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Phase relations in ternary oxide systems of Group III and VB elements in a subsolidus region. Ternary oxide compounds

M G Zuev

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Abstract. Phase relations in the subsolidus region are considered for 54 ternary systems including $M_2O_3-V_2O_5-R_2O_5$, $Y_2O_3(La_2O_3, Sc_2O_3)-Nb_2O_5-Ta_2O_5$, $M_2O_3-B_2O_3-R_2O_5$, $M_2O_3-Ga_2O_3-R_2O_5$, $Al_2O_3-V_2O_5-R_2O_5$ (where M is a rare-earth element and R = Ta, Nb). The criteria determining the formation of ternary oxide compounds were found to include the cation sizes and the ratios between the radii of the ions constituting the anionic part of the compounds. The crystal-chemical characteristics are presented for MR_2VO_9, $LaRB_2O_7$, La_4VBO_{10}, Ln_7VBO_{17} (Ln = La, Pr, Nd), $La_3Ga_{5.5}R_{0.5}O_{14}$. The vibrational spectra of polycrystals of ternary compounds and solid solutions based on them are described in detail. The bibliography includes 154 references.

I. Introduction

One of the primary tasks of chemistry is the development and creation of new materials. Simple and complex oxides have found very wide use in many branches of industry. Synthesis of new materials based on complex oxides and the improvement of existing technologies for the production of these materials are based both on the study of the phase diagrams of oxide systems and on fundamental investigations into the 'composition – structure – properties' relationships.

Owing to the vast diversity of their properties, complex oxides of V, Ta, Nb and elements of the Group III of the Periodic Table are of special interest. For example, oxide crystals of Group III and VB elements are used as photo-, cathodo- and X-ray active luminophores. A topical task is the search for medical and luminescent materials that possess new spectroscopic parameters which might be expected among compounds of transition elements.

For instance, efficient tantalum-based X-ray active luminophores have acquired ever growing importance in recent years.[1–3] They possess higher specific density [$(7.5-9.7)\times10^3$ kg m^{-3}] than other X-ray active luminophores used in common practice and a number of other advantages allowing the production of intensifying X-ray screens with higher resolution and speed. This makes it possible to decrease significantly the radiation dose that affects the patients during X-ray examinations, a feature especially important for X-ray diagnostics of children.

Rare-earth element (REE) tantalates are crystals which efficiently absorb X-ray radiation with a quantum energy from 10 to 150 keV and are widely used in medicine. Complex tantalum-containing REE oxides are used as novel X-ray contrast agents (RCA) that are precipitated on body tissues and absorb X-ray radiation. This enhances contrast, which allows one to perform more accurate diagnostics at lower irradiation doses absorbed by the patient.[4–8] The physicochemical properties of these compounds have not been studied sufficiently yet. Studies of the phase diagrams of complex oxides and their solid solutions used as RCA will aid in filling this gap.

Compounds of the general formula MR_2VO_9 exist in ternary systems $M_2O_3-V_2O_5-R_2O_5$ (M = REE; R = Nb, Ta).[9] Based on these compounds, a new type of complex-oxide phosphor crystal has been developed. Synthesis of these compounds is accompanied by spontaneous formation of optical centres VO_4^{4-} owing to which the crystals of MR_2VO_9 possess narrow-band luminescence, predominantly in the red region of the spectrum. These phosphor crystals have an unusual temperature dependence of irradiation: the intensity of red luminescence of the centres increases on heating, whereas that of the support is quenched.[10] This effect contradicts the law of thermal luminescence quenching and has not been rationalised yet.

A physicochemical substantiation of the properties of complex oxides listed above requires primarily a detailed study of the regularities of their formation by considering phase relations in ternary systems. The types of phase diagram often vary for REE-containing systems:[11] purely eutectic systems exist in equilibrium with chemical compounds. In addition, one or several compounds can exist only for some of the elements rather than for the entire REE series. As a result, isostoichiometric series are formed which are grouped in complete or incomplete morphotropic and isostructural series. The change in the type of phase diagrams of ternary systems depending on the nature of the REE is shown below.

The purpose of this review is to generalise data on the phase relations in ternary † oxide systems of Group III and VB elements

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† The phase composition of restriction-type binary systems, *viz.*, $M_2O_3-R_2O_5$ (M = B, Al, La, Y, Sc, Ln; R = Ta, Nb, V), $M_2O_3-B_2O_3$ (M = La, Y, Sc, Ln,), $La_2O_3-Ga_2O_3$, $V_2O_5-R_2O_5$ (R = Ta, Nb), $Ta_2O_5-Nb_2O_5$, as well as the chemistry of the compounds formed from them have been described in detail elsewhere.[12–82]

in a subsolidus region, to reveal the regularities of the formation of ternary oxide systems and to analyse their vibration spectra. The vibration spectra not only provide information on the structure of the crystal lattices of ternary compounds but also make it possible to predict the luminescent properties of phosphor crystals. Based on the analysis of vibration spectra with the use of the concept of elementary lattice excitations (phonons), one can make conclusions on the filling of the energy gaps between the excited states of optical centres and describe the processes responsible for the excitation energy transfer in phosphor crystals.

II. Phase relations in $M_2O_3-V_2O_5-Ta_2O_5$ systems (M = REE)

Figure 1‡ shows phase relations in tantalum-containing $M_2O_3-V_2O_5-Ta_2O_5$ systems in a subsolidus region up to 1200 °C.[83–98] For each REE, ternary oxides with the composition MTa_2VO_9 (henceforth referred to as vanadatotantalates) were found in these systems. When a mixture of the starting compounds is heated, thermodynamic equilibrium is established faster the higher the temperature. Under isothermal sintering conditions at temperatures > 1100 °C, the $M_2O_3-V_2O_5$ systems are equilibrated in 6–8 h, while the $M_2O_3-Ta_2O_5$ systems require 30–70 h (for comparison: the equilibrium in the $M_2O_3-Ta_2O_5$ system at 900 °C is established in > 100 h). It takes more than 10 h to equilibrate the $V_2O_5-Ta_2O_5$ system.[18,44] Equilibration of the ternary systems $M_2O_3-V_2O_5-Ta_2O_5$ takes approximately the same time as that of the $M_2O_3-Ta_2O_5$ systems.[9] Vanadatotantalates decompose above 1200 °C to give the corresponding REE metatantalates and an unknown phase.[86] In a subsolidus region, all compounds of the ternary system are stable. The difference in triangulation depends only on the existence of certain binary compounds in the $M_2O_3-V_2O_5$ (up to 50 mol. % M_2O_3) and $M_2O_3-Ta_2O_5$ systems (50 mol. % – 100 mol. % Ta_2O_5).

According to the data of laser radiation second harmonics generation (SHG) measurements, ternary oxides of scandium and cerium subgroup elements can be assigned centrosymmetrical crystals.[9] X-Ray diffraction data[9] suggest that the structures of MTa_2VO_9 (M = La, Y, Pr, Nd, Sm, Eu) are close to those of the corresponding tantalates MTa_7O_{19} which possess hexagonal symmetry. For this reason, solid solutions can be formed in the $MTa_2VO_9-MTa_7O_{19}$ system. Table 1 lists the unit cell parameters for MTa_2VO_9 crystals. It should be noted that YTa_2VO_9 has two crystal modifications conventionally designated as α and β. The α modification is structurally similar to $LaTa_2VO_9$, while the β modification is similar to $ScTa_2VO_9$.

‡ Hereinafter, isothermal sections are shown in the phase diagrams.

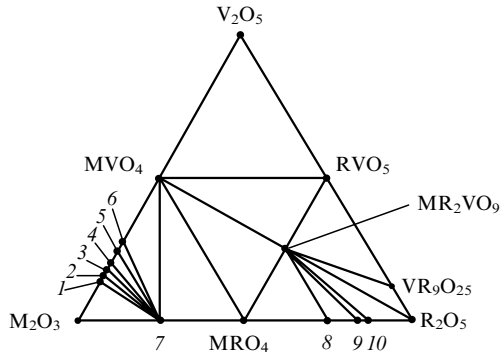


Figure 1. Phase relations in the $M_2O_3-V_2O_5-R_2O_5$ systems (M = REE, R = Ta, Nb).
(*1*) $M_{12}V_2O_{23}$ (M = Pr, Nd); (*2*) M_5VO_{10} (M = Y, Sm, Eu, Er); (*3*) $M_{1.62}V_{0.38}O_{3.38}$ (M = La, Nd, Eu, Gd, Tb), (*4*) $M_8V_2O_{17}$ (M = Y, La, Ce–Eu, Dy–Yb); (*5*) M_3VO_7 (M = La, Nd, Eu); (*6*) $La_{1.42}V_{0.58}O_{3.58}$; (*7*) M_3RO_7 (R = Ta, M ≠ Ce; R = Nb, M ≠ Sc, Ce); (*8*) MR_3O_9 (R = Ta, M ≠ Sc; R = Nb, M = La–Sm); (*9*) MR_5O_{14} (R = Ta, M = La, Ce; R = Nb, M = La–Nd, Er); (*10*) MR_7O_{19} (R = Ta, M ≠ Sc, Yb, Lu; R = Nb, M = La, Ce).

Table 1. Unit cell parameters of hexagonal crystals of MTa_2VO_9.

M	a[a] /nm	c[a] /nm	V /nm^3
La	0.6231	1.9573	0.658
Ce	0.6152	0.9932	0.653
Pr	0.6124	1.9831	0.643
Nd	0.6143	1.9864	0.648
Sm	0.6192	1.9723	0.654
Eu	0.6121	1.9812	0.643
Y[b]	0.6189	1.9831	0.655

[a] The error of determination is ±0.0005 nm. [b] The α-YTa_2VO_9 phase.

The structures of vanadatotantalates of scandium and yttrium subgroup elements differ from those of compounds of cerium subgroup elements. The structure of MTa_2VO_9 crystals has not been determined yet.

One can see from Table 1 that the parameters a and c and the unit cell volumes of vanadatotantalates do not depend linearly on the lanthanide ionic radii, as opposed to simple tantalates[99] and mixed-cation compounds.[100] It is believed[99] that the decrease in the unit cell parameters of tantalates with the decrease in the REE ionic radii can be explained by a decrease in the degree of covalence of the M–O bond, which changes essentially along the series from scandium to yttrium, lanthanum and from cerium to lutetium. Evidently, other factors are important in the case of vanadatotantalates.

It is well known that REE compounds display periodicity of structural and structure-dependent properties. These properties change non-monotonically for several reasons; the major of these include the energetic and spatial deepening of orbitals, the alteration of the type of exchange interactions between unpaired electrons, spin-orbital stabilisation, the nepheloauxetic effect and the stabilising effect of the crystal field.[11]

Table 1 shows that praseodymium and europium vanadatotantalates have the smallest parameters a and unit cell volumes. Hence, it can be assumed that an additional decrease in the energy of the 4f orbitals occurs in $PrTa_2VO_9$ and $EuTa_2VO_9$ due to spin-orbital interaction. This affects the contribution of the f orbitals to the formation of chemical bonds and probably the shape of the coordination polyhedra of these compounds. It is noteworthy that there is a small 'gadolinium' inflexion of a values for $LnTa_7O_{19}$ crystals (Ln = Ce–Lu).[101]

No sharp changes in the X-ray diffraction parameters are observed in the series $LnTa_2VO_9$ (Ln = Gd–Lu). These crystals are isostructural, which is corroborated by the data from vibrational spectra (see Section VI).

Some crystal-chemical features of vanadatotantalates were established using NMR spectroscopy.[83] In particular, the type of coordination polyhedra formed by oxygen around the vanadium ions was determined. The spectra were assigned using NMR data for known compounds.[102–106] The spectra for a sample of YTa_2VO_9 were recorded at frequencies of 105.2 and 78.86 MHz without and with magic-angle spinning (MAS). The spectrum consisted of a single line. The magic-angle spinning enabled fairly accurate determination of the isotropic shift. The MAS spectra recorded at two operating frequencies of the spectrometer display quadrupole splitting of the central transition. Figure 2 (curve *1*) shows a ^{51}V NMR spectrum for YTa_2VO_9 measured at 78.86 MHz without consideration of the quadrupole correction $\delta_{iso} = -665\pm2$. The small anisotropy of the chemical shift and the value of δ_{iso} indicate that the vanadium atom is located in an almost regular tetrahedral environment. According to data reported elsewhere,[107] the insignificant distortion of the tetrahe-

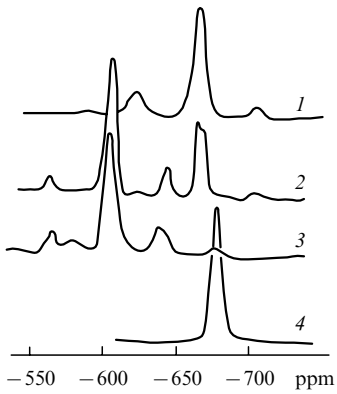


Figure 2. ^{51}V NMR spectra of YTa_2VO_9 (*1*), YNb_2VO_9 (*2*), $ScNb_2VO_9$ (*3*), La_4VBO_{10} (*4*).

dron can suggest that one of its oxygen atoms simultaneously belongs to an adjacent VO_4 tetrahedron. The NMR spectrum of the vanadatotantalate $GdTa_2VO_9$ could not be recorded, probably due to quadrupole effects resulting in line broadening.

Thus, it is possible to distinguish a full isostoichiometric series in the $LnTa_2VO_9$ class of compounds (where Ln indicates lanthanides) existing at normal temperature and pressure. However, this is not a full isostructural series: for Ln = Gd, there is a morphotropic transition from one structural type ($LnTa_7O_{19}$) for Ln = Y, La – Eu to another one for Ln = Gd – Lu.

III. Phase relations in the systems $M_2O_3-V_2O_5-Nb_2O_5$ (M = REE) and Y_2O_3 (La_2O_3, Sc_2O_3) – $Nb_2O_5-Ta_2O_5$

Figure 1 shows phase relations in the $M_2O_3-V_2O_5-Nb_2O_5$ systems in the subsolidus region up to 1100 °C (for M = Sc, up to 1000 °C).[83, 89, 94, 108–114] Compounds with the composition MNb_2VO_9 (henceforth referred to as vanadatoniobates) were found in ternary systems for every M.

Under isothermal annealing conditions at temperatures > 900 °C, the time required to establish equilibria in the $M_2O_3-Nb_2O_5$ and $V_2O_5-Nb_2O_5$ systems is the same as in the corresponding tantalum-containing systems. Ternary $M_2O_3-V_2O_5-Nb_2O_5$ systems come to equilibrium in 30 – 70 h.[9] Vanadatoniobates decompose above 1150 °C to give ortho- (Sc, Y) and metaniobates (La, Ln) and an unknown phase.[86] In the subsolidus region, all compounds of the ternary systems are stable.

The structure of vanadatoniobates has not been determined yet. According to SHG measurements, Sc, Y and La vanadatoniobates are centrosymmetrical crystals. It follows from comparison of the X-ray diffraction characteristics of MTa_2VO_9 and MNb_2VO_9 (M = Sc, Y, La) that $ScTa_2O_9$ and $ScNb_2O_9$ are isostructural; the structures of vanadatoniobates YNb_2VO_9 and $LaNb_2VO_9$ differ from each other and from those of vanadatotantalates YTa_2VO_9 and $LaTa_2VO_9$, respectively.

The structure of vanadatoniobates formed by cerium subgroup lanthanides differs from that of the corresponding vanadatotantalates. Within the series $LnNb_2VO_9$ (Ln = Ce – Eu), the structures of $PrNb_2VO_9$ and $NdNb_2VO_9$ are similar and differ from the structures of $CeNb_2VO_9$, $SmNb_2VO_9$ and $EuNb_2VO_9$, which have similar lattice symmetry. Probably, as in vanadatotantalates of cerium subgroup elements, the additional decrease in the energy of the *f* orbitals participating in the chemical bonds in vanadatoniobates of the elements of this subgroup affects the shape of the coordination polyhedra of the crystals.

The structure of vanadatoniobates of yttrium subgroup elements has some specific features. In the X-ray diffraction patterns of compounds in the series Gd – Lu, the interplanar distance (*d*) between the most intense reflexions decreases from 0.359 [relative intensity (I/I_0) 69%] to 0.354 nm (relative intensity 68%) in the case of $GdNb_2VO_9$ and to 0.350 (relative intensity 100%) in the case of $EuNb_2VO_9$. For $TmNb_2VO_9$, $YbNb_2VO_9$ and $LuNb_2VO_9$, only one reflexion with 100% intensity and $d = 0.351$ nm is observed. Thus, the vanadatoniobates $LnNb_2VO_9$, where Ln = Gd, Tb, Dy, Ho, Er, are isostructural, and the structures differ from those of compounds with Ln = Tm, Yb, Lu. This behaviour is probably determined by the Ln^{3+} ionic radius and the degree of covalency of the Ln – O bond. It should be noted that the structures of the cerium- and yttrium-subgroup compounds are different. The type of coordination polyhedron of the vanadatoniobate lattice was determined using NMR spectroscopy (see Fig. 2, curves *2*,*3*).[83] In polycrystals of YNb_2VO_9, the V^{5+} ions occupy two non-equivalent crystallographic positions. The isotropic shifts δ_{iso1} and δ_{iso2} are -665 ± 2 and -604 ± 2, respectively, without the quadrupole correction. The small anisotropy and the magnitudes of the isotropic shifts suggest that the vanadium atom is located in an almost regular tetrahedral environment and can have one common atom with the adjacent VO_4 tetrahedron. It is of note that compounds YNb_2VO_9 and YTa_2VO_9 are not isostructural but have almost similar tetrahedral environments with $\delta_{iso} = -665$.

Two lines are observed in the ^{51}V NMR spectrum of $ScNb_2VO_9$. The use of the MAS technique made it possible to determine the isotropic shifts for these lines: -581 ± 5 (line *I*) and -603 ± 2 (line *II*). The presence of two lines in the spectrum suggests that the lattice contains two non-equivalent vanadium ions. The shape of line I implies an axial anisotropy of the chemical shift tensor equal to $\delta_\perp = -350$, whereas line *II* is almost symmetrical. The magnitude of anisotropy, its type and the magnitude of the isotropic shift make it possible to assume that line *I* belongs to the vanadium ions in a distorted octahedral environment, while line *II* belongs to the vanadium ions in a slightly distorted tetrahedral environment. The tetrahedral environments in $ScNb_2VO_9$ and in YNb_2VO_9 ($\delta_{iso} = -604$) are almost the same. In the vanadatoniobate $ScNb_2VO_9$, the VO_4 tetrahedra are linked to each other through one common oxygen atom. The reason for distortion of the VO_6 octahedra is that each VO_6 octahedron has two common oxygen atoms with the adjacent octahedron.[107]

Based on the X-ray diffraction characteristics obtained for $LnNb_2VO_9$ (Ln = REE), it can be stated that this isostoichiometric series of compounds is not a full isostructural series. Five different structure types exist in the series of $LnNb_2VO_4$ vanadatoniobates: the first one for Ln = La, the second one for Ln = Pr and Nd, the third one for Ln = Ce, Sm and Eu, the fourth one for Ln = Gd, Tb, Dy, Ho, Er and the fifth one for Ln = Tm, Yb and Lu. Thus, a morphotropy phenomenon is observed.

The $Y_2O_3-Nb_2O_5-Ta_2O_5$ system.[115] Figure 3 presents phase relations in the $Y_2O_3-Nb_2O_5-Ta_2O_5$ system in a subsoli-

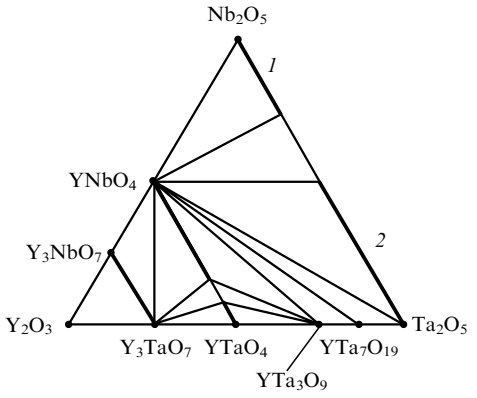


Figure 3. Phase relations in the $Y_2O_3-Nb_2O_5-Ta_2O_5$ system. (*1*) α-$Nb_{2(1-x)}Ta_{2x}O_5$; (*2*) β-$Ta_{2(1-x)}Nb_{2x}O_5$.

dus region up to 1350 °C. Solid solutions in this system were studied by optical-immersion analysis. A continuous series of solid solutions with the compositions $Y_3Nb_xTa_{1-x}O_7$ with a probable structure of the pyrochlore type was found in the quasibinary section $Y_3TaO_7-Y_3NbO_7$, and solid solutions of two types were found in the quasibinary section $YTaO_4-YNbO_4$. The first type has the composition $YNb_xTa_{1-x}O_4$ and is based on the fergusonite M′-modification in the concentration range $0 \leqslant x \leqslant 0.15$, while the second type has the same composition and is based on the fergusonite M-modification in the concentration range $0.3 \leqslant x \leqslant 1$. A mixture of solid solutions of the first and second types is formed in the intermediate region, *viz*., $0.15 < x < 0.3$. Above 1400 °C, a continuous series of solid solutions with M-fergusonite structure exists in this section.

The $La_2O_3-Nb_2O_5-Ta_2O_5$ system.[116] In order to determine the location of the quasibinary sections and to perform the triangulation of the $La_2O_3-Nb_2O_5-Ta_2O_5$ system, physicochemical analysis was used to study the phase composition of 30 points located in various hypothetical sections and regions of the system. Figure 4 presents phase relations in the $La_2O_3-Nb_2O_5-Ta_2O_5$ system in a subsolidus region up to 1250 °C. Various solid substitution solutions were found in the region containing more than 50 mol. % La_2O_3. The hatched regions *1* and *2* contain solid solutions based on $LaNbO_4$ and La_3NbO_7, respectively. In addition, a limited series of solid solutions of the general formula $LaTa_{1-x}Nb_xO_4$ ($0 \leqslant x \leqslant 0.15$) based on $LaTaO_4$ was found in the $LaNbO_4-LaTaO_4$ section. A continuous series of solid solutions of the general formula $La_3Nb_{1-y}Ta_yO_7$ ($0 \leqslant y \leqslant 1$) exists in the $La_3NbO_7-La_3TaO_7$ section.

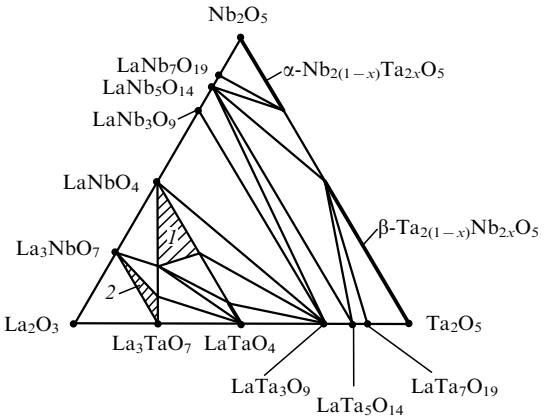


Figure 4. Phase relations in the $La_2O_3-Nb_2O_5-Ta_2O_5$ system. The hatched zones indicate the areas of existence of solid solutions based on $LaNbO_4$ (*1*) and La_3NbO_7 (*2*).

The $Sc_2O_3-Nb_2O_5-Ta_2O_5$ system.§ The phase composition of the system was studied up to 1400 °C; no ternary compounds were found (Fig. 5). A continuous series of solid substitution solutions of the general formula $ScTa_{1-x}Nb_xO_4$ with the wolframite structure exists in the quasibinary section $ScNbO_4-ScTaO_4$.

§ The system was studied by E V Arkhipova (Institute of Solid State Chemistry of the Urals Branch of the Russian Academy of Sciences).

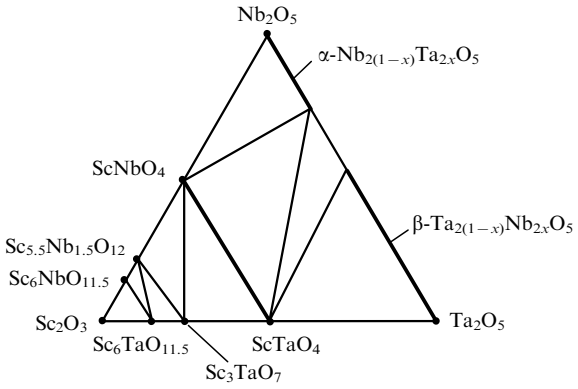


Figure 5. Phase relations in the $Sc_2O_3-Nb_2O_5-Ta_2O_5$ system.

IV. Phase relations in systems containing B, Al and Ga

The $M_2O_3-B_2O_3-Ta_2O_5$ systems.[83, 117–119] Figure 6 *a*,*b* presents phase relations in the $Sc_2O_3-B_2O_3-Ta_2O_5$ and $Y_2O_3-B_2O_3-Ta_2O_5$ systems in a subsolidus region up to 1100 °C. No ternary compounds were found in these systems.

Figure 7 demonstrates phase relations in the $La_2O_3-B_2O_3-Ta_2O_5$ system in a subsolidus region up to 1000 °C. A ternary compound with the composition $LaTaB_2O_7$, which exists in

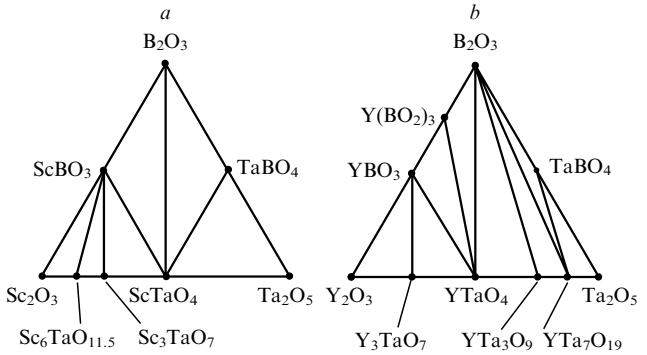


Figure 6. Phase relations in the $Sc_2O_3-B_2O_3-Ta_2O_5$ (*a*) and $Y_2O_3-B_2O_3-Ta_2O_5$ (*b*) systems.

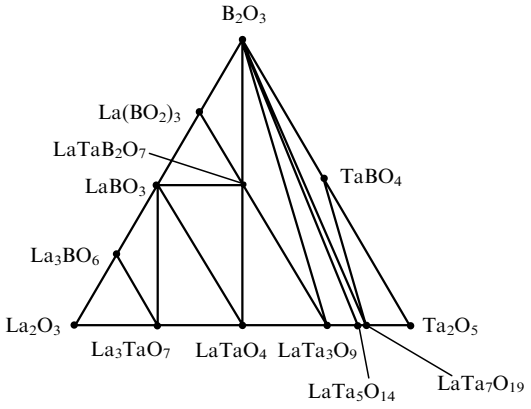


Figure 7. Phase relations in the $La_2O_3-B_2O_3-Ta_2O_5$ system.

equilibrium with $LaBO_3$, $La(BO_2)_3$, B_2O_3, $LaTa_3O_9$ and $LaTaO_4$, was found in the quasibinary section $La(BO_2)_3 - LaTa_3O_9$. Lanthanum boratotantalate decomposes at $\sim$ 1200 °C in accordance with the peritectic reaction

$$LaTaB_2O_7 = LaTaO_4 + B_2O_3.$$

In the $M_2O_3 - B_2O_3$ systems, thermodynamic equilibrium at temperatures above 1000 °C is established in several tens of hours.[66] The time required to reach equilibrium in ternary systems is even longer, *viz*., $\sim$ 200 h.[9] All phases of the systems described above are stable in a subsolidus region.

According to SHG laser irradiation measurements, lanthanum boratotantalate has centrosymmetrical crystals. X-Ray diffraction studies suggest that it has orthorhombic symmetry. The unit cell parameters *a*, *b* and *c* for $LaTaB_2O_7$ are 1.28692, 1.17562 and 1.13692 nm, respectively; the unit cell volume is 1.72004 nm^3; the number of formula units in the lattice (*z*) is 14; the picnometric density is 6.16×10^3 kg m^{-3}.

The coordination of boron in these crystals was studied by NMR spectroscopy.[120] Figure 8 shows the ^{11}B NMR spectrum of the boratotantalate $LaTaB_2O_7$ (relative to aqueous H_3BO_3, magic-angle spinning). The spectrum is a superposition of two doublet components ($\delta - 7.96$ and -21.59) and a narrow central peak ($\delta - 16.53$). The assignment was made using the known literature data (see, *e.g*., Ref. 121). It was found that the doublet belongs to the boron nuclei located in a trigonal oxygen environment (the quadrupole coupling constant is 2.5 MHz), while the narrow line belongs to the boron nuclei in a tetrahedral environment. It should be noted that the central component in the spectra is shifted by 7 ppm, and the doublet is shifted by 14 ppm with respect to diamagnetic compounds. This is probably caused by paramagnetic admixtures in the samples.

The ternary $M_2O_3 - B_2O_3 - Ta_2O_5$ systems with the following lanthanides were studied: cerium, praseodymium, neodymium, samarium and europium.[122, 123] No ternary compounds were found in these systems. Figure 9 *a*,*b* presents phase relations in these systems in a subsolidus region up to 1000 °C. It is seen that borates are in equilibrium with lanthanide tantalates.

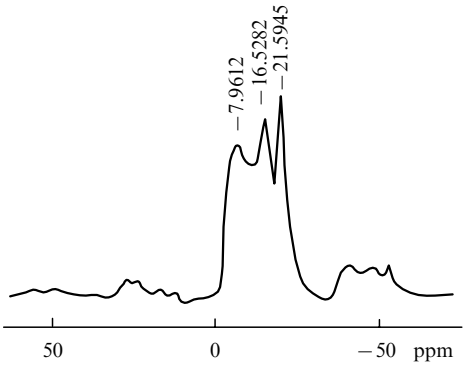


Figure 8. ^{11}B NMR spectrum of boratotantalate $LaTaB_2O_7$.

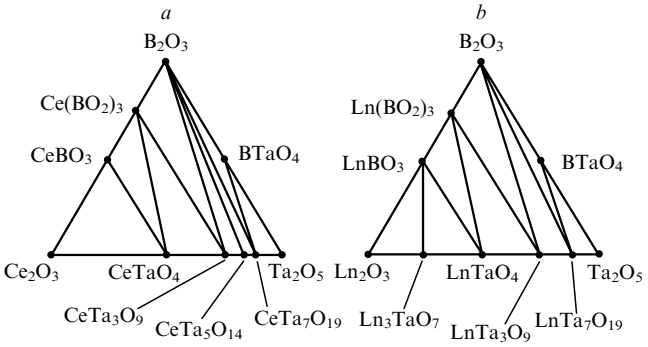


Figure 9. Phase relations in the $Ce_2O_3 - B_2O_3 - Ta_2O_5$ (*a*) and $Ln_2O_3 - B_2O_3 - Ta_2O_5$ (Ln = Pr, Nd, Sm, Eu) (*b*) systems.

The $M_2O_3 - B_2O_3 - Nb_2O_5$ systems.[83, 118, 119] These systems, where M = REE, are similar to the corresponding tantalum-containing ternary systems in many respects. The equilibrium in these systems is also established in $\sim$ 200 h.[9] No ternary compounds were found in the $Sc_2O_3 - B_2O_3 - Nb_2O_5$ and $Y_2O_3 - B_2O_3 - Nb_2O_5$ systems, the phase relations in which in a subsolidus region up to 1000 °C are presented in Fig. 10 *a*,*b*.

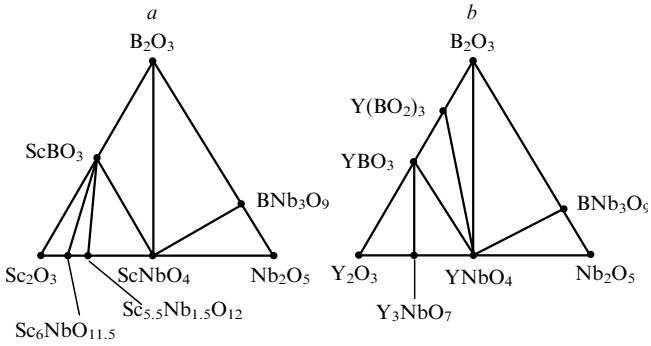


Figure 10. Phase relations in the $Sc_2O_3 - B_2O_3 - Nb_2O_5$ (*a*) and $Y_2O_3 - B_2O_3 - Nb_2O_5$ (*b*) systems.

More complex phase relations are observed in the $La_2O_3 - B_2O_3 - Nb_2O_5$ system.[117, 119] The ternary compound $LaNbB_2O_7$ is formed in this system; this compound exists in equilibrium with $LaNbO_4$, $LaNb_3O_9$, $LaBO_3$, $La(BO_2)_3$ and B_2O_3. The boratoniobate $LaNbB_2O_7$ is isostructural to the boratotantalate $LaTaB_2O_7$. It decomposes peritectically above 1200 °C to give $LaNbO_4$ and B_2O_3. Figure 11 shows phase relations in this system in a subsolidus region up to 1000 °C. The unit cell parameters *a*, *b* and *c* of $LaNbB_2O_7$ are 1.2771(5), 1.1722(5) and 1.1223(5) nm; the unit cell volume is 1.679231 nm^3.

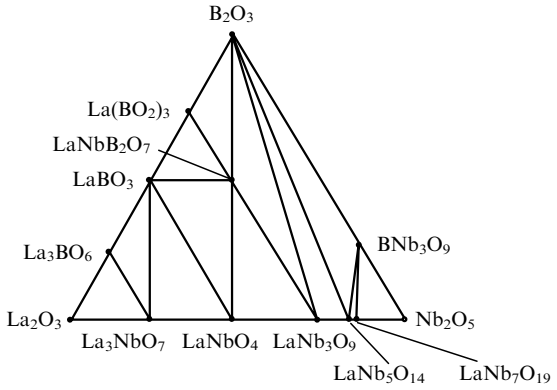


Figure 11. Phase relations in the $La_2O_3 - B_2O_3 - Nb_2O_5$ system.

The $M_2O_3 - B_2O_3 - V_2O_5$ systems. The equilibrium in these systems is established in more than 800 h,[9] which is much longer than in the $M_2O_3 - B_2O_3 - R_2O_5$ systems (R = Ta, Nb).

Figure 12 demonstrates phase relations in the $Y_2O_3 - B_2O_3 - V_2O_5$ system in a subsolidus region up to 1000 °C. No ternary compounds were found in this system.[124]

Figure 13 presents phase relations in the $La_2O_3 - B_2O_3 - V_2O_5$ system in a subsolidus region up to 900 °C.[125] It was found that lanthanum orthovanadate is in equilibrium with all compounds of the binary systems $La_2O_3 - B_2O_3$ and $B_2O_3 - V_2O_5$ except La_3BO_6. A ternary compound with the composition La_4VBO_{10} is formed in this system in the region with high La_2O_3 content; this compound

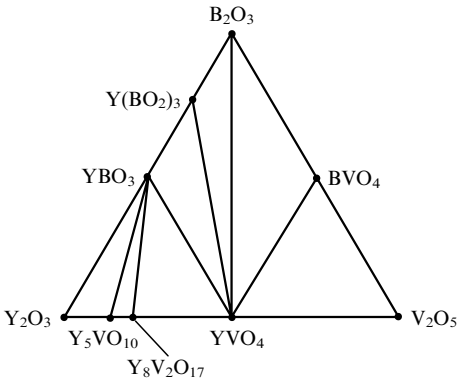


Figure 12. Phase relations in the $Y_2O_3-B_2O_3-V_2O_5$ system.

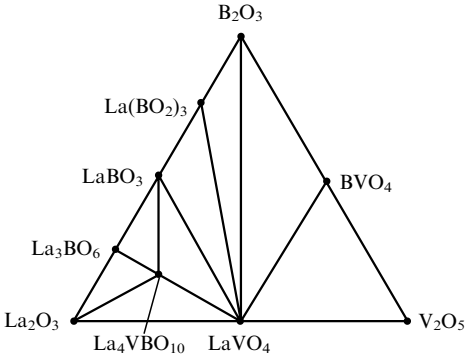


Figure 13. Phase relations in the $La_2O_3-B_2O_3-V_2O_5$ system.

is in equilibrium with La_2O_3, La_3BO_6, $LaBO_3$ and $LaVO_4$. The melting point of La_4VBO_{10} is unknown. According to SHG measurements, this compound has centrosymmetrical crystals.

Figure 2 (curve *4*) shows the ^{51}V NMR spectrum of La_4VBO_{10} polycrystals. The spectrum is a single line with $\delta_{iso} = -674$. The magnitude of the quadrupole correction indicates that vanadium is located in a nearly regular tetrahedral environment.[126] As in vanadatoniobates, the VO_4 tetrahedra can have one common oxygen atom with the adjacent tetrahedra. The signal of the boron nuclei is very weak, probably due to quadrupole effects.

Hence, $LaTaB_2O_7$, $LaNbB_2O_7$ and La_4VBO_{10} are merely the first members of the corresponding isostoichiometric series under ordinary conditions. An attempt to obtain compounds of scandium, yttrium and lanthanides with compositions indicated above failed.[83]

Gokhman *et al.*[127] synthesised ternary oxides with the composition $Ln_7V_2BO_{17}$ (Ln = La, Pr, Nd). The samples were obtained in air by multi-step sintering of the starting oxides Ln_2O_3, V_2O_5 and H_3BO_3. The temperature of the final sintering step was 1240 °C; the overall sintering time was 30 h. The melting points of the compounds are unknown. Ternary oxides for Ln = Sm, Eu, Gd and Tb could not be obtained. Table 2 lists the unit cell parameters for the crystals of $Ln_7V_2BO_{17}$, which possess monoclinic symmetry.

Table 2. Unit cell parameters of $Ln_7V_2BO_{17}$ crystals.

Ln	*a* /nm	*b*/nm	*c*/nm	*β* /deg	*V* /nm^3
La	0.695(1)	1.786(1)	1.227(1)	99.6(1)	1.501(2)
Pr	0.687(1)	1.747(7)	1.205(3)	99.7(3)	1.425(7)
Nd	0.680(1)	1.723(2)	1.205(1)	99.4(1)	1.392(2)

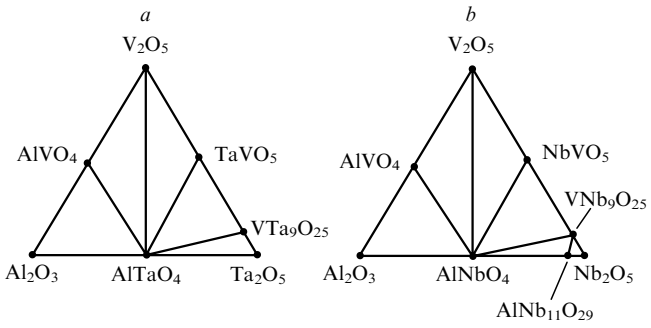


Figure 14. Phase relations in the $Al_2O_3-V_2O_5-Ta_2O_5$ (*a*) and $Al_2O_3-V_2O_5-Nb_2O_5$ (*b*) systems.

The $Al_2O_3-V_2O_5-R_2O_5$ systems. Figure 14 *a* shows phase relations in the $Al_2O_3-V_2O_5-Ta_2O_5$ system in a subsolidus region up to 1350 °C, and Fig. 14 *b* shows phase relations in the $Al_2O_3-V_2O_5-Nb_2O_5$ system in a subsolidus region up to 1100 °C. The times required to establish equilibria in these systems are the same as those for $M_2O_3-V_2O_5-R_2O_5$ (M = REE, R = Ta, Nb). No ternary compounds were found in these systems.[9, 128–130]

It was found that the $AlTaO_4$ phase has two crystal modifications in the section $AlTaO_4-V_2O_5$ (see Fig. 14 *a*). In the vicinity of the section point where the concentrations of the components, *i.e.*, Al_2O_3, V_2O_5 and Ta_2O_5, are 38 mol.%, 24 mol.% and 38 mol.%, respectively, the $AlTaO_4$ crystals are isostructural to alumotantite (its formula is $Al_{0.98}Ta_{0.99}Nb_{0.02}O_4$) with orthorhombic symmetry.[131] In the other points of this section studied, the $AlTaO_4$ crystals have a structure different from that of alumotantite.[132] It should also be noted that for all points of this section containing less than 50 mol. % V_2O_5 (except for the point specified above), the diffractograms of freshly prepared $AlTaO_4$ samples recorded at room temperature contain additional lines. These lines disappear after storage of the samples in air for a month. These reflexions probably originate from structural ordering of $AlTaO_4$ crystals with involvement of lattice defects.

The $AlNbO_4$ structure is described in the database of X-ray spectra.[133]

The $M_2O_3-Ga_2O_3-Nb_2O_5$ (Ta_2O_5) systems (M = La, Pr).[42] The isothermal sections in these systems have not been studied. It was found that the $La_2O_3-Ga_2O_3-Nb_2O_5$ system contains a ternary compound with the composition $La_3Ga_{5.5}Nb_{0.5}O_{14}$ having the structure of $Ca_3Ga_2Ge_4O_{14}$ ($a = 0.8218$ nm, $c = 0.5122$ nm; the densities obtained from X-ray estimation and from experimental measurement are 5.934×10^3 and 5.903×10^3 kg m^{-3}, respectively). The compound has a narrow homogeneity range and is stable up to 1450 °C.

The compound $La_3Ga_{5.5}Ta_{0.5}O_{14}$ ($a = 0.8151$ nm, $c = 0.5105$ nm) is formed in the $La_2O_3-Ga_2O_3-Ta_2O_5$ system, and the compounds $Pr_3Ga_{5.5}Nb(Ta)_{0.5}O_{14}$ exist in the $Pr_2O_3-Ga_2O_3-Nb_2O_5$ (Ta_2O_5) systems. Starting with M = Nd, no similar compounds isostructural to $Ca_3Ga_2Ge_4O_{14}$ are formed.

V. Phase formation regularities in ternary systems

It follows from the experimental phase relation diagrams that vanadatoniobates MNb_2VO_9 exist in equilibrium preferentially with compounds which have the structural type of fergusonite, perovskite, zircon, wolframite ($ScNbO_4$) and with compounds α-$LaNb_5O_{14}$ and MNb_7O_{19} (M = La, Ce). Vanadatotantalates MTa_2VO_9 coexist with such compounds as fergusonite, perovskite, wolframite ($ScTaO_4$), $LaTaO_4$, MTa_5O_{14} (M = La, Ce) and with compounds of hexagonal symmetry such as MTa_7O_{19}. All vanadatotantalates and -niobates exist in equilibrium with tetragonal phases such as VR_9O_{25} and RVO_5 (R = Ta, Nb). Lanthanum boratotantalate and -niobate $LaRB_2O_7$ (R = Ta, Nb) coexist

Table 3. Ionic sizes (Ref. 134) of Group III and VB elements and ratios of ionic radii.

Ion (1) [a]	Radius (r_1) /nm	Ion (2) [a]	Radius (r_2) /nm	r_1/r_2
B^{3+} (3)	0.01	V^{5+} (4)	0.0355	~ 0.3
		Nb^{5+} (4)	0.048	~ 0.2
		Nb^{5+} (6)	0.064	~ 0.16
		Ta^{5+} (6)	0.064	~ 0.16
V^{5+} (4)	0.0355	Nb^{5+} (4)	0.048	~ 0.74
		Nb^{5+} (6)	0.064	~ 0.55
		Ta^{5+} (6)	0.064	~ 0.55
Ga^{3+}	0.047 – 0.062 [b]			

[a] The numbers in parentheses indicate the coordination numbers. [b] Values for different coordination numbers are given.

with such compounds as perovskite, aragonite, fergusonite, $LaRO_4$ and monoclinic $La(BO_2)_3$, whereas lanthanum boratovanadate La_4VBO_{10} coexists with such compounds as monazite, aragonite and monoclinic La_3BO_6. All ternary compounds described above exist in equilibrium with simple oxides R_2O_5 (R = Ta, Nb, V), B_2O_3, La_2O_3.

Solid solutions in the $Y_2O_3-Nb_2O_5-Ta_2O_5$ system coexist with such compounds as fergusonite, pyrochlore, perovskite, Y_2O_3, R_2O_5 (R = Ta, Nb); those in the $La_2O_3-Nb_2O_5-Ta_2O_5$ system coexist with such compounds as weberite, perovskite, $LaTaO_4$ and La_2O_3, and those in the $Sc_2O_3-Nb_2O_5-Ta_2O_5$ system coexist with such oxides as Sc_3TaO_7 and R_2O_5 (R = Nb, Ta).

Thus, it can be stated that ternary phases formed in systems of Group III and VB oxides (except for $La_2O_3-B_2O_3-V_2O_5$) exist in equilibrium with compounds that have the fergusonite and perovskite structural types and with compounds characteristic of each individual system.

It is well known that no theory formulating the phase formation criteria in complex systems exists at present. The phase formation in quasi-binary vanadate systems was analysed by estimation of cation radii and with the use of the spatial-energetical P parameter.[44]

Let us consider the regularities in the formation of mixed crystals for Group III and VB elements depending on the ion sizes and on the ionic radii ratios in ternary compounds (Table 3).

If the ratio of the ionic radius of boron to that of tantalum or niobium is ~ 0.2, no ternary compounds of lanthanides, scandium and yttrium are formed in the $M_2O_3-B_2O_3-Ta_2O_5$ (Nb_2O_5) systems (M = Sc, Y, Ce – Lu). The existence of the starting members of the series with M = La, *viz*., $LaTaB_2O_7$ and $LaNbB_2O_7$, can be explained by the fact that the radius of the La^{3+} ion is larger than those of scandium and lanthanides. In the $Al_2O_3-V_2O_5-Ta_2O_5$ (Nb_2O_5) systems, ternary compounds with hypothetical composition $Al_xTa(Nb)_yV_zO_k$ are not formed, either. Probably, the cation radii should also be taken into account in addition to the ionic radii ratios in the anionic parts of the compounds. The ion radius of Al^{3+} is 0.0390 to 0.0535 nm depending on the coordination number; it is smaller than the ion radii of scandium, yttrium, lanthanum and lanthanides. This is probably the reason why ternary compounds are not formed in the $Al_2O_3-V_2O_5-Ta_2O_5$ (Nb_2O_5) systems [unlike in the $M_2O_3-V_2O_5-Ta_2O_5$ (Nb_2O_5) systems (M = Sc, Y, La – Lu) where the MR_2VO_9 compounds exist]. In the $M_2O_3-B_2O_3-V_2O_5$ systems (M = La, Pr, Nd) at temperatures > 900 °C, the $M_7V_2BO_{17}$ compounds exist (see Ref. 127), whereas only one compound, namely, M_4VBO_{10} with M = La, was found at temperatures < 900 °C. Hence, one can probably expect the formation of compounds with molecular composition M_4VBO_{10} for M = Pr and Nd.

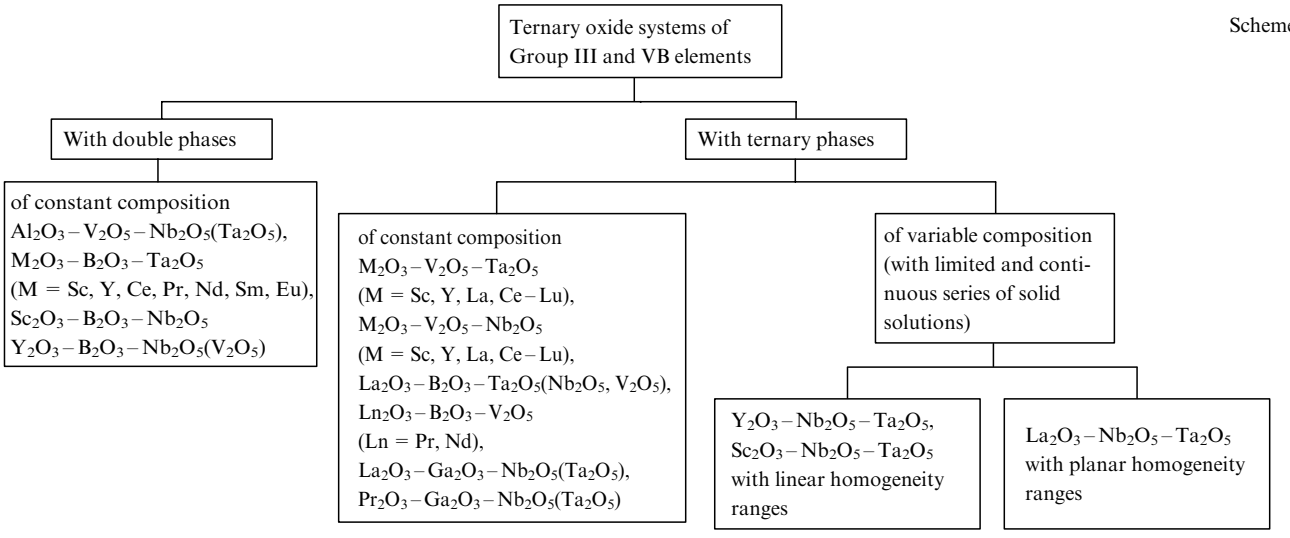
Table 4. Ratios of ionic radii in ternary compounds.

Compounds	M	Ion (1)	Ion (2)	r_1/r_2
MR_2VO_9 (R = Nb, Ta)	Sc, Y, La – Lu	V^{5+}	R^{5+}	0.55 – 0.74
MRB_2O_7 (R = Nb, Ta)	La	B^{3+}	R^{5+}	0.2
M_4VBO_{10}	La	B^{3+}	V^{5+}	0.3
$M_7V_2BO_{17}$	La, Pr, Nd	B^{3+}	V^{5+}	0.3
$M_3Ga_{5.5}R_{0.5}O_{14}$ (R = Nb, Ta)	La, Pr	Ga^{3+}	R^{5+}	0.97

Thus, the dimension-related criterion for the formation of ternary compounds in oxide systems includes two conditions: (1) the cation radius should be larger than 0.0535 nm; (2) the radii ratios for the ions forming the anionic parts should be greater than 0.2 but smaller than 1. It follows from the data in Table 4 that if the ionic radii ratio is $r_1/r_2 \approx 0.2$, ternary compounds exist only in the case of M = La, whereas if this ratio is 0.55 – 0.74, these exist in the case of M = Sc, Y, La – Lu. However, if the radius of the M ion is smaller than that of the Sc ion, ternary compounds are not formed for $r_1/r_2 = 0.55-0.74$ [where ion(1) = V^{5+}; ion(2) = Ta^{5+}, Nb^{5+}]. In the $M_2O_3-Nb_2O_5-Ta_2O_5$ systems, no ternary compounds with hypothetical composition $M_xNb_yTa_zO_r$ are formed either if $r_1/r_2 = 1$ and M = Sc, Y, La.

Thus, the following classification of ternary oxide systems of Group III and VB elements can be made: (1) systems with an equilibrium between the original components and binary compounds; (2) systems where ternary phases are formed. In turn,

Scheme 1



ternary phases can have a constant composition (chemical compounds) or a variable composition (solid solutions). The arbitrary character of this classification is due to the fact that constant composition phases always contain very narrow homogeneity regions which can be neglected. Scheme 1 shows the classification of ternary oxide systems; this classification can apparently be used to predict the existence of phase equilibria, *e.g.*, in the $Ln_2O_3-Nb_2O_5-Ta_2O_5$ and $Ln'_2O_3-Nb_2O_5-Ta_2O_5$ systems, where Ln and Ln′ are lanthanides belonging to the yttrium and cerium subgroups, respectively.

VI. Vibrational spectra of ternary oxides

Using NMR spectroscopy in MR_2VO_9 (R = Ta, Nb) and La_4VBO_{10} crystals, the VO_4 and VO_6 anionic groups were revealed; they are generally linked through one or two oxygen atoms with the adjacent VO_4 or VO_6 groups, respectively. The $LaTaB_2O_7$ crystals were shown to contain BO_3 triangles. Thus, one of the goals in the analysis of the vibrational spectra of ternary oxides is to determine whether the anionic part of a compound is a united complex anion or it consists of anionic groups.

1. MTa_2VO_9 crystals

The IR spectra of the MTa_2VO_9 crystals, where M indicates cerium subgroup elements, contain narrow intense bands in the range of 430–437 cm^{-1}, whereas the remaining bands in the spectrum are broad and have medium intensity. The band positions in the range of 600–900 cm^{-1} depend on the nature of the M^{3+} ion: the vibration frequencies are shifted to the long-wave region with a decrease in the ionic radii in the series Ce–Eu (Fig. 15). It is well known that a decrease in the ionic radius increases the covalence of bond between a lanthanide ion and the environment and enhances the effect of the crystal field,[11] hence these bands can originate from the stretching vibrations of the Ta–O bonds involving the M–O bonds. The shape of the IR spectra of MTa_2VO_9 crystals, where M indicates yttrium subgroup elements, depends on the nature of the metal and changes non-monotonically (Fig. 16).[88]

The most significant differences between the spectra of MTa_2VO_9, where M indicates yttrium and cerium subgroup elements, are observed in the region of 200–500 cm^{-1}, which probably corresponds to the deformation vibrations of the lattice polyhedra. The IR spectra of $LaTa_2VO_9$ (Fig. 17, spectrum *1*) and $ScTa_2VO_9$ (Fig. 17, spectrum *3*) are similar to the spectra of MTa_2VO_9, where M indicates yttrium and cerium subgroup elements, respectively. Replacement of 50% of yttrium in YTa_2VO_9 by europium stabilises the α-phase, and the IR spectrum of the solid solution $Y_{0.5}Eu_{0.5}Ta_2VO_9$ (Fig. 17, spectrum *2*) resembles that of $LaTa_2VO_9$. Tables 5–8 list the frequencies of vibrational spectrum maxima for compounds of the general formula MTa_2VO_9 (M = Sc, Y, La–Lu). The bands in the regions of 865–900, 790–835, 455–485 and 370–385 cm^{-1} can probably be assigned to the ν_1, ν_3, ν_4 and ν_2 vibrations of the VO_4 tetrahedra, respectively, while the bands in the regions of 910–930, 580–710 and 430–455 cm^{-1} can be assigned to the ν_1, ν_3 and ν_5 vibrations of the TaO_6 octahedra, respectively. Only the most intense lines in the Raman spectra of $LaTa_2VO_9$ and $TbTa_2VO_9$ were recorded.¶ The Raman spectra of the vanadatotantalates $CeTa_2VO_9$ and $ScTa_2VO_9$ could not be recorded, probably due to strong absorption of radiation.

The Raman spectra of MTa_2VO_9, where M = Pr, Nd, Sm, Eu, Gd, Dy, Tm, Yb, Lu, in the region of 780–1000 cm^{-1} are similar (Fig. 18–20): each of them contains an intense line at 855–900 cm^{-1} and two lines around 780–835 cm^{-1}. The differences between the spectra of the compounds containing cerium and yttrium subgroup elements are mostly observed in the range below 780 cm^{-1}. The Raman spectra of the vanadatotantalates $HoTa_2VO_9$ and $ErTa_2VO_9$ differ from those described above (see Fig. 19, spectra *2* and *3*). The spectrum of $HoTa_2VO_9$ was recorded using argon laser excitation (excitation with a helium–neon laser results in a weak vibrational spectrum at the background level). It contains a group of narrow high-intensity lines at

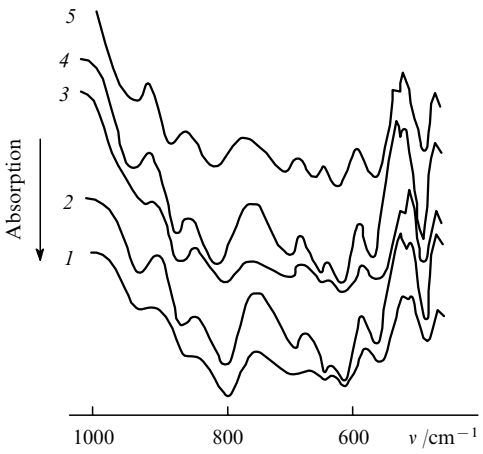


Figure 15. IR spectra of MTa_2VO_9, where M = Ce (*1*), Pr (*2*), Nd (*3*), Sm (*4*), Eu (*5*).

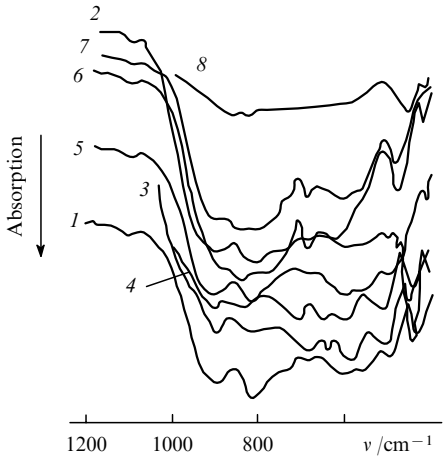


Figure 16. IR spectra of MTa_2VO_9, where M = Gd (*1*), Tb (*2*), Dy (*3*), Ho (*4*), Er (*5*), Tm (*6*), Yb (*7*), Lu (*8*).

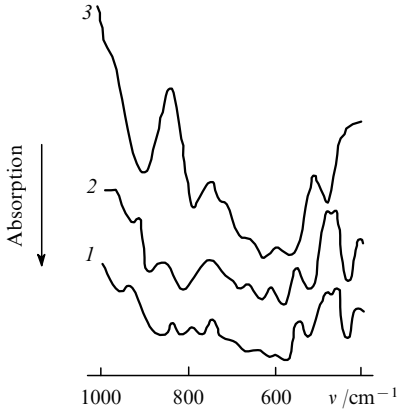


Figure 17. IR spectra of $LaTa_2VO_9$ (*1*), $Y_{0.5}Eu_{0.5}Ta_2VO_9$ (*2*) and $ScTa_2VO_9$ (*3*).

¶ All Raman spectra were recorded with excitation by a helium–neon laser (λ = 632.8 nm) unless stated otherwise.

Table 5. Frequencies (cm^{-1}) of maxima in vibrational spectra of MTa_2VO_9 (M = La, Ce, Pr, Nd).

La		Ce (IR)	Pr		Nd		Assignment
IR	Raman		IR	Raman	IR	Raman	
–	–	–	–	–	–	1150	stretching vibrations of VO_4, TaO_6, VO_6
–	–	–	–	990	–	990	
965	–	957	960	–	940	–	
885	–	–	885	890	884	–	
860	–	873	–	–	–	–	
–	870	–	–	855	–	870	
–	845	–	–	–	–	–	
826	–	800	802	820	802	–	
808	–	–	–	790	–	–	
–	–	–	–	780	–	795	
783	–	–	–	–	–	785	
–	–	–	–	750	–	760	
675	–	677	679	–	683	–	
–	–	–	–	650	–	–	
620	–	–	623	–	626	–	
–	–	618	–	–	–	610	
585	–	585	592	570	590	–	
525	–	520	530	530	527	535	deformation vibrations of VO_4, TaO_6, VO_6
475	–	467	469	–	472	–	
–	–	–	–	460	–	470	
440	435	431	437	–	437	450	
	380			420	–	–	
				370	–	370	
				–	360	–	
				350	–	350	
				305	–	305	v(M – O)
				290	270	–	
				250		245	
				225, 215, 180, 155, 110, 75, 70		225	translation and rotation of VO_4, VO_6

910, 930, 940(sh.), 985, 1000 and 1045 cm^{-1}. These lines may be due to resonance phenomena caused by diffusion of laser light near the $^5F_4$ state of the Ho^{3+} ion. The spectrum of $ErTa_2VO_9$

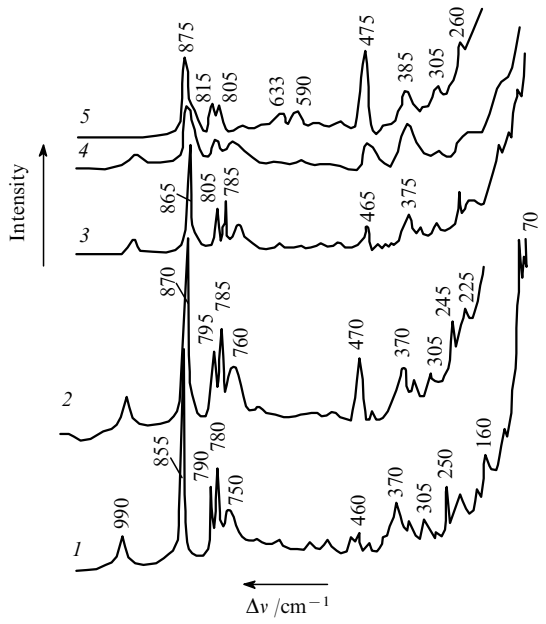


Figure 18. Raman spectra of MTa_2VO_9, where M = Pr (*1*), Nd (*2*), Sm (*3*), Eu (*4*), Gd (*5*).

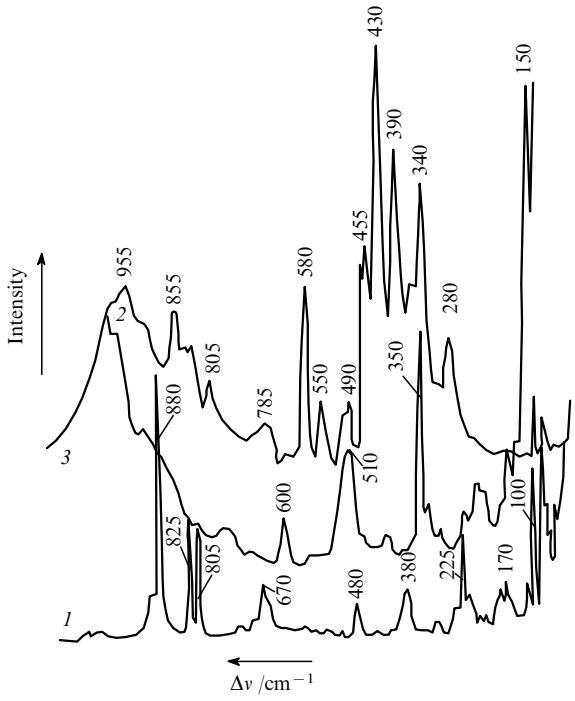


Figure 19. Raman spectra of MTa_2VO_9, where M = Dy (*1*), Ho (*2*), Er (*3*).

Table 6. Frequencies (cm^{-1}) of maxima in vibrational spectra of MTa_2VO_9 (M = Sm, Eu, Gd, Tb).

Sm		Eu		Gd		Tb		Assignment
IR	Raman	IR	Raman	IR	Raman	IR	Raman	
–	–	–	–	–	–	–	1080	stretching vibrations of VO_4, TaO_6, VO_6
–	990	–	990	–	–	–	–	
960	–	940	–	–	–	–	–	
887	–	884	–	895	–	895	–	
–	865	–	870	–	875	–	900	
–	845	–	–	–	840	–		
810	805	802	–	810	–	810		
–	790	–	825	–	815	–		
–	–	–	780	–	805	–		
–	–	–	–	–	770	–		
–	750	–	–	735(sh)	–	735		
682	675	683	690	680	670	681		
–	–	–	–	–	635	–		
627	625	626	–	–	–	–		
–	–	–	610	–	–	–		
590	580	590	560	595	590	590		
530	510	527	–	550	535	550		deformation vibrations of VO_4, TaO_6, VO_6
469	470	–	–	490	475	–		
–	445	–	485	–	–	490		
433	–	437	–	–	–			
398	415	398	–	400(sh)	–			
–	370	–	385	–	385			
360	–	362	–	364	–			
336	345	322	–	322	–			ν(M – O)
312	315	306	310	–	305			
	–	288	–	264	260			
	250	264	245					
	215, 160, 130, 110, 75		210, 150					translation and rotation of VO_4, VO_6

Table 7. Frequencies (cm^{-1}) of maxima in vibrational spectra of MTa_2VO_9 (M = Dy, Ho, Er, Tm).

Dy		Ho		Er		Tm		Assignment
IR	Raman	IR	Raman	IR	Raman	IR	Raman	
–	–	–	–	–	–	–	1010	stretching vibrations of VO_4, TaO_6, VO_6
–	–	–	–	–	985	–	–	
950(sh)	–	–	–	–	955	–	–	
–	–	–	–	–	930	–	–	
–	–	892	–	900	–	885	–	
–	–	–	890	–	895	–	–	
–	880	–	870	–	–	–	890	
–	–	–	–	–	855	–	–	
–	825	–	830	–	–	–	835	
820	–	824	–	–	845	840	–	
–	805	–	–	812	805	792	815	
–	–	–	760	–	785	–	–	
–	735	–	745	–	–	–	–	
–	–	–	730	–	–	–	–	
690	675	695	685	680	670	685	670	
640	–	640	625	–	630	630	–	
590	600	590	605	592	580	–	–	
520	–	530	–	554	550	560(sh)	–	deformation vibrations of VO_4, TaO_6, VO_6
–	–	–	510	–	505	–	–	
480(sh)	–	–	–	494	490	–	–	
–	480	–	–	–	–	–	485	
–	–	–	–	–	465	476	–	
430	440	430	–	–	455		–	
400(sh)	–	–	–	–			–	
–	375	–	–	–			385	
365	–	–	–	362			–	

Table 7 (continued).

Dy		Ho		Er		Tm		Assignment
IR	Raman	IR	Raman	IR	Raman	IR	Raman	
325	315	325	330	–			–	
310	275	308	–	276			280	ν(M – O)
260	255	250	–	–			250	
236	245	240	–	–			–	
224	220, 185, 175, 165, 115, 100, 80, 65	220	225, 205, 150	220			210, 170	translation and rotation of VO_4, VO_6

Table 8. Frequencies (cm^{-1}) of maxima in vibrational spectra of MTa_2VO_9 (M = Yb, Lu, Sc, Y).

Yb		Lu		Sc (IR)	Y		Assignment
IR	Raman	IR	Raman		IR	Raman	
–	1090	–	–	–	–	–	
–	1050	–	–	–	–	1045	
–	–	–	1020	–	–	1025	
–	–	–	1010	–	–	–	
–	–	–	–	990(sh)	–	–	
–	–	–	–	–	960(sh)	–	
–	–	–	930	910	–	910	
895	–	890	–	–	895	895	
–	900	–	890	–	–	885	stretching vibrations of VO_4, TaO_6, VO_6
838	–	–	–	–	840	–	
–	815	–	835	–	–	830	
800	810	815	820	792	–	810	
–	–	–	790	–	–	–	
730(sh)	740	–	775	730(sh)	–	730	
–	–	–	765	–	–	–	
685	680	–	710	680(sh)	692	670	
–	–	–	665	630	640	640	
600	–	–	625	–	590	610	
560(sh)	–	–	–	574	535	–	
479	–	–	–	490	490	–	
	480	–	455	–	–	485	
	–	–	–	–	–	–	deformation vibrations of VO_4, TaO_6, VO_6
	–	450	–	–	430	450	
	–	–	415	–		420	
	385	–	370	–		375	
	–	360	–	350	–	–	
	–		315	296		–	
	–		265	268		275	
	255		255			255	ν(M – O)
	–		230			245	
						230	
	215, 175		210, 170, 150, 100, 65			200, 175, 95, 90, 75	translation and rotation of VO_4, VO_6

contains a group of intense lines in the region of 340 – 455 cm^{-1}. Probably, resonance phenomena involving virtual states due to diffusion of laser light near the $^4F_{9/2}$ state of the Er^{3+} ion also occur in this case. Similar phenomena were reported for the $^7F_0$ state of the Eu^{3+} ion and the $^4I_{9/2}$ state of the Nd^{3+} ion in $EuTa_7O_{19}$ and $LnTaO_4$ crystals (Ln = Nd, Eu).[135]

The empirical assignment of frequencies in the vibrational spectra of YTa_2VO_9 is based on the fact that its lattice contains almost regular VO_4 tetrahedra.[136, 137] The region of the stretching vibrations of these tetrahedra [730 – 900 cm^{-1}, *cf.* the assignment of the stretching vibration frequencies of VO_4 tetrahedra [138, 139] for the $[VO_4]^{3-}$ ion and for the $Na_3M(VO_4)_2$ compounds, where M = Sc, Y, La – Lu] displays quite a few maxima (see Table 8), which may be due to vibrations of VO_4 groups linked through one oxygen atom.

The tantalates MTa_7O_{19} (M = La, Ce) with the structures similar to that of YTa_2VO_9 are characterised by the presence of distorted TaO_6 octahedra. Probably, the structure of MTa_2VO_9 also contains distorted TaO_6 octahedra. The presence of vanadium-based polyhedra in the lattice of vanadatotantalates primarily results in variation of the frequencies originating from internal vibrations of the TaO_6 octahedra (ν and δ for Ta – O and Ta – O – Ta) and in elongation of the bonds in the octahedra

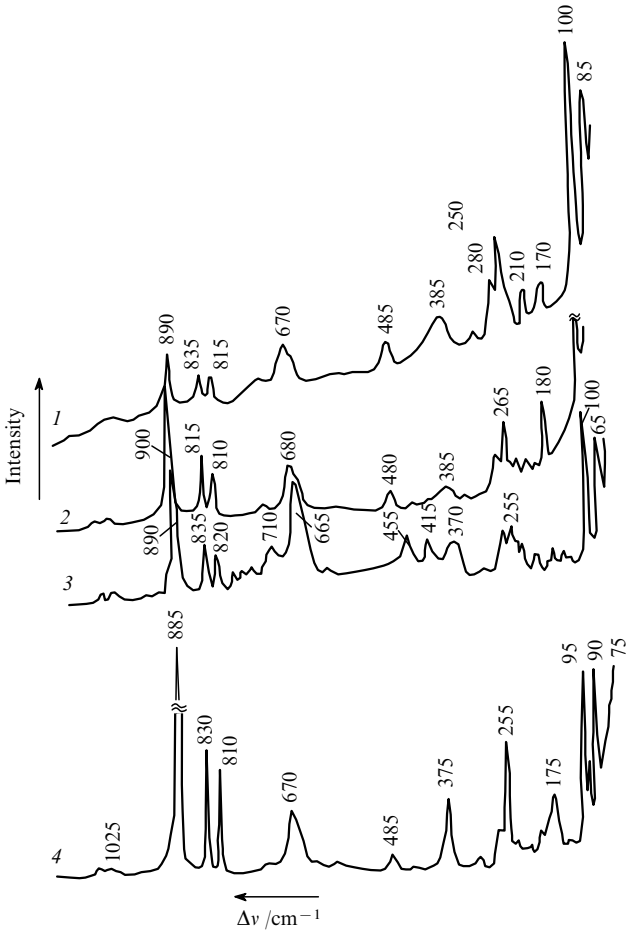


Figure 20. Raman spectra of MTa_2VO_9, where M = Tm (*1*), Yb (*2*), Lu (*3*), and the Raman spectrum of vanadatotantalate YTa_2VO_9 (4).

accompanied by a decrease in the vibration frequencies of the Ta–O terminal bonds.

Some frequencies in the spectra of YTa_2VO_9 were assigned to vibrations of distorted TaO_6 octahedra (see Table 8 and the frequency assignment in Refs 140 and 141). The spectra of orthovanadates MVO_4 and the assignment of the vibration frequencies of VO_4 tetrahedra have been documented.[142] For example, the frequencies for YVO_4 are as follows: $\nu_1 = 888$, $\nu_2 = 376$, $\nu_3 = 836.8$, $\nu_4 = 487\ cm^{-1}$. Taking into account the line shapes in the Raman spectrum of the vanadatotantalate YTa_2VO_9, some of the lines were assigned to the vibration frequencies of the VO_4 tetrahedron: $\nu_1 = 885$, $\nu_2 = 375$, $\nu_3 = 830$, $\nu_4 = 485\ cm^{-1}$. It is well known that for some tetrahedra, such as VO_4^{3-}, ReO_4^{3-}, FeO_4^{-}, RuO_4^{2-}, FeO_4^{2-},[143] and for MTa_2VO_9 the frequency ν_3 is smaller than ν_1.

2. MNb_2VO_9 crystals

The structures of MNb_2VO_9 crystals have not been determined. Tables 9–12 list the frequencies of the maxima in the vibration spectra of the vanadatoniobates MNb_2VO_9 (M = Sc, Y, La–Lu).[9] The bands at 865–890, 795–840, 470–490 and 370–385 cm^{-1} can probably be assigned to the ν_1, ν_3, ν_4 and ν_2 vibrations of the VO_4 tetrahedra, respectively.

The bands in the IR spectra of these compounds differ in shapes and intensities. For vanadatoniobates of cerium subgroup lanthanides, comparatively intense medium-width bands at 200–600 cm^{-1} and one broad band at 600–1000 cm^{-1} are observed (Fig. 21). For instance, the $NdNb_2VO_9$ spectrum has some specific features: the band at 828 cm^{-1} is particularly intense. In the spectra of MNb_2VO_9, where M = Ce, Pr, Sm, Eu, this band is less intense and is shifted from 828 cm^{-1} towards

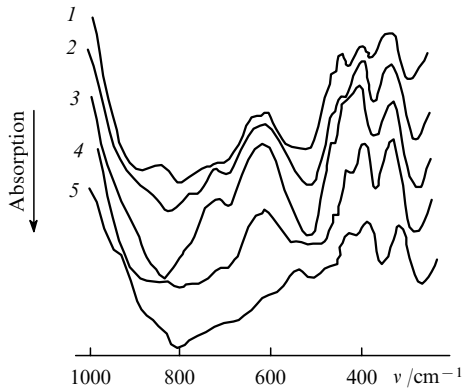


Figure 21. IR spectra of MNb_2VO_9, where M = Ce (*1*), Pr (*2*), Nd (*3*), Sm (*4*), Eu (*5*).

higher or lower frequencies. Such frequency shifts are less pronounced in the deformation vibration region. The IR spectra of yttrium subgroup compounds are similar: the frequency region characteristic of deformation vibrations displays comparatively intense medium-width bands; the stretching vibration bands merge into one broad band (Figs 22, 23). It should be noted that the IR spectra of $LaNb_2VO_9$ (Fig. 24, spectrum *1*) and vanadatoniobates of yttrium subgroup elements are similar to the spectra of vanadatoniobates of cerium subgroup elements. The spectra of YNb_2VO_9 and $ScNb_2VO_9$ (Fig. 24, spectra *2*, *3*) mainly differ in the intensity of the absorption bands. It is noteworthy that for compounds with M = Gd, Tb, Dy, Ho the broad band in the region of deformation vibrations splits into two narrow bands at

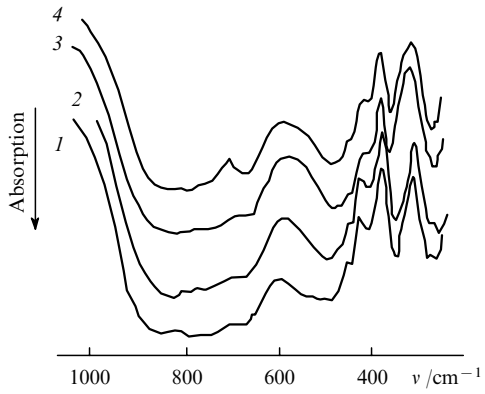


Figure 22. IR spectra of MNb_2VO_9, where M = Gd (*1*), Tb (*2*), Dy (*3*), Ho (*4*).

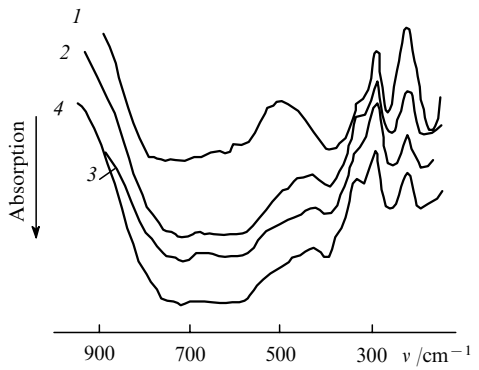


Figure 23. IR spectra of MNb_2VO_9, where M = Er (*1*), Tm (*2*), Yb (*3*), Lu (*4*).

Table 9. Frequencies (cm^{-1}) of maxima in vibrational spectra of MNb_2VO_9 (M = La, Ce, Pr, Nd).

La		Ce (IR)	Pr		Nd		Assignment
IR	Raman		IR	Raman	IR	Raman	
–	–	–	–	–	–	1070	stretching vibrations of VO_4, TaO_6, VO_6
–	1000	–	–	–	–	–	
–	–	–	–	990	–	–	
885	910	–	–	–	–	–	
865	–	875	–	–	–	–	
–	850	–	–	855	–	–	
850	–	–	–	–	–	–	
816	–	–	820	–	828	–	
800	–	800	–	–	–	–	
–	–	–	–	795	–	–	
–	–	–	–	785	–	–	
775	–	–	760	–	770	–	
–	–	690	690	–	684	–	
675	670	–	–	670	–	–	
–	–	630 – 620	620 – 615	–	625 – 620	–	
–	610	–	–	610	–	–	
–	–	560	–	–	–	–	deformation vibrations of NbO_n, VO_4, VO_6
–	–	510	510	–	508	–	
495	–	–	–	–	–	–	
–	470	–	–	480	–	–	
–	–	–	–	–	–	–	
–	–	450	450	–	450	–	
430	–	–	–	–	–	–	
	–	420	420	–	420	–	
	370	–	–	370	–	–	
	–	365	365	–	360	–	
	340	–	–	–	–	310	
	–	280	276	–	286	–	ν(M – O)
	270			255		–	
	210, 150, 115			220, 175, 135, 125, 100		185	translation and rotation of VO_4, VO_6

Table 10. Frequencies (cm^{-1}) of maxima in vibrational spectra of MNb_2VO_9 (M = Sm, Eu, Gd, Tb).

Sm		Eu (IR)	Gd		Tb		Assignment
IR	Raman		IR	Raman	IR	Raman	
–	990	–	–	–	–	1000	stretching vibrations of NbO_n, VO_4, VO_6
–	935	–	–	–	–	–	
–	885	–	–	–	880	890	
–	870	–	870	880	–	–	
860	–	–	–	–	–	–	
–	830	–	–	820	–	840	
–	–	–	–	–	840	–	
–	810	–	810	–	–	810	
800	–	803	–	–	–	–	
760	–	–	770	–	–	770	
690	680	670	690 – 670	685	685 – 670	670	
620	620	590	–	610	–	620	
550	–	–	–	–	–	–	deformation vibrations of NbO_n, VO_4, VO_6
510 – 480	–	506 – 467	505	–	510	–	
–	490	–	–	–	–	–	
–	470	–	475	–	480	–	
450	–	450	460	–	455	–	
–	–	–	420	420	–	420	
415	–	412	–	–	415	–	
–	370	–	–	–	–	385	
365	–	–	360	–	360	–	
–	350	352	–	–	–	–	

Table 10 (continued).

Sm		Eu (IR)	Gd		Tb		Assignment
IR	Raman		IR	Raman	IR	Raman	
–	–	–	290	–	290	–	
270	–	268	270	–	260	270	ν(M – O)
	255		–	260		–	
	210, 175, 150		170	210, 170, 115		175, 110	translation and rotation of VO_4, VO_6

Table 11. Frequencies (cm^{-1}) of maxima in vibrational spectra of MNb_2VO_9 (M = Dy, Ho, Er, Tm).

Dy		Ho		Er		Tm (IR)	Assignment
IR	Raman	IR	Raman	IR	Raman		
–	1050	–	–	–	–	–	
–	–	–	–	–	940	–	
–	–	–	–	–	–	907	
–	–	–	–	890	–	–	
–	880	–	–	–	–	–	
–	–	860	–	865	–	–	
–	–	–	–	–	–	850	
840	–	840	–	–	–	–	
–	815	–	–	–	–	–	stretching vibrations of NbO_n, VO_4, VO_6
810	805	810	–	805	–	810	
–	–	780	–	775	–	–	
–	–	–	–	–	–	740	
–	–	–	–	725	–	–	
–	–	690	690	680	–	685	
–	–	–	650	–	–	–	
–	620	–	–	620	–	–	
–	–	–	–	–	605	–	
–	–	–	590	–	595	–	
–	–	–	–	–	550	–	
–	–	–	540	–	545	545	
–	–	–	–	–	510	–	
495	–	500	505	500	–	–	
475	–	485	–	480	–	488	
–	480	–	–	–	–	–	
455	–	455	–	455	–	455	deformation vibrations of NbO_n,
–	–	–	430	–	440	–	VO_4, VO_6
415	–	420	–	415	–	414	
–	–	–	405	–	–	–	
–	–	–	390	–	–	–	
–	370	–	–	–	–	–	
370	–	370	370	365	–	–	
–	–	–	–	–	–	356	
–	–	–	300	290	–	–	
270	265	270	–	270	–	280	ν(M – O)
	–		–		260	–	
	220, 150, 115		230, 175		175, 125, 90		translation and rotation of VO_4, VO_6

260 – 270 cm^{-1}. This can be due to distortion of the polyhedra formed by the M^{3+} ions (M = Gd, Tb, Dy, Ho). The positions of certain bands depend on the nature of the M^{3+} cation: the decrease in the ionic radii in the $Ce^{3+} - Lu^{3+}$ series is accompanied by a shift of the band at 420 cm^{-1} to 412 cm^{-1} (Ho^{3+} is an exception). This may originate from an increase in the covalency of the bond of the lanthanide with the environment and enhancement of the crystal field effect as the M^{3+} ionic radius decreases. The Raman spectra could be recorded only for the compounds with M = La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er; only the most intense lines were recorded for $NdNb_2VO_9$. In the spectra of lanthanum, praseodymium, samarium and gadolinium vanadatoniobates, the most intense narrow band is shifted from 850 to 880 cm^{-1} (Fig. 25). Similarly, the decrease in ionic radius in the series La^{3+}, Pr^{3+}, Sm^{3+}, Gd^{3+} results in displacement of the relatively broad band at 670 cm^{-1} to 685 cm^{-1}. The pair of lines at 650 and 690 cm^{-1} in the spectrum of $HoNb_2VO_9$ has the highest intensity (Fig. 26, spectrum *2*). This is probably due to the resonance enhancement of the Raman spectrum upon helium – neon laser excitation of the holmium ion near the $^5F_5$ state. The enhancement of the line at 940 cm^{-1} occurs due to resonance effects, *viz*., laser light scattering near the $^4F_{9/2}$ state of the erbium ion in $ErNb_2VO_9$. The bands at 850 – 880 and 670 – 690 cm^{-1} in the spectra of vanadatoniobates, like those in the case of vanada-

Table 12. Frequencies (cm^{-1}) of maxima in vibrational spectra of MNb_2VO_9 (M = Yb, Lu, Sc, Y).

Yb	Lu	Sc	Assignment	Y	Assignment
–	–	990		990	stretching
895	900	–	stretching		vibration of NbO_m
850	850	850	vibrations of		
810	810	–	NbO_m, VO_4,		
–	–	765	VO_6, V–O–V	810	stretching
730	730	–			vibration of VO_4
685	685	–			
–	–	–	deformation	665,	deformation
–	–	615	vibrations	575	vibrations
–	550	555	of NbO_m		of NbO_m
490	488	–			
				470	$\nu_4(VO_4)$
455	455	475	deformation		
415	412		vibrations of		
350	352		VO_4, VO_6		
280	285		ν(M–O)		

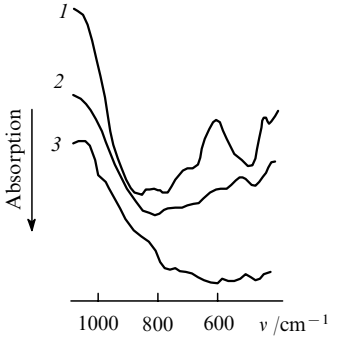


Figure 24. IR spectra of MNb_2VO_9, where M = La (*1*), Y (*2*), Sc (*3*).

totantalates, originate from the stretching vibrations of the Nb–O bonds involving the M–O bonds.

NMR data were used for empirical assignment of certain frequencies in the vibrational spectra of MNb_2VO_9. In the vanadatoniobate YNb_2VO_9, vanadium occupies two non-equivalent regular tetrahedral positions; the vanadium environment in one of them coincides with the tetrahedral environment of

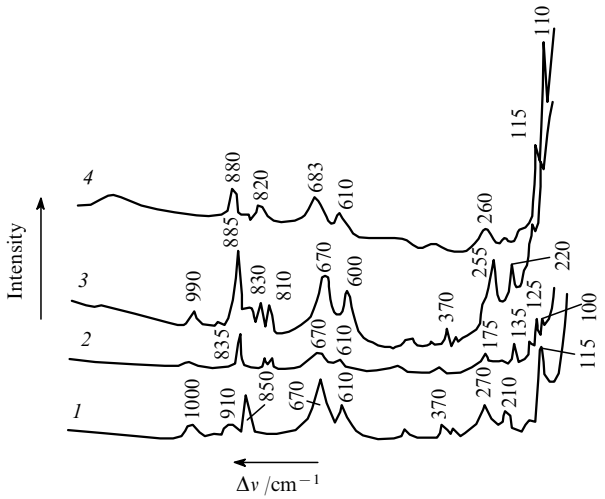


Figure 25. Raman spectra of MNb_2VO_9, where M = La (*1*), Pr (*2*), Sm (*3*), Gd (*4*).

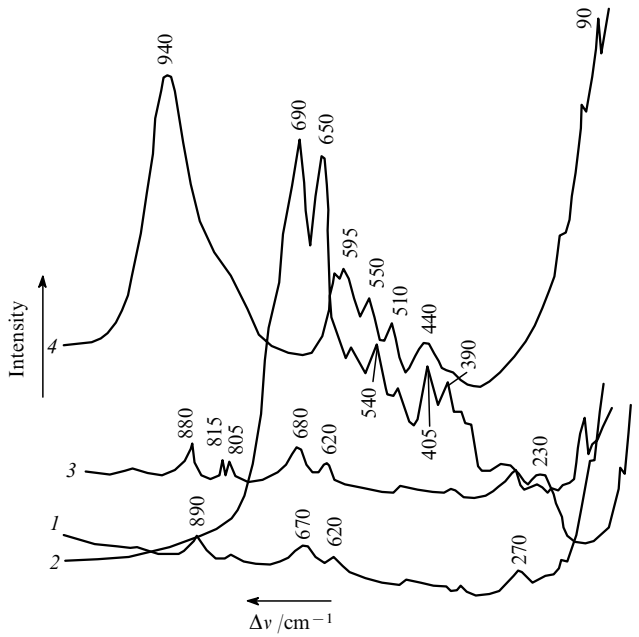


Figure 26. Raman spectra of MNb_2VO_9, where M = Tb (*1*), Ho (*2*), Dy (*3*), Er (*4*).

vanadium in the vanadatotantalate YTa_2VO_9. In $ScNb_2VO_9$ crystals, vanadium occupies two non-equivalent crystallographic positions: one position corresponds to a distorted octahedral environment while the other corresponds to a slightly distorted tetrahedral environment; the type of the VO_4 tetrahedra in $ScNb_2VO_9$ is similar to one of the types of tetrahedron in YNb_2VO_9. The YNb_2VO_9 and YTa_2VO_9 compounds have different structures. On the other hand, YNb_2VO_9 and $ScNb_2VO_9$ have niobium-formed polyhedra of the same symmetries.

The IR and Raman spectra of the vanadatoniobates MNb_2VO_9, where M = Sc, Y, La, are virtually similar and mostly differ in the band intensities. Therefore, the structures of MNb_2VO_9 are likely to contain the same set of polyhedra, namely VO_4, VO_6 and NbO_m; the structural difference between these compounds is that the polyhedra in the lattices of MNb_2VO_9 crystals are connected in different ways. The existence of vanadium polyhedra in YNb_2VO_9 and $ScNb_2VO_9$ was established reliably; probable assignment of bands in the IR spectra of these compounds was made on this basis (see Table 12).[138, 140, 144, 145]

The majority of lines in the Raman spectra of MNb_2VO_9 are broadened. This implies that the lattice atoms occupy non-equivalent crystallographic positions and form several types of similar polyhedra with different symmetries. The lines in the Raman spectra of MTa_2VO_9 crystals are less broadened, hence the MTa_2VO_9 structure has fewer non-equivalent atomic positions.

As in the case of vanadatotantalates, certain frequencies in the Raman spectra of vanadatoniobates were assigned based on the intensities, shapes and positions of particular lines. Comparison of these data with those for MVO_4 orthovanadates (see Refs 146, 147) resulted in the assignment given in Tables 9–12 ($\nu_3 < \nu_1$, as in the case of MTa_2VO_9).

The changes in the ν_1 and ν_3 frequencies in the Raman spectra of MTa_2VO_9 and MNb_2VO_9 polycrystals were analysed (see Ref. 9). The spectral lines are sufficiently narrow, hence it is quite reasonable to construct various functional dependences for them. Figure 27 presents the dependences of the ν_1 and ν_3 frequencies in the Raman spectra of $LnTa_2VO_9$ and $LnNb_2VO_9$ on the atomic number (z) and the ionic radius (r_{Ln}) of Ln^{3+} (the ionic radii were taken from Ref. 134). The ν_1 frequency is given only for $LnTa_2VO_9$ crystals. Figure 27 *a* clearly shows the scatter of experimental points near the straight line drawn using the least-

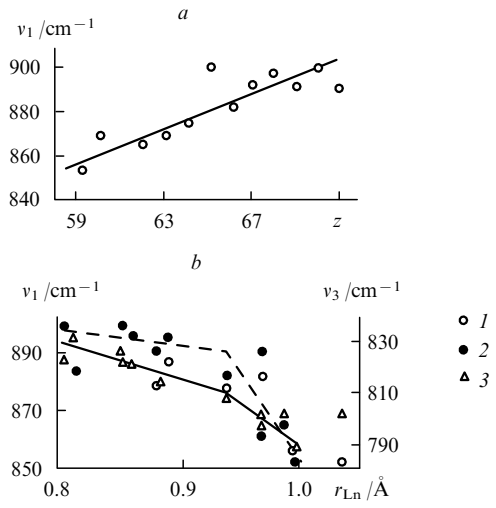


Figure 27. Dependence of vibration frequencies v_1 and v_3 of VO_4 tetrahedra on the atomic number in $LnTa_2VO_9$ (*a*) and the Ln^{3+} ionic radius in $LnTa_2VO_9$ (*1*, *2*) and $LnNb_2VO_9$ (*3*) (*b*). The experimental points refer to the frequencies v_1 (*1*, *3*) and v_3 (*2*); the calculated curves are drawn for the frequencies v_1 (solid line) and v_3 (dashed line).

squares method. The v_1 frequency for the $LnTa_2VO_9$ compounds increases as the lanthanide atomic number changes in the series Pr – Lu. This phenomenon can be explained by the lanthanide contraction. The scatter of v_1 values around the straight line is different for different lanthanides. The greatest deviations are observed for Tb, Nd and Lu. It is well known that non-uniform spreading of *f* orbitals, which depends on *z* and originates from spin-orbital coupling, is superimposed on the lanthanide contraction.[11] This effect might explain the scatter of v_1 for the compounds under consideration. Figure 27 *b* shows the same kind of scatter of experimental data and an increase in v_1 and v_3 with a decrease in the Ln ionic radius; in addition, the straight lines have sharp breaks around $r_{Ln} = 0.094$ nm (the ionic radius of Gd^{3+}). The dependences of other properties in the series of *f* elements are also characterised by similar breaks.[11] As shown by Muck *et al.*,[148] the $v_1(VO_4)$ frequency in the IR spectra of $Y(PO_4)_x(VO_4)_{1-x}$ mixed crystals increases as *x* changes from 0 to 0.7. This can be due to the effect on the bond vibrations in VO_4 tetrahedra exerted, for example, by other VO_4 groups.

3. $LaTaB_2O_7$, La_4VBO_{10}, $Ln_7V_2BO_{17}$ crystals and solid solutions based on them

Table 13 lists the frequencies of maxima in the vibrational spectra of solid solutions based on $LaTaB_2O_7$. The bands in the regions of 718 – 720 and 610 – 620 cm^{-1} can probably be assigned to the v_2 and v_4 vibrations of the BO_3 triangles. Frequencies up to

Table 13. Frequencies (cm^{-1}) of maxima in vibrational spectra of $La_{1-x}Sm_xTaB_2O_7$.

x						Assignment
0	0 [a]	0.001	0.01	0.05	0.1	
	155, 179, 215, 267					
300	–	300	300	300	300	v(La – O), v(O – B – O), v(O – Ta – O)
315	–	310	311	310	310	
–	321	320	325	321	320	
350	–	–	352	352	352	
375	370	372	370	372	370	
386	–	390	390	390	390	
400	–	425	423	425	427	
492	–	493	490	490	493	
525(sh)	–	525	525	525	525	
540	536	540	540	540	542	
560	564	557	560	557	562	
580	–	577	580	570	581	
590	–	–	–	595	–	
614	620	615	615	610	615	deformation vibrations of BO_3; stretching vibrations of TaO_n
667	–	–	665	665	667	
677	–	675	675	673	677	
–	700	–	–	–	–	
–	–	718	–	720	720	
–	749	–	–	–	–	stretching vibrations of TaO_n
765	775	764	765	775	768	
802	–	802	802	802	805	
895	–	890	890	890	890	
923	920	920	920	–	900	
960	958	960	960	960	965	
1029	–	1026	1027	1030	1030	
–	1045	–	–	–	1050	
1085	–	1085	1085	1085	1090	stretching vibrations of BO_3
–	–	–	–	1160	–	
1170	–	1165	1165	1170	1170	
1187	–	–	–	–	–	
–	–	–	1230	1230	–	

Table 13 (continued).

x						Assignment
0	0 [a]	0.001	0.01	0.05	0.1	
1235	–	1235	1240	–	1240	stretching vibrations of BO_3
–	1250	–	–	–	–	
1270	–	1270	1275	1272	1275	
	–	1293	1295	1300	1300	
	1316					
	1412					

[a] Raman spectroscopy data.

Table 14. Frequencies (cm^{-1}) of maxima in vibrational spectra of $La_{4(1-x)}Ln_{4x}VBO_{10}$ (Ln = Eu, Sm).

x					Assignment	x					Assignment
0	0.01(Eu)	0.05(Eu)	0.05(Sm)	0.01(Sm) [a]		0	0.01(Eu)	0.05(Eu)	0.05(Sm)	0.01(Sm) [a]	
				175	translation and rotation of VO_4	–	–	–	–	850	stretching vibrations of VO_4, V–O–V
						865	864	860	860	–	
				275, 395	ν(L–O), ν(O–B–O)	890	885	885	883	–	
–	–	–	425	–		906	–	–	–	905	
445	440	440	445	–		927	928	928	925		
486	482	480	485	–		945	941	942	941		
515	515	510	510	505		–	–	–	975		
–	575	–	–	–		1000	1000	1000	–		
593	594	594	592	–	$\nu_4(BO_3)$	1025	1025	1025	1025		
613	612	612	612	–		1080	1080	1080	1080		
715	718	715	717	–	$\nu_2(BO_3)$	1120	1120	1120	1120		
748	746	740	745	–		1135	1135	1135	1135		
–	–	–	760	–		1145	1145	1145	1145		
780	775	775	775	–	stretching vibrations of VO_4, V–O–V	1180	1180	1180	1180		
800	795	800	795	–		1250	1242	1245	1245		
832	830	828	829	830		1280	1275	1275	1276		

[a] Raman spectroscopy data.

1000 – 1100 cm^{-1} correspond to the fundamental lattice vibrations of the simple rare-earth element tantalates (see Ref. 141). The vibrations of the B–O bonds occur in the region up to 1400 cm^{-1} (see Ref. 149). Thus, the frequencies in the region of 1170 – 1412 cm^{-1} in mixed-anion crystals probably correspond to vibrations of the B–O bonds in BO_3. The bands in the region of 155 – 1100 cm^{-1} belong to the vibrations of groups containing tantalum, boron and lanthanum. The bands at 1170 – 1270 cm^{-1} probably arise from ν_3 antisymmetric stretching vibrations of isolated BO_3 triangles.

It is well known that the isolated BO_3^{3-} anion is characterised by vibrations in the region of 1100 – 1300 (degenerate antisymmetric stretching vibration) and 700 – 900 cm^{-1} (nonplanar degenerate deformation vibration). The reduction of boron symmetry in the case of $LaBO_3$ or the L-modification of $SmBO_3$ causes the frequency of 940 cm^{-1} to appear, which corresponds to symmetric stretching vibrations.[150, 151] Association of anions in rings or chains distorts their structures, which leads to broadening and splitting of bands, overlap of regions of different vibrations and often to a high-frequency shift of the stretching vibration bands. The character and span of frequencies of this group of vibrations in the IR spectra of $La_{1-x}Sm_xTaB_2O_7$ is not inconsistent with association of borate anions in rings and chains. Comparison of the spectra presented here with the results obtained for REE tantalates provides a reason to assume that the frequencies 600 – 830 cm^{-1} include the stretching vibrations of TaO_n polyhedra in addition to the deformation vibrations of the BO_3 groups, whereas vibrations at 200 – 500 cm^{-1} can be due to various deformation modes of O–B–O and O–Ta–O. The Raman spectrum of the boratotantalate $LaTaB_2O_7$ contains a dominant line with ν = 370 cm^{-1} (Fig. 28 *a*). The presence of an intense line in the region of 370 – 430 cm^{-1} of the Raman spectrum is characteristic of REE tantalates and comes from the deformation vibration of O–Ta–O.

The IR spectra of $La_{1-x}Sm_xTaB_2O_7$ solid solutions lack certain frequencies that are present in the spectra of $LaTaB_2O_7$ (Fig. 28 *b*); in addition, a series of frequencies appears (see Table 13). This means that replacement of lanthanum ions with samarium ions results in deformation of lattice polyhedra in solid solutions. This probably changes the selection rule of the vibrations. The same is true for the vibrational spectra of $La_{1-x}Eu_xTaB_2O_7$ solid solutions (see Ref. 152). Table 14 presents the frequencies of maxima in the vibrational spectra of $La_{4(1-x)}Ln_{4x}VBO_{10}$ solid solutions (Ln = Sm, Eu). According to NMR data, the lattices of the crystals indicated above contain almost regular VO_4 tetrahedra which have one common oxygen atom with the adjacent VO_4 tetrahedra. The IR spectra of the pure compound and its solid solutions are characterised by the presence of three intense absorption bands at 400 – 600, 650 – 950 and 1150 – 1350 cm^{-1} (see Ref. 153). The spectra of solid solutions lack some frequencies and contain some new frequencies in comparison with the spectrum of La_4VBO_{10} (Fig. 29 *a*).

The bands in the region of 480 – 486 cm^{-1} can be assigned to the ν_4 vibrations of the VO_4 tetrahedra, while those in the regions of 1275 – 1280, 941 – 945, 715 – 748 and 592 – 621 cm^{-1}, to the ν_3, ν_1, ν_2 and ν_4 vibrations of the BO_3 triangles, respectively.

The Raman spectrum of the $(La_{0.09}Sm_{0.01})_4VBO_{10}$ solid solution contains five high-intensity lines (Fig. 29 *b*) and two

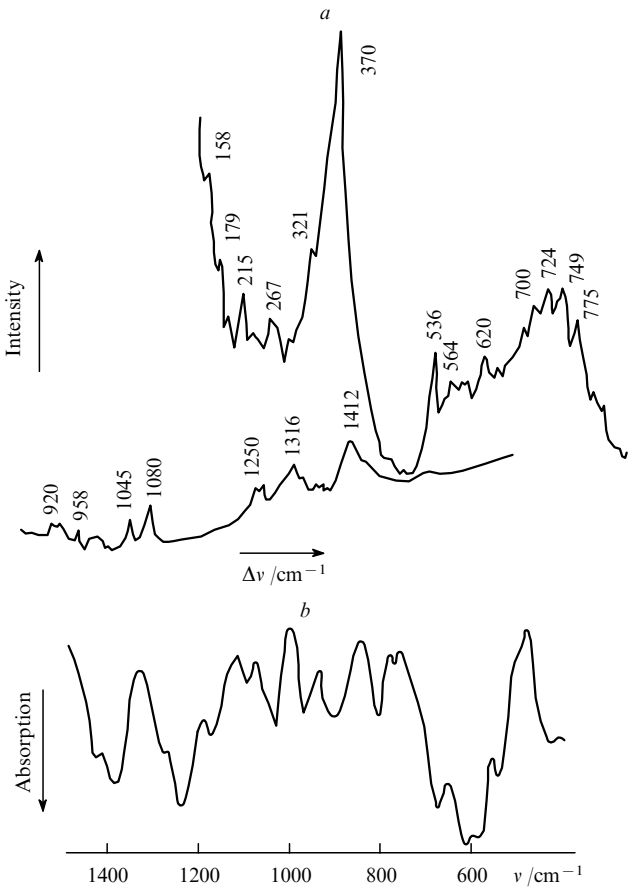


Figure 28. Vibrational spectra of $LaTaB_2O_7$.
(*a*) Raman spectrum; (*b*) IR spectrum.

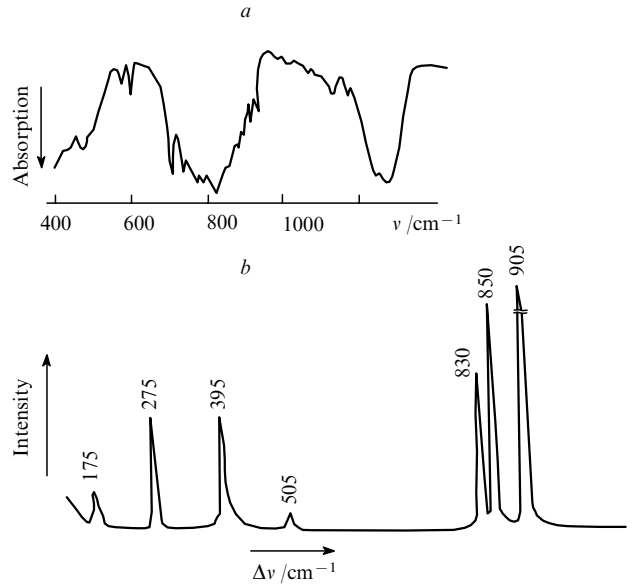


Figure 29. IR spectrum of La_4VBO_{10} (*a*) and Raman spectrum of $(La_{0.99}Sm_{0.01})_4VBO_{10}$ (*b*).

medium-intensity lines. Using the data for the vibration frequencies of BO_3 groups (see Refs 138, 150), a series of IR bands were assigned to the vibrations of BO_3 borate triangles (see Table 14). It follows from the assignment presented in Table 14 that La_4VBO_{10} is a mixed-anion compound. Probably, the La–O bond in the complex borates in question is essentially ionic, as shown for $LaMgB_5O_{10}$, $LaBO_3$, *etc.*[154]

The IR spectra of $Ln_7V_2BO_{17}$ contain bands ascribed to deformed BO_3 groups;[127] in particular, at 1172, 1215, 1310 and 1350 cm^{-1} for Ln = Nd.

* * *

Thus, the possibility of formation of ternary oxide compounds in ternary oxide systems of Group III and VB elements depends both on the ratio of the ionic radii of elements in the anionic part of the compound and on the cation radius. The vibrations of complex anionic groups in ternary oxide crystals can be interpreted as vibrations of quasi-isolated polyhedra, such as VO_4, VO_6 and RO_n, and BO_3 triangles. The chemical bonds of solid solutions with complex anions involve the *f* orbitals, as is evident from the lattice dynamics of these objects. As a rule, ternary compounds decompose to binary ones on heating. This is also characteristic of ternary compounds of other Groups of the Periodic Table. For example, titanoniobates and -tantalates, $LnTiNb(Ta)O_6$, undergo peritectic decomposition to give rutile and the corresponding niobates and tantalates, $LnNb(Ta)O_4$.[13] The decomposition products of compounds with mixed cations, *e.g.*, $Ln_2Ca_3(BO_3)_4$ or $LnAl_3(BO_3)_4$, contain double borates, *viz.*, $LnBO_3$ and $AlBO_3$.[66]

The data presented in this review can serve as a basis for studies of more complex multicomponent oxide systems, *e.g.*, $M_2O_3-V_2O_5-Nb_2O_5-Ta_2O_5$,
$M_2O_3-M'_2O_3-V_2O_5-Nb_2O_5-Ta_2O_5$, *etc.* The use of spectrometric methods allows one to understand the regularities of the formation of phases and their structures in the systems under consideration.

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