombic, and Yb metatantalate is monoclinic (Table 7). The lattice parameters and unit-cell volume[40,55] of the metaniobates $Ln_{1/3}NbO_3$ and metatantalates $R_{1/3}TaO_3$ fall regularly with increase in the atomic number of the lanthanide.

Since the metaniobates with perovskite structure are known only for the metals of the cerium subgroup, the very existence of compounds of composition $A_{1/3}BO_3$ depends in a definite manner on the size of the r.e.e. cation. As Table 8 shows, metaniobates with the perovskite structure can exist at Goldschmidt stability factors $\leqslant 0.9$. Therefore the metaniobates of Fe, Cr, Sc, and other 3*d*- or *p*-metals with perovskite structure can hardly be obtained. Nevertheless the hitherto unknown $Bi_{1/3}TaO_3$ should be stable. The lower limit of the stability factor for the metatantalates of composition $A_{1/3}TaO_3$ should be somewhat lower than for the niobates and seems to be 0.83–0.84.

The structure for the metaniobates and metatantalates of composition $R_{1/3}BO_3$ has been determined for $La_{1/3}NbO_3$ [55] and $La_{1/3}TaO_3$, [55,117] and also $Y_{1/3}TaO_3$. [117] All the compounds have a perovskite structure, $P4/mmm$. [55,117] However, unlike the ideal structure of perovskite, for the compounds $A_{1/3}BO_3$ only one-third of the sites in the A sublattice can be occupied and the remaining two-thirds of the sites remain vacant.

Table 7. Lattice parameters of the metaniobates and metatantalates $A_{1/3}BO_3$.

Compound	Symmetry	Lattice parameters				
		a, Å	*b*, Å	*c*, Å	*V*, Å³	*Z*
$La_{1/3}NbO_3$ [55]	o-rh.	3.911	3,917	7.908	121.2	2
$Ce_{1/3}NbO_3$ [55]	o-rh.	3.901	3.917	7.886	120.5	2
$Pr_{1/3}NbO_3$ [55]	o-rh.	3.891	3.915	7.862	119.8	2
$Nd_{1/3}NbO_3$ [55]	o-rh.	3.878	3.907	7.840	118.8	2
$Eu_{1/3}NbO_3$ [50]	o-rh.	3.624	3.806	7.90	108.9	2
$La_{1/3}TaO_3$ [55]	tetr.	3.918	—	7.913	121.5	2
$Ce_{1/3}TaO_3$ [55]	tetr.	3.915	—	7.878	120.7	2
$Pr_{1/3}TaO_3$ [55]	o-rh.	3.845	3.910	7.836	119.3	2
$Nd_{1/3}TaO_3$ [55]	o-rh.	3.876	3.916	7.829	118.8	2
$Sm_{1/3}TaO_3$ [55]	o-rh.	3.882	3.896	7.785	117.7	2
$Eu_{1/3}TaO_3$ [110]	o-rh.	3.843	3.854	7.915	117.0	2
$Gd_{1/3}TaO_3$ [55]	tetr.	3.874	—	7.795	117.0	2
$Tb_{1/3}TaO_3$ [110]	o-rh.	3.861	3.865	7.807	116.7	2
$Dy_{1/3}TaO_3$ [55]	tetr.	3.847	—	7.769	115.0	2
$Ho_{1/3}TaO_3$ [55]	tetr.	3.841	—	7.756	114.0	2
$Er_{1/3}TaO_3$ [55]	tetr.	3.825	—	7.754	113.5	2
$Yb_{1/3}TaO_3$ [40*]	mon.	3.793	3.805	7.708	111.2	2
$Y_{1/3}TaO_3$ [55]	tetr.	3.824	—	7.758	113.5	2

* $\beta = 91.6°$

An increase in the lattice parameter along the *c* axis by a factor of two in comparison with the initial perovskite cell is characteristic for all the compounds. This doubling is due to the alternation of the empty layers with the layers two-thirds filled with atoms A. The atoms A are distributed statistically in two-thirds filled cubo-octahedra. The sometimes suggested[118] doubling of the lattice parameters also along axes *a* and *b*, which for the composition $Ln_{1/3}NbO_3$ requires $Z = 8$, can hardly be correct.

The niobium and tantalum atoms are surrounded by six oxygen atoms, which are situated at the vertices of an almost regular NbO_6 (or TaO_6) octahedron. The structure and interatomic distances for $Ln_{1/3}NbO_3$ are given in Fig. 6. Clearly the distance Nb–O (or Ta–O) in the r.e.e. metaniobates and metatantalates differs from the B–O distance in the ideal perovskite. This is due to some displacement of the Nb (Ta) atom along the *c* axis. Similar structural features are characteristic for ferroelectrics of the oxygen-octahedral type, for example, $BaTiO_3$, $KNbO_3$, etc. [119]

E. Niobates and Tantalates of Composition A_3BO_7

The niobates of composition A_3BO_7 belong to three structural groups, depending upon the nature of the r.e.e. and the temperature. The La, Nd, and Sm niobates, which form the first group, are orthorhombic, weberite structure type[38], space group $Pncm$. [120,121] Eu_3NbO_7 and Gd_3NbO_7, which belong to the second structural group, are monoclinic, space group $P2/m$. [122] All the niobates R_3NbO_7 (R = Dy–Lu, Y, Sc) of the third group are cubic, fluorite type [120–122]—according to other investigators[38], pyrochlore type.

Table 8. Relation between the ionic radius and stability factor for certain niobates of composition $A_{1/3}NbO_3$ with a perovskite structure.

Element A	Ionic radius, r_A, Å	Stability factor, *t*	Compound
La	1.04	0.924	$La_{1/3}NbO_3$ [40,55]
Nd	0.99	0.907	$Nd_{1/3}NbO_3$ [40,45]
Sm	0.97	0.900	unknown
Eu	0,97	0.900	$Eu_{1/3}NbO_3$ [50]
Gd	0,94	0.888	unknown
Lu	0,80	0.835	unknown
Y	0,97	0.900	unknown
Sc	0.83	0.844	unknown
Bi	1,20	0.988	unknown
Sb	0,90	0.874	$Sb(NbO_3)_3$ structure $PbNb_2O_6$ [90]
Fe	0.67	0.785	unknown
Al	0,57	0.744	unknown
Ga	0,62	0.765	unknown
In	0.92	0.883	unknown

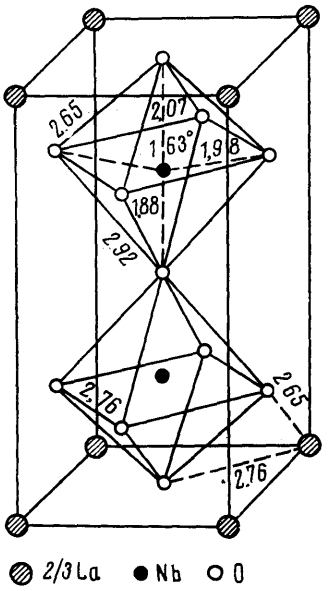


Figure 6. Unit cell of $La_{1/3}NbO_3$. [55]

Table 9 gives the lattice parameters of the compounds R_3NbO_7. With increase in the atomic radius of the r.e.e. the fluorite lattice parameter increases. The niobates Ln_3NbO_7 of the first and second groups undergo polymorphic transformations above 1300°C with change to a stable fluorite cubic structure [121,122] (Table 9).

The tantalates of composition R_3TaO_7 (where R = La, Nd, Sm, Gd, Dy, Y, and Sc) are cubic[38]. However, Rooksby and White[38] could not find any difference between the disordered fluorite structure and the ordered pyrochlore structure. According to Romashov and coworkers[110] the R_3TaO_7 (R varies from Sm to Lu and Y) have a pyrochlore structure. The lattice parameters change regularly along the lanthanide series.

Table 9. Lattice parameters of certain niobates and tantalates R_3BO_7.

Compound	Symmetry	Lattice parameters				Structure type*	Polymorphic transformation
		a, Å	b, Å	c, Å	β		
La_3NbO_7 [38]	o-rh.	7.84	10.86	7.70	—		W $\xrightarrow{1300°}$ F[122]
Nd_3NbO_7 [38]	o-rh.	7.66	10.98	7.70	—	W	W $\xrightarrow{1300°}$ F[122]
Sm_3NbO_7 [123]	o-rh.	7.56	10.81	7.59	—	W	W→P2/m→F[122]
Eu_3NbO_7 [121]	mon.	10.672	10.679	10.666	90°25′	—	P2/m $\xrightarrow{1300°}$ F[121]
Gd_3NbO_7 [38]	cub.	5.32 (F); 10.64 (P)	—	—	—	F,P	P2/m→F[121]
Dy_3NbO_7 [38]	cub.	5.26 (F); 10.53 (P)	—	—	—	F,P	—
Lu_3NbO_7 [120]	cub.	5.33	—	—	—	F	—
Y_3NbO_7 [38]	cub.	5.24 (F); 10.49 (P)	—	—	—	F,P	—
Sc_3NbO_7	cub.	4.88 (F); 9.99 (P)	—	—	—	F,P	—
La_3TaO_7 [38]	o-rh.	7.84	10.87	7.70	—	W	—
Nb_3TaO_7 [38]	o-rh.	7.66	10.98	7.52	—	W	—
Sm_3TaO_7 [38]	cub.	5.36 (F); 10.75 (P)	—	—	—	F,P	—
Gd_3TaO_7 [38]	cub.	5.32 (F); 10.64 (P)	—	—	—	F,P	—
Dy_3TaO_7 [38]	cub.	5,26 (F); 10,58 (P)	—	—	—	F,P	—
$HoTaO_7$ [110]	cub.	10.45	—	—	—	P	—
Er_3TaO_7 [110]	cub.	10,50	—	—	—	P	—
Tm_3TaO_7 [110]	cub.	10.33	—	—	—	P	—
Lu_3TaO_7 [110]	cub.	10.33	—	—	—	P	—
Y_3TaO_7 [38]	cub.	5.24 (F); 10,49 (P)	—	—	—	F,P	—
Sc_3TaO_7 [38]	cub.	4.88 (F); 9,66 (P)	—	—	—	F,P	—

*W = weberite; F = fluorite; P = pyrochlore.

F. Niobates and Tantalates of Composition LnB_5O_{14}

According to Badiot[58] the pentaniobates $LnNb_5O_{14}$ (Ln = La, Ce, Pr, and Nd) are orthorhombic, the lattice parameters for $LaNb_5O_{14}$ being: $a = 20.12$, $b = 12.42$, $c = 7.74$ Å, $Z = 8$, space group C_{2V}^9. The tantalates RTa_5O_{14} (R = La, Ce, Nd, Pr, Sm, Dy, Tm, and Y) have an orthorhombic basocentric lattice, corresponding to a distorted ReO_3 structure[124]. The lattice parameters for $LaTa_5O_{14}$ are: $a = 17.56$, $b = 16.98$, $c = 3.851$ Å. According to Ferguson[111], $LaTa_5O_{14}$ is not isostructural with $LaNb_5O_{14}$, despite Iyer and Smith's claim[55].

3. CRYSTAL-CHEMISTRY OF THE ANTIMONY AND BISMUTH NIOBATES AND TANTALATES

According to Roth and Waring[84] compounds of composition ABO_4 (A = Sb or Bi; B = Nb or Ta) at room temperature are isostructural and have the same structure as the natural mineral cervatite $SbSbO_4$,[91] stibiocolumbite (Sb, Bi)(Nb, Ta)O_6, or bismutotantalite (Bi, Sb)(Ta, Nb)O_4.[125]

Table 10 gives the orthorhombic lattice parameters. X-ray diffraction investigation of $SbTaO_4$ [13,91] and $SbNbO_4$,[13,85] as examples, indicated the space group of the ABO_4: $Pna2_1 = C_{2V}^9$, $Z = 4$. The $SbTaO_4$ structure is shown in Fig. 7. It is characteristic of an octahedral environment for the atoms Nb and Ta. The atoms Sb and Bi also have a coordination number of 6. Fig. 8 gives the bond lengths in the $SbNbO_4$ structure[85]. The NbO_6 and TaO_6 octahedra form toothed chains. The monolayers of BO_6 octahedra are separate in the z direction. The ions A occupy the vacancies between the BO_6 octahedra.

Table 10. Lattice parameters of antimony and bismuth orthotantalates and orthoniobates[84].

Compound	a, Å	b, Å	c, Å	Z	ρ_{expt}, g cm^{-3}	$\rho_{X\text{-ray}}$, g cm^{-3}
$SbNbO_4$	4.929	11.797	5.559	4	5.75[87]	5.79
$BiNbO_4$	4.980	11.709	5.675	4	7.37[93]	7,34
$SbTaO_4$	4,911	11.814	5.535	4	7,57[147]	7.65
$BiTaO_4$	4.957	11,763	5.633	4	9.26[147]	9,22

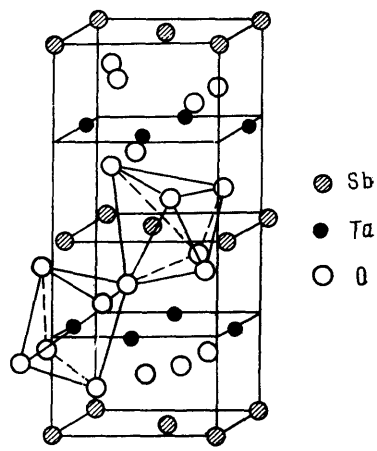


Figure 7. Structure of antimony orthotantalate $SbTaO_4$.[91]

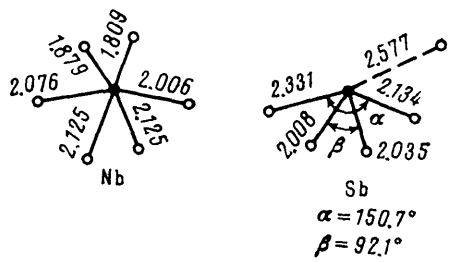


Figure 8. Lengths of the Nb–O and Sb–O bonds and valence angles in the $SbNbO_4$ structure[85].

According to Popolitov and coworkers[98] the orthorhombic single crystals of $BiNbO_4$ and $BiTaO_4$ prepared under hydrothermal conditions have the centrosymmetric space group $D_{2h}^6 = Pnna$.

In addition to the orthorhombic modification α-ABO_4 a high-temperature modification β-ABO_4 is characteristic

for bismuth orthoniobate and orthotantalate. The triclinic high-temperature modification for $BiNbO_4$ and $BiTaO_4$ was first obtained by heating mixtures of Bi_2O_3 and Nb_2O_5 [or Ta_2O_5 (Ed. of Translation)] in air at 1100–1200°C.[88] α-$BiNbO_4$ and α-$BiTaO_4$ are irreversibly converted into the triclinic β-modification when heated to 1020° and 900°C respectively[84,89].

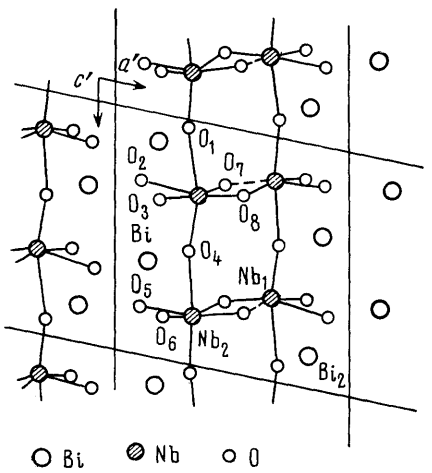


Figure 9. Projection of the β-$BiNbO_4$ structure on [010].[126]

The lattice parameters of the triclinic β-$BiBO_4$ are[88]:

	a, Å	b, Å	c, Å	α	β	γ
β-$BiNbO_4$	7.61	5.53	7.91	83.99°	74.43°	82.15°
β-$BiTaO_4$	7.62	5.58	7.77	89.92°	77.12°	96.45°

The space group of β-$BiNbO_4$ is[126]: $P1$, $Z = 4$.

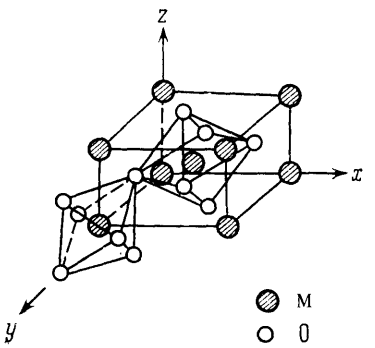


Figure 10. Rutile structure for compounds of the ABO_4 type (A = Ti, V, Cr, or Fe).

The structure of β-$BiNbO_4$ [126,127] (Fig. 9) consists of corrugated lattices constructed from NbO_6 octahedra parallel to the plane oc. Each octahedron is connected by vertices with four other octahedra. The NbO_6 lattices are maintained by Bi atoms. The Bi atoms have a coordination number of eight. The Bi polyhedron is a distorted tetragonal antiprism. The Bi–O distance is in the range 2.105–3.017 and the Nb–O distance in the range 1.803–2.313 Å.

$SbNb_3O_9$ is orthorhombic with lattice parameters a = 17.635, b = 3.968, c = 17.219 Å. The structure is analogous with the ferroelectric $PbNb_2O_6$, $Z = 10$.[90] The compound $Bi_3Nb_{17}O_{47}$ has the structure of a tungsten "bronze".[37,128] The orthorhombic lattice parameters are: a = 12.516, b = 37.14, c = 3.922 Å, $Z = 2$. Space group $Pba2$. Some of the niobium atoms have coordination number 7. The coordination polyhedron is a pentagonal bipyramid. The remaining 8 niobium atoms are arranged in octahedra. The Nb–O distance is 1.48–2.46 Å.[92]

4. CRYSTAL-CHEMISTRY OF THE *d*-ELEMENT NIOBATES AND TANTALATES

Compounds of Composition ABO_4 (A = Ti, V, Cr, Fe)

The orthoniobates and orthotantalates of composition ABO_4 crystallise according to rutile type[13,18,129]. The TiO_2 rutile structure is tetragonal, space group D_{2h}^{14} [D_{4h}^{14}? (Ed. of Translation)]. The number of formula units for TiO_2 is $Z = 2$; that for ABO_4 is $Z = 1$. The lattice parameters of the compounds of composition ABO_4 are a = 4.6, c = 3.0 Å (Table 11). Fig. 10 shows the ABO_4 structure. Atoms A and B are arranged randomly in the cell of the double oxide[13,129] and have coordination number 6, occupying identical positions.

Table 11. Lattice parameters of the *d*-element orthoniobates and orthotantalates with a rutile structure.

Compound	a, Å	c, Å	$\rho_{X\text{-ray}}$, g cm^{-3}	ρ_{expt}, g cm^{-3}
$TiNbO_4$ [13]	4.712	2.996	5.100	5.01
$VNbO_4$ [13]	4.681	3.033	5.194	5.13
$CrNbO_4$ [18]	4.635	3.005	—	—
$FeNbO_4$ [18]	4.68	3.05	—	—
$TiTaO_4$ [129]	4.645	3.020	—	—
$VTaO_4$ [129]	4.667	3.047	—	—
$CrTaO_4$ [129]	4.638	3.018	—	—
$FeTaO_4$ [129]	4.679	3.047	—	—
TiO_2 [130]	4.594	2.959	—	—

For iron orthoniobate $FeNbO_4$, in addition to the tetragonal form mentioned there are another two polymorphic modifications—monoclinic and orthorhombic[131]. Roth and Waring[132] think that the low-temperature modification, stable up to 1085°C, is monoclinic, space group $P2_1/a$. The lattice parameters are a = 5.001, b = 5.620, c = 4.653 Å, β = 90°16′. The orthorhombic phase (a = 5.005, b = 5.613, c = 4.647 Å) is stable from 1085° to 1380°C. The rutile modification exists from 1380°C up to the melting point (~ 1475°C).[132] Conversion of the low-temperature rutile modification into the high-temperature orthorhombic modification, with wolframite structure, is observed for iron orthotantalate $FeTaO_4$. The lattice parameters are a = 4.63, b = 5.64, c = 5.04 Å.[133]

The above crystallographic results show that the niobates and tantalates of tervalent elements form two structural groups: with tetrahedral and octahedral environment of the Nb or Ta. Tetrahedral coordination is encountered only in the orthoniobates and orthotantalates ABO_4. However, even for this composition it is not the only possibility. Isolated BO_4^{3-} tetrahedra exist only in the r.e.e. orthoniobates and (in part) orthotantalates (except for La, Ce, and Pr) with the fergusonite structure, which has many features in common with the scheelite structure. The remaining tervalent metal niobates and tantalates for which structural results have been published are compounds of octahedral type.

A comparison of the available results shows that the change from tetrahedral to octahedral configuration even in the series of ABO_4 compounds is not determined by the increase in the ionic radius of the r.e.e. This transformation is usually due to the change in the nature of the A–O bond and the competition of the A atoms with the Nb(Ta) atoms for possession by the oxide ligands.

The niobates and tantalates of tervalent metals with an octahedral configuration crystallise according to the $LaTaO_4$ type, perovskite, cervantite, or rutile. In all these structures the BO_6 octahedra are usually connected by their vertices with the formation of two-dimensional or three-dimensional skeletons, unlike the fergusonite structure with isolated BO_4^{3-} tetrahedra.

Table 12. Interplanar spacings (Å) in niobates and tantalates with octahedral coordination.

Structure type	$(B-O)_{min}$		$(B-O)_{max}$		$(B-O)_{av}$	
	Nb–O	Ta–O	Nb–O	Ta–O	Nb–O	Ta–O
$LnTaO_4$	—	1.91	—	2.05	—	2.00
Perovskite ($La_{1/3}BO_3$)	1.88	1.90	2.07	2.06	1.98	1.98
Cervantite ($SbBO_4$)	1.81	2.06	2.07	2.09	2.00	2.09
Rutile ($ATaO_4$)	—	1.95	—	2.04	—	2.00
Mean value (B–O)	1.85	1.95	2.07	2.07	1.99	2.01

The B–O interatomic distances in the compounds of octahedral type according to the available information are given in Table 12. A regular dependence of the B–O distances on the nature of the metal A is not observed. The Ta–O distance is somewhat greater than the Nb–O distance. The mean interatomic B–O distances in the octahedral compounds (2.00 Å) is greater than the mean B–O distance in the tetrahedral compounds (1.77–1.78 Å for scheelite). Distortion of the octahedron is observed in all the compounds of octahedral type, the shortest bond always being *trans* to the longest B–O bond (cf. Figs. 6 and 8). This fact can be due to the displacement of the Nb (Ta) atom from the centre of the octahedron along one of the fourth-order axes. These structural features are known to facilitate the production of a spontaneously polarised state in tantalates, niobates and molybdates of a series of *s*- and *p*-elements.

V. PROPERTIES OF NIOBATES AND TANTALATES OF TERVALENT METALS

1. PHYSICOCHEMICAL PROPERTIES

The information about the chemical stability and solubility of the niobates and tantalates of tervalent metals is disconnected. However, the available information suggests that all the compounds considered have high chemical stability. Both the niobates and tantalates are almost insoluble in water. For example, when the r.e.e. tantalates were treated with boiling water for 10 h there was no change in the structure of the compound, and r.e.e. ions could not be detected in the water[63].

The niobates and tantalates do not react with dilute HCl, HNO_3, $HClO_4$, H_3PO_4 or solutions of alkalis. However, when heated with concentrated acids or alkalis they are partly decomposed, and in hot H_2SO_4 some of the niobates and tantalates[63] can decompose completely. They also dissolve in hydrofluoric acid.

Niobates and tantalates are also highly resistant towards solutions of organic acids, and to many molten salts and metals. The niobates and tantalates are stable also towards moderate heating. Thus the r.e.e. (except Eu) orthoniobates are not reduced in an atmosphere of hydrogen at 1100–1200°C.[134] Under the same conditions $EuNbO_4$ is reduced to the metaniobate with perovskite structure (a = 3.95 Å)[134].

2. MELTING POINTS

Tables 13 and 14 give the melting points of the niobates and tantalates of some tervalent metals. As might be expected, the tantalates melt at a higher temperature than the corresponding niobates.

Table 13. Melting points of certain niobates of tervalent metals, °C.

Element A	$ANbO_4$	$A_{1/3}NbO_3$	A_3NbO_7	Other compounds
Al	1560[12]	—	—	—
Ga	1450[22]	—	—	—
In	1740[22]	—	—	—
Sc	1950[32]	—	—	—
Y	2000[77]	—	—	—
La	1620[48]	1460[48]	1760[48]	$La_2Nb_{12}O_{33}$—1330[59]
Ce	1660[48]	1480[48]	1790[48]	$Ce_2Nb_{12}O_{33}$—1350[59]
Pr	1720[48]	1550[48]	1800[48]	—
Sb	1160[87]	—	—	—
Bi	1245[59]	—	—	—

Another obvious regularity is observed for the r.e.e. niobates and tantalates. With increase in the molar ratio A : B in the compounds, that is, in the series AB_3O_9–ABO_4–A_3BO_7, the melting points of the compounds of a single element A increase (Tables 13 and 14). The compounds of composition A_3BO_7, which contain the greatest possible proportion of tervalent metal, have the highest melting point. A tendency towards an increase in the melting points of the compounds in the series La–Lu is not observed. The melting points for all types of compound undergo a jump at gadolinium and they reach a maximum for the La–Lu series.

3. ELECTROPHYSICAL PROPERTIES

As noted above, in most of the niobates and tantalates the NbO_6 (or TaO_6) octahedra are usually distorted owing to the displacement of the B atoms from the centres of the octahedra. This is characteristic of many ferroelectrics, for example, $KNbO_3$, $KTaO_3$, $PbNb_2O_6$, the antiferroelectric $NaNbO_3$, the piezoelectrics $Sr_xBa_{1-x}Nb_2O_6$, and other commercially important niobates and tantalates[119].

Table 14. Melting points of certain r.e.e. tantalates[63], °C.

Element A	$ATaO_4$	$A_{1/3}TaO_3$	A_3TaO_7	Element A	$ATaO_4$	$A_{1/3}TaO_3$	A_3TaO_7
Y	2100	1920	2380	Tb	1980	1820	2230
La	1860	1780	1960	Dy	2030	1820	2270
Ce	1890	—	—	Ho	2010	1835	2270
Pr	1845	1750	1990	Er	2010	1810	2360
Nd	1825	1820	1980	Tm	1990	1770	2260
Sm	1930	1810	2050	Yb	2030	1780	2360
Eu	1830	1805	2000	Lu	1980	1760	2340
Gd	2050	1840	2280				

A. Al, Ga, and In Niobates and Tantalates

Manakov and coworkers[135] were the first to study the dielectric properties of the Al_2O_3–Nb_2O_5 system. Ionic conductivity was observed for the entire composition region. As the temperature is raised (100–1600°C) in the Al_2O_3–Nb_2O_5 system the curve of electrical conductivity σ against temperature shows an inflection characteristic of ionic conduction, and this inflection corresponds to the melting point[135].

The curves showing the temperature dependence of ϵ and σ for the Al_2O_3–Nb_2O_5 and Ga_2O_3–Nb_2O_5 systems have anomalies characteristic of ferroelectric materials close to the Curie point. The most pronounced maximum on the curve of ϵ against temperature is observed at the composition $Al_2O_3 : Nb_2O_5 = 1 : 5$. However, the absence of a hysteresis loop did not confirm the hypothesis of ferroelectric properties for these materials[31,107]. The dielectric properties of ceramic specimens of $AlNbO_4$ and $GaNbO_4$ have also been studied[20,136]. The variation of ϵ and tan δ with the temperature for all the specimens agrees with the temperature dependence of electrical conductivity. It is therefore thought[20] that the inflections on the above curves are due to relaxation processes.

Anomalies in the dielectric properties have not been observed for Al and Ga tantalates[31]. Their dielectric constant is much less than for the corresponding niobates in the temperature range up to 350°C.

B. Niobates and Tantalates of Scandium Subgroup Elements

(1) Orthoniobates of composition $RNbO_4$. The electrical properties of compounds of the type ABO_4 have been studied only for $YNbO_4$,[9,42] $NdNbO_4$,[6,137] $GdNbO_4$,[137] and $HoNbO_4$,[9] and for $LaNbO_4$, $YbNbO_4$, $YTaO_4$, and $YbTaO_4$.[8] These r.e.e. orthoniobates are antiferroelectrics with a rather high Curie temperature (500–830°C)[8,9]. The Curie temperature is inversely proportional to the radius of cation A and lies in the range 500–730°C for ABO_4, where A = Y, La, Yb.[8]

The dielectric constant and slope of the dielectric loss vary slightly up to 160°C.[42] When the temperature is raised further there is an increase in ϵ and tan δ;[8,137] the curves have a characteristic inflection at the Curie point (Fig. 11). The reciprocal of the dielectric constant $1/\epsilon$ is a linear function of temperature, which agrees with the Curie law[137]. The electrical conductivities σ of the $LnNbO_4$ (Ln = Nd, Gd) also increase with the temperature[6,137]. Above 130°C for $NdNbO_4$ and 230°C for $GdNbO_4$ lg σ varies linearly with $1/T$.[137] The $NdNbO_4$ and $GdNbO_4$ exhibit *n* type conduction.[137]

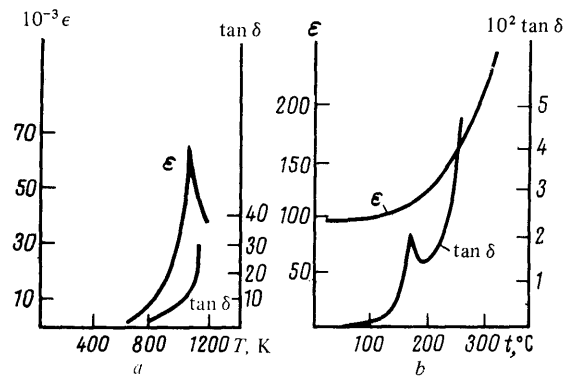


Figure 11. Variation of the dielectric constant ϵ and slope of the dielectric loss tan δ with temperature: *a*) $NdNbO_4$;[137] *b*) $Nd_{1/3}NbO_3$.[138]

(2) Metaniobates of composition $Ln_{1/3}NbO_3$. The niobium compounds of oxygen-octahedral type of composition $MNbO_3$ (M = K or Na) with perovskite structure usually exhibit ferroelectric or antiferroelectric properties[119]. This very feature is responsible for the more detailed study of the dielectric properties of the r.e.e. metaniobates.[6,7,133,138].

On the curves for the temperature dependence of ϵ and tan δ for $Ln_{1/3}NbO_3$ there are distinct inflections[31,138] which allow them to be associated with a phase transformation (Fig. 11). However, neither the shape nor the size of these maxima are characteristic of ferroelectrics[138] but seem to be characteristic of relaxation[6,138]. The latter is explained by the ordered alternation of filled layers and vacancies in the A sublattice[138].

The electrical conductivity σ of the r.e.e. metaniobates is similar, as regards absolute value and temperature dependence, to that for the orthoniobates[6]. All the metaniobates exhibit an ability to accumulate a large residual charge[6,7]. The existence of residual charges capable of being retained for a long time (up to 1–5 years) and the reversal of the sign of the charge shows the $Ln_{1/3}NbO_3$ to possess electret properties, this being connected with the residual polarisation of the specimens. The residual charge of the r.e.e. metaniobates[6] (Table 15) usually exceeds that for the other known ceramic electrets, for example, those based on titanates[139], consequently materials based on r.e.e. metaniobates are interesting not only as electrets but also as low-power sources of current.

C. Antimony and Bismuth Niobates and Tantalates

The detailed study of the dielectric properties of the antimony and bismuth orthoniobates and orthotantalates of composition ABO_4 with cervantite structure began after the discovery in 1970 that the natural mineral stibiotantalite $(Sb,Bi)(Ta,Nb)O_4$ exhibits ferroelectric properties[5,140]. Later on, ferroelectric properties were also observed in synthetic specimens of $SbNbO_4$ [87,96,97] and $SbTaO_4$.[95,96] Phase transformations, the nature of which is still disputed, are shown clearly on the curves of ϵ and $\tan\delta$ against temperature (Fig. 12). Some investigators[86,87,97] identify the phase transformation at 410°C with the Curie temperature, that is, with a change from a spontaneously polarised state into a pyroelectric phase. These results agree with the Curie temperature of $T_C = 410°C$ for the natural mineral stibiotantalite[5].

Table 15. Residual charge of certain ceramic electrets.

Composition	ϵ	P, C cm^{-2}	Composition	ϵ	P, C cm^{-2}
$La_{1/3}NbO_3$	200	$(4.5-8)\cdot10^{-4}$	$MgTiO_3$	15	$1.3\cdot10^{-7}$
$Pr_{1/3}NbO_3$	70	$(3-5)\cdot10^{-3}$	$CaTiO_3$	150	$1.0\cdot10^{-7}$
$Nd_{1/3}NbO_3$	50	$(1-2.5)\cdot10^{-3}$			

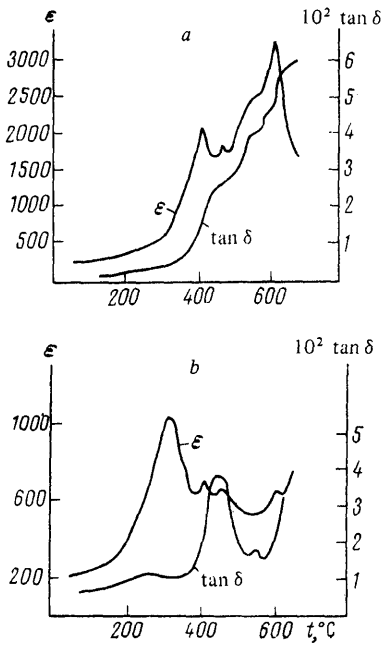


Figure 12. Variation of the dielectric constant ϵ and of the slope of the dielectric loss tan δ with temperature[96]: *a*) $SbNbO_4$; *b*) $SbTaO_4$.

Combined studies of single-crystalline ceramic specimens of ABO_4 showed[94,96,98] that the Curie point lies at temperatures higher than thought earlier, namely T_C = 600°C for $SbNbO_4$, 605°C for $SbTaO_4$. Below the Curie point they have an antiferromagnetic phase, but Ivanova and coworkers[96] think that ferroelectric properties appear at 400–410°C. The compounds $BiNbO_4$ and $BiTaO_4$ are antiferroelectrics with T_C = 570°C.[98]

The existence of a spontaneously-polarised state in the compounds ABO_4 agrees with the appearance of pyro- and piezo-electric properties. The hydrostatic piezo-modulus d_h at room temperature is 8×10^6 cgse units for $SbNbO_4$. The combination of this d_h with low dielectric constant shows the high piezoelectric sensitivity of $SbNbO_4$ in relation to omnidirectional pressure[86].

In addition, the high resistance to heat and moisture, the chemical inertness, and the mechanical strength of the antimony and bismuth niobates and tantalates will facilitate their wide use in various branches of technology.

D. Niobates and Tantalates of the 3*d*-Metals

Among the niobates and tantalates of the 3*d*-metals, the dielectric properties of the Ti, V, Cr, and Fe orthotantalates[141] and orthoniobates[142] have been studied.

The temperature dependence of the electrical conductivity of $ATaO_4$ [141,143,144] and $FeNbO_4$ [145] has been investigated. All the compounds exhibit electron conductivity. An insignificant fraction of an ionic component appears only at 1000°C. The temperature dependence of the conductivity of the $ATaO_4$ is of a semiconductor nature[144].

It has also been shown that the $ANbO_4$ (where A is Ti, V, Cr, or Fe) are semiconductors with a narrow forbidden gap[142]. The mechanism for the establishment of electrical conductivity and its nature have been discussed from the standpoint of ideas about the formation of the chemical bond in the $ATaO_4$.[141,143] Study of the temperature dependence of the dielectric constant ϵ has shown that $TiTaO_4$, $VTaO_4$, $CrTaO_4$, and $FeTaO_4$ are ferroelectrics[141,146].

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Faculty of Chemistry,
Shevchenko Kiev State University