Reviews

The vibrational spectra of complex oxides with a perovskite-type structure

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Some aspects of the crystal chemistry and vibrational spectroscopy of complex oxides with a perovskite-type structure have been considered. The results of investigations of rhenium, tungsten, niobium, and tantalum complex oxides with a perovskite-type structure by vibrational spectroscopy methods (IR absorption, spontaneous Raman scattering) have been surveyed.

Key words: spectra; vibrations; structure; perovskite.

Among the complex-oxide materials used in modern engineering, compounds with a perovskite-type structure are of great importance. The possibility of wide variations in the composition and directional realization of fine structural peculiarities within the limits of a single structural type ensure a diversity of the significant properties of these compounds in practice and make it possible to use them as functional materials in electronic engineering. In view of the foregoing, it is not surprising that they have received much attention from researchers. All of the studies being carried out, including the investigation and justification of physical properties, are based on known (or supposedly known) structural details.

Vibrational spectroscopy (IR absorption and spontaneous Raman scattering) is among the most widely used methods for investigating the structures of substances. The use of these techniques allows one to gain information on the structural details of both single crystals and polycrystalline specimens. In the present work, we give an account of the general principles of the analysis of vibrational spectra of complex oxides with a perovskite-type structure and survey the results of some spectroscopic studies carried out in this field.

The perovskite, cryolite, and elpasolite structural types

General regularities

"Perovskites," *i.e.*, isostructural compounds of the composition ABO_3, have received their name from the corresponding mineral, $CaTiO_3$.[1] The perfect perovskite-type structure has a cubic unit cell with an edge of ~4 Å containing one formula unit and is described by the *Pm3m* space group. The B cations are located in the centers of regular oxygen octahedra, and the A cations have a cubo-octahedral coordination. In the structure, the octahedra are linked into an infinite three-dimensional framework.

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The A and B cations may have various oxidation states forming compounds $A^{I}B^{V}O_3$, $A^{II}B^{IV}O_3$, and $A^{III}B^{III}O_3$. The most general geometric criterion which determines the possibility of the occurrence of the perovskite structure is the tolerance factor, $t = (R_A+R_O)/\sqrt{2(R_B+R_O)}$. According to evaluations made by various authors, $0.8 < t < 1.05$. At $t > 1$, the B cations have ample space in the octahedra and shift from their centers, which may result, in particular, in the appearance of ferroelectric properties. If $t < 1$, then the A cations have ample space, and, consequently, bending of the chains of the octahedra and a rhombic distortion of the structure occur.

A generalized formula of the oxide compounds which belong to the perovskite family is as follows[2]: $(A_{\alpha_1}...A_{\alpha_m})(B_{\beta_1}...B_{\beta_n})O_3$. It also comprises the complex oxides with the cryolite (the $Na_2[NaAlF_6]$ mineral) and elpasolite (the $K_2[NaAlF_6]$ mineral) structures that also may be regarded as derivatives of perovskite. The unit cell of elpasolite (oxides with the elpasolite structure having the general formula $A_2B'B''O_6$ are usually referred to as 1 : 1 ordered perovskites) contains four formula units. The crystal lattice is described by the space group *Fm*3*m*.

The A cations, as in the case of perovskite, occupy cubo-octahedral twelve-coordinate positions; the alternating B′ and B′′ cations are located at the centers of the neighboring octahedra. The statistical arrangement of A and B cations results in the cryolite structure,[3] and the statistical arrangement of B′ and B′′ throughout the octahedral positions yields the perovskite structure. As has been noted previously,[4] for an ordered distribution of various cations to occur, the difference between the charges of the cations equal to or greater than four and the difference between their ionic radii greater than 0.12 Å are only required.

The nature of the cations and the character of their distribution throughout the crystallographic positions determine the degree of distortion of the lattice. In the case of octahedral coordination of Group V and VI elements (V, Nb, Mo, W), π-interaction tends to be localized at one, two, or three *cis*-arranged bonds, which leads to a decrease in the electron density at the three other bonds, owing to the *trans*-effect.[5] As a consequence, not only linear, but also angular distortions of the coordination octahedra occur. The degree and character of the deformations are associated with the tendency of the anions (oxygen atoms) to occupy equilibrium positions. It is important to keep in mind that the statistical arrangement of the distorted octahedra (distribution of the cations) may result in some cases in a cubic unit cell. It has been noted[6] that the displacements of the A^{II} cations from the perfect positions with the O_h symmetry in the $A^{II}BO_3$ structure lead to rhombic distortions of the lattice, and the antiparallel shifts of these cations from the T_d positions in $A_2^{II}B'B''O_6$ result in monoclinic distortions. In the case of the statistical distribution of the B′ and B′′ cations, the shifts of the A^{II} cations are also disordered and the symmetry of the compound $A_2^{II}B'B''O_6$ remains orthorhombic. The above-noted characteristic features of the structure are embodied in the vibrational spectra.

Vibrational spectra

In the case of the ordered cubic perovskite $A_2B'B''O_6$, all of the atoms occupy specific crystallographic positions. The group-theoretic analysis of vibrations of the crystals having this structure at $k = 0$ yields the following full irreducible representation:

$$\Gamma = A_{1g} + E_g + F_{1g} + 2F_{2g} + 5F_{1u} + F_{2u}.$$

Acoustic vibrations are described by the irreducible representation F_{1u}. Vibrations of the $A_{1g} + E_g + 2F_{2g}$ type are Raman active, and $4F_{1u}$ are active in the IR absorption spectra. The F_{1g} and F_{2u} vibrations are inactive in the optical spectrum. The site symmetry of atoms and the set of irreducible representations of vibrations for each sublattice of the crystal are given in Table 1.

The forms of normal vibrations[7] calculated and constructed using the symmetry coordinates assume that during the A_{1g} and E_g vibrations of the anionic sublattice, all of the cations are at rest, and the angles between the bonds do not vary, while the F_{2g} vibrations, in addition to the oxygen anions, involve the A cations, which move parallel to the edges of the unit. Since the Raman active vibrations are of three different symmetry types, polarization measurements on single crystals allow the correct assignment of the spectral bands to be carried out. The fully symmetrical A_{1g} stretching vibration is manifested as the most high-frequency intense peak. In terms of its form, it is a stretching vibration of the $B''O_6$ octahedron in which the oxygen atoms move along the B′—O—B′′ axes and, therefore, its frequency is determined by the nature of the B′ and B′′ cations and also by the B′—O and B′′—O interatomic distances.

Despite the fact that the bulky A cation does not participate in the type A_{1g} vibrations, its size has an effect on the B′—O (but not B′′—O) bond length and thus on the frequency of this vibration. In those cases where the octahedral positions are occupied by bulky

Table 1. The symmetry of the positions of atoms and the results of group-theoretic analysis of vibrations of a crystal of the ordered cubic perovskite

Atom	Position	Symmetry of the position	Irreducible representations of vibrations
A	8c	T_d	$F_{2g} + F_{1u}$
B′	4b	O_h	F_{1u}
B′′	4a	O_h	F_{1u}
O	24e	C_{4v}	$A_{1g} + E_g + F_{1g} + F_{2g} + 2F_{1u} + F_{2u}$

cations, for example, alkaline earth cations, contraction of the neighboring octahedra occurs, and one would expect an increase in the $\nu_1(A_{1g})$ frequency. However, this is not the case, probably due to the fact that, along with the squeezing of the octahedra, bending of the B′—O—B′′ chains and a decrease in the full returning force acting on the oxygen atoms of the $B''O_6$ octahedra take place.

During the doubly degenerate vibration with the $\nu_2(E_g)$ frequency, the $B''O_6$ octahedron is compressed along one of its axes. This vibration has not been recorded for all of the compounds. It has been suggested[8] that it is governed by the electronic configuration of the B′′ ion and the character of the B′′—O bond. In conformity with this suggestion, this vibration has a noticeable intensity in the Raman spectra when the ion has a d^{10} configuration and is missing from the spectra at a d^0 configuration of the ion. One of the F_{2g} vibrations may be regarded, with a certain admission, as a ν_5 symmetrical deformation vibration of the $B''O_6$ group with some participation of the A cations.

The most high-frequency broad absorption band in the IR spectrum is associated with the asymmetrical stretching vibrations (ν_3) of the $B''O_6$ octahedron, and the next band in frequency (ν_4) corresponds to the asymmetrical deformation vibrations of this group. The latter is prone to mix to a lesser or greater extent with lower-frequency translational vibrations.

The slight distortions of the structure resulting from the presence of bulky B′′ cations are more pronounced in the Raman spectra.[9] The decrease in the symmetry of the $B''O_6$ octahedra is manifested as the removal of the degeneracy of the vibrations (splitting of the bands into components) and as the appearance of inactive modes. The behavior of the Raman line corresponding to the F_{2g} deformation vibration, which may be broadened or split, is the most demonstrative in this respect. The vibration with the $\nu_6(F_{2u})$ frequency is inactive in both the IR absorption and Raman spectra of the perovskites with cubic symmetry. A simple formula for the calculation of this frequency has been offered: $\nu_6 = \nu_5/\sqrt{2}$. In the expected frequency region of the IR spectra of some compounds with substantially distorted crystal structure, absorption bands assigned to this vibration have been recorded.

In the subsequent text we will pay special attention to the vibrations of cationic sublattices. In accordance with formal symmetry considerations, in this case, the following modes should be realized: the $T_1(F_{2g})$ and $T_3(F_{1u})$ vibrations of the cations occupying cubo-octahedral positions; the $T_2(F_{2u})$ vibrations of the cations in octahedral positions; interaction of the T_2 and T_3 vibrations as well as participation of oxygen atoms in them cannot be ruled out.

Studies of the vibrational spectra of a number of compounds with an ordered cubic perovskite structure (molybdates, tungstenates, niobates, tantalates, uranates, and tellurates and solid solutions based on them) made it possible to identify some general regularities.[7–15] It was shown[11] that in terms of the interpretation of the vibrational spectra, the ordered perovskites $A_2^{II}B'B''O_6$ may be divided into three groups: (1) compounds with the $B''O_6$ octahedra having the O_h symmetry; (2) those with a reduced point symmetry of the $B''O_6$ octahedra; and (3) those with several types of the $B''O_6$ octahedra.

The Raman spectra provide more information than the IR spectra for assigning a compound to one of these groups, in particular, because of the fact that in the former case, mixing of vibrations with different symmetry types is impossible.

The assignment to the first or second group can be easily carried out by analyzing the profile of the F_{2g} band, which is normally recorded at ν_5 = 300 to 400 cm^{-1}. The first-group perovskites exhibit a singlet; those from the second group display a doublet or triplet (removal of the degeneracy). One more criterion for the assignment to these groups is the appearance of bands in the region of the $T_1(F_{2g})$ vibrations and the observance (for the first group) or the violation (for the second group) of the alternative prohibition rule.

Compounds that belong to the third group are best identified by the presence of several bands in the region of nondegenerate $\nu_1(A_{1g})$ vibration. The presence of several sorts of octahedra in the structure is indicated by multiplet signals recorded in the region of $\nu_5(A_{2g})$, $T_1(F_{2g})$, and $\nu_3(F_{1u})$ vibrations.

It should be noted that there is no one-to-one correspondence between the symmetry of the lattice and the assignment of perovskites to these groups. Compounds having a cubic symmetry of the crystal lattice belong, as a rule, to the first group, but such compounds in other groups are also known. The distorted perovskites are mostly related to the second and third groups.

Of special importance for the estimation of the distribution of the cations over the A and B′ positions is the analysis of the IR active $T_2(F_{1u})$ and $T_3(F_{1u})$ lattice vibrations. The frequencies of these vibrations are affected by both the charge and the mass of the cation. Experimental results indicate that the frequency of the T_2 cation depends, in addition, on the nature of the B′′ cation, but a clear-cut relationship between the frequency variation and the mass of the cation cannot always be followed. On the contrary, the cations in the A positions exert no effect on the T_2 vibration. A partial replacement of ions in the B positions by ions having a substantially different charge and size may be accompanied by splitting of the T_2 band into components. The T_3 and T_1 vibration frequencies also depend on the nature of the cations in various sublattices.

The problems of the ordering of cations in octahedral positions in the context of vibrational spectroscopy have been considered[12,16] by looking at the behavior of the ν_1 band in the Raman spectra. In the case where the distribution of the cations throughout the octahedral positions of the crystal lattice is disordered, the separa-

tion of the vibrations into internal (vibrations of the $B''O_6$ octahedra) and external vibrations is not quite correct; nevertheless, it may be used as a first approximation. The statistical distribution of the B′ and B″ cations results in the appearance of several dissimilar types of the $B''O_6$ octahedra. This is attested, first of all, by the presence of several bands at ν_1 in the Raman spectra and also by splitting of the ν_3 and ν_4 into more than three components. For some specimens, a violation of the alternative prohibition rule has been found. The results of investigations[17] show that vibrational spectroscopy can be used for studying the disordering phenomena in those cases in which the X-ray methods are not very sensitive.

Barium and alkali metal hexaoxorhenates

According to the results of an X-ray structural study,[18,19] complex rhenium oxides of the composition Ba_2LiReO_6 and Ba_2NaReO_6 have been assigned to the structural type of cubic perovskite with an ordered distribution of rhenium and alkali metal atoms throughout the crystal lattice positions. The number and the activity of vibrations in the spectra of these compounds[20] to the greatest extent correspond to the above-outlined selection rules. Each of the Raman spectra exhibits (Table 2) four bands, and none of them undergo an isotopic shift when ^6Li is replaced by ^7Li.

However, the frequencies of vibrations of these compounds are noticeably different. For example, the two highest frequencies increase, and the lowest frequencies decrease, as lithium is replaced by sodium. The band in the 550—600 cm^{-1} region has a shoulder on its low-frequency slope. In the IR absorption spectra, four bands are also recorded. For two of them, an isotopic shift was observed in the case of the lithium-containing compound. The corresponding bands in the spectrum of Ba_2NaReO_6 are recorded at lower frequencies. The frequency of the high-frequency IR band increases on going from Ba_2LiReO_6 to Ba_2NaReO_6, and the band itself is clearly split into two components. The latter as well as the asymmetry of the bands (shoulders) are due to distortions of the crystal lattice.

In the high-frequency region of the spectrum (above 500 cm^{-1}), vibrations of the anionic sublattice (oxygen anions) are only exhibited. Since for sodium-containing compounds the frequencies of these vibrations are higher than for lithium-containing compounds, while the effect of the cation mass, in the case in which the cation participates in the vibration, would have given rise to the opposite results, a substantial polarizing effect of alkali metal cations on the Re—O bonds has been assumed. Since the cations in these compounds are likely to retain their positions in the crystal lattice points, the distortion of the structure is associated with deformation of the oxygen polyhedra. One more characteristic feature of the spectra is the presence of Raman lines of medium intensity at 568 cm^{-1} (for Ba_2LiReO_6) and 598 cm^{-1} (for Ba_2NaReO_6), which correspond to the $\nu_2(E_g)$ stretching vibration.

Table 2. The vibration frequencies for hexaoxorhenates (ν/cm^{-1})

$Ba_2{}^6LiReO_6$		$Ba_2{}^7LiReO_6$		Ba_2NaReO_6		Assignment
Raman	IR	Raman	IR	Raman	IR	
801		801		818		$\nu_1(A_{1g})$
	650		650		698	$\nu_3(F_{1u})$
					661	
568		568		598		$\nu_2(E_g)$
545 sh		545 sh		565 sh		
454		454		439		$\nu_5(F_{2g})$
	368		362		345	$\nu_4(F_{1u})$
	317		298		266	$T_2(F_{1u})$
	132		132		118	$T_3(F_{1u})$
119		119		104		$T_1(F_{2g})$

From an analysis of the spectra it follows that vibrations of the lithium cations in the octahedral positions are exhibited at 317—298* cm^{-1}, and those for sodium cations are at 266 cm^{-1}. Despite the fact that vibrations of the oxygen octahedra are highly characteristic and interact weakly with each other, as shown by normal coordinate analysis, the cations of rhenium and other elements (lithium, sodium, and barium) accomplish joint movement with lower frequencies (136 cm^{-1} and below).

Phases in the Ba_3WO_6—Sr_3WO_6 system

The phases formed in the Ba_3WO_6—Sr_3WO_6 system crystallize in a perovskite-type structure. It is known[20—23] that as barium is replaced by strontium the crystal lattice of mixed tungstenates, $Ba_{3-x}Sr_xWO_6$, consecutively changes from the orthorhombic symmetry, in the case of Ba_3WO_6, to the tetragonal symmetry, cubic symmetry with a superlattice, cubic symmetry without a superlattice, then to the monoclinic, once more cubic without a superlattice, and finally to the triclinic symmetry in the case of Sr_3WO_6. Using the techniques of vibrational spectroscopy, investigators have studied the character of the distortion of the structure of phases, homogeneity regions of the solid solutions, and the order of the replacement of the cations.[24]

The frequencies recorded in the IR absorption spectra were schematically divided into four groups (Table 3) corresponding to the four IR-active vibrations of the ordered cubic perovskite: 450—750 cm^{-1} for $\nu_3(F_{1u})$, 250—400 cm^{-1} for $\nu_4(F_{1u})$, 150—200 cm^{-1} for $T_2(F_{1u})$, and 100—130 cm^{-1} for $T_3(F_{1u})$. In the complex struc-

* From here on, for isotope-substituted specimens, the first and second frequencies correspond to compounds with the lighter and the heavier isotope, respectively.

Table 3. The frequencies of vibrations of $Ba_{3-x}Sr_xWO_6$ (ν/cm^{-1}) at various x values

0.0		0.05	0.1		0.15	0.2		0.25	0.4	0.5		0.75		0.8	0.85	1.0		1.5		3.0		Assign-
IR	Ra- man	Ra- man	IR	Ra- man	Ra- man	IR	Ra- man	Ra- man	Ra- man	IR	Ra- man	IR	Ra- man	Ra- man	Ra- man	IR	Ra- man	IR	Ra- man	IR	Ra- man	ment
875												885				880						$\nu_1(A_{1g})$
	843	843		846	844		842				842											
817	812	808	820	817	812	820	815	817	816	810	816		816	817	818		818		819	827	821	
	793	796						771				773	775						772	770	773	
725	760	761	730	759	757		758	761	762		760		756			760		760				
																665		670		630		$\nu_3(F_{1u})$
565			572			570	570	560	575	575		575				580		585		580		
																				535		
495			500			495				495		495				495		495		515		
	420	423																			421	
	410	408		413	409		410	408	408		407		405	408	405		411		411			$\nu_5(E_g)$
	394	395		395	395	375								374			403					$\nu_4(F_{1u})$
350			340			335				335										338		
306			305			310				310		320				310		320		320		
																		281		274		
							242	242	238													$\nu_6(F_{2u})$
						195				188		182				185		180		180		$T_2(F_{1u})$
154			152			148				150												
112			112			110				110		106				114		106		124		$T_3(F_{1u})$
																				105		
	107	107		101	96		98	99	99		98		97	97	99		99		100		100	
	94	93		93																		$T_1(F_{2g})$
	71	71		68	66		68															
				61				57	60													

ture of the band associated with the ν_3 asymmetrical stretching vibration of the WO_6 octahedron, three or four components can be distinguished. The splitting is especially pronounced for compositions ($x \leq 0.15$; $x \geq 0.8$) with low symmetries of the crystal lattice. The behavior of the components is dissimilar: whereas the position of the band at ~500 cm^{-1} almost does not change for all of the x values, the components recorded at higher frequencies shift to longer wavelengths as the proportion of strontium increases.

On the basis of the variation of the T_2 vibration frequency, the distribution of the alkaline earth metal cations in the octahedra has been followed. Already at $x \geq 0.75$, the 154 cm^{-1} band corresponding to the T_2(Ba) vibration is manifested as a shoulder on the low-frequency slope of the band that appears due to the corresponding vibration of the strontium cations in an octahedral environment (T_2(Sr) at 180 cm^{-1}). Thus, in conformity with general crystal-chemical regularities, the strontium atoms fill first of all the octahedra. The band recorded at the lowest frequency (T_3 at 124—105 cm^{-1}) behaves as a singlet, except for compound Sr_3WO_6. In the spectrum of the latter it is split into two components. The relative insensitivity of the frequency of this vibration to the substitution of strontium for barium suggests that heavy tungsten atoms substantially participate in it; therefore, it is difficult to study filling of the cubo-octahedral positions with alkaline earth cations by observing the behavior of the corresponding band.

All of the vibrations active in the Raman spectra correspond to different symmetry types, and their assignment, resorting to the literature data available, presented no problems: 750—850 cm^{-1} corresponds to $\nu_1(A_{1g})$, 370—420 cm^{-1} is due to $\nu_5(F_{2g})$, and 60—100 cm^{-1} was assigned to $T_1(F_{2g})$. The activity of several components of the nondegenerate vibration at ν_1 indicates that the phase structure contains four dissimilar types of the WO_6 octahedra at $x = 0$ to 0.1; three types of the octahedra at $x = 0.15$ to 0.75; two types at $x = 0.8$ or $x \geq 1.5$; and one type at $x = 0.85$ or $x = 1.0$. Splitting of the bands of triply degenerate (ν_5 and T_1) vibrations into components in the case of phases with high proportions of barium allows one to conclude that the cubic cell is deformed due to displacement of the octahedra

resulting from the arrangement of bulky barium cations in octahedral positions.

In the spectra under consideration, some deviations from the general regularities of the behavior of bands for series of solid solutions have been found. For example, the monotony in the variation of the number of components of the symmetrical vibration of ν_1 is broken. Variations of the vibrational frequencies have also a discontinuous character. On the basis of the analysis of all of the characteristic features of the spectra, five homogeneity regions have been identified. They include phases of an orthorhombic symmetry ($x \leq 0.05$), a tetragonal symmetry ($x = 0.1$), a cubic symmetry with a superlattice ($0.75 < x < 1.5$), and a triclinic symmetry ($x > 1.5$). The spectra of the phases in these concentration intervals mostly exhibit a two-mode character of vibrations. The phases of the composition $Ba_{2.25}Sr_{0.75}WO_6$ and $Ba_{1.5}Sr_{1.5}WO_6$, crystallizing in a cubic structure without a superlattice, at the boundaries of these regions should be regarded, as has been suggested, as transition disordered states between the regions of homogeneity. The normal coordinate analysis for Ba_3WO_6 shows[25] that vibrations are rather specific and localized at the corresponding fragments of the structure, which also is in agreement with the two-mode behavior of the bands in the spectra of solid solutions.

Niobates, tantalates, and the inversion of cations

The replacement of cations in the cryolite structure according to the scheme $M^{II} + W^{VI} \rightarrow Ln^{III} + B^{V}$ affords niobates and tantalates of the composition $M^{II}LnB''O_6$, where M^{II} is Ca, Sr, or Ba. The appearance of a rare earth element in the structure allows various degrees of filling of the cationic positions with these cations. In calcium-containing niobates and tantalates, the lanthanides from the initial part of the series are known[26,27] to occupy eight-vertex units, where they are statistically arranged together with the calcium atoms, whereas heavy lanthanides predominantly occupy octahedra alternating with niobium or tantalum. Analysis of the spectra of these compounds[28,29] was based on a comparison with the spectra of rhenates and tungstates, on regularities identified in the behavior of frequencies along the series of the cations, on the isotopic effect observed on replacement of ^{40}Ca by ^{44}Ca, and on a comparison with the spectrum of $Ca_2(Mg_{0.5}Ti_{0.5})NbO_6$, in the structure of which the calcium atoms are known to occupy cubo-octahedra.

In the 740—810 cm^{-1} frequency region, the Raman spectra of virtually all of the calcium compounds[28] contain one line, a component of the fully symmetrical vibration (Table 4), which indicates that one type of the $B''O_6$ octahedra is present in the structure. The frequency of this vibration increases over the series of lanthanides, and beginning with dysprosium, when lanthanide cations fill the octahedral positions, it increases more quickly. The clearly defined splitting of bands in the region of deformations of the octahedra (380—490 cm^{-1}) for gadolinium and neodymium-containing compounds correlates with the relatively large values for the angle of the monoclinic crystal lattice; for compounds containing heavy lanthanides it has been suggested that it is due to the increase in the dynamic interaction between the vibrations of the $B''O_6$ octahedra *via* the lanthanide atoms. The weak diffuse bands in the 500—600 cm^{-1} region may be due to the manifestation of the vibration at $\nu_2(E_g)$, which is normally not observed for this type of compound.

The bands at 510—670 cm^{-1} in the IR absorption spectra have been assigned to the asymmetric stretching vibrations of $B''O_6$, and those at 320—455 cm^{-1} correspond to the deformations. The bands in the 216—320 cm^{-1} region have been assigned to the vibration at $\nu_6(F_{2u})$, which is inactive in cubic perovskites. These bands are split into components due to the decrease in the symmetry of the crystal lattice to monoclinic.

In the case of $Ca_2LaB''O_6$ and $Ca_2LuB''O_6$, two Raman lines in the 197—260 cm^{-1} region undergo the greatest shifts (4—11 cm^{-1}) as a result of calcium isotope substitution. A similar pair of bands (226 and 251 cm^{-1}) were detected in the spectrum of $Ca_2(Mg_{0.5}Ti_{0.5})NbO_6$. Slight isotopic shifts (3—4 cm^{-1}) were noted for a group of bands in the 143—170 cm^{-1} region. All of these were assigned to the translations of the calcium atoms in cubo-octahedra.

The regular redistribution of the intensities of two bands (197—191 and 231—224 cm^{-1} for Ca_2LaNbO_6, 197—193 and 232—229 cm^{-1} for Ca_2LaTaO_6), which accompanies the transition from lanthanum to lutetium, is associated with the inversion in the population of the positions with calcium and lanthanide atoms. The bands in the long-wavelength region of the spectrum (below 125 cm^{-1}) shifting to lower frequencies over the lanthanide series were assigned to the librations of the $B''O_6$ octahedra. Owing to the substantial mixing of the vibrations, virtually all of the bands below 400 cm^{-1} in the IR absorption spectra undergo isotopic shifts after calcium isotope substitution and do not provide unambiguous information on the vibrations of cationic sublattices.

The results of the normal coordinate analysis for Ca_2LaNbO_6 and Ca_2LuNbO_6 showed that the high-frequency vibrations (above 480 cm^{-1}) are highly characteristic and localized at the NbO_6 octahedra. It was found that going from lanthanum to lutetium results in an extension of the frequency region of the stretching vibrations of NbO_6, due to intensification of the interaction *via* the lutetium cations in octahedral positions. The difference between the force constants obtained for the two compounds is slight. The latter allows one to say with confidence that the similarity of dynamic characteristics of the octahedral and cubo-octahedral positions, along with the dimensional factors, are respon-

Table 4. The frequencies of vibrations of $Ca_2LnB''O_6$ (ν/cm^{-1})

Ca_2LaNbO_6				Ca_2LaTaO_6				Ca_2LuNbO_6				Ca_2LuTaO_6				Assignment
IR		Raman		IR		Raman		IR		Raman		IR		Raman		
^{40}Ca	^{44}Ca	^{40}Ca	^{44}Ca	^{40}Ca	^{44}Ca	^{40}Ca	^{44}Ca	^{40}Ca	^{44}Ca	^{40}Ca	^{44}Ca	^{40}Ca	^{44}Ca	^{40}Ca	^{44}Ca	
760	760			775	775											ν_1
		744	745			759	760			783	786			802	801	
										760				780		
660	660			672	672			680	680							ν_3
612	612			625	625											
545	546			560	560			570	570			590	590			
								500	500			530	530			
		500	500			515	515			550	550			589	582	ν_2
														578		
												460	460			ν_4
402	400			388	382			410	405			400	393			
								375	364			363	363			
350	360			350	350			350	348				358			
					338			320				320	336			
										474	474			478	479	ν_5
		430	432			434	437			445	443			449	448	
										392				392	393	
		376	371			380	379			374	373			377	376	
		303	314			285	285			319	318			322	321	
				282	275			275	278			266	266			ν_6
258	258			258	255			250	220			240	231			
225	220			216	221			206	198			190	188			T_2
	202				207											
				186				187	177			162				
								175								
166	165			156	140			145	?			145	132			
		231	224			232	229			260	250			261	252	T_1
										237	238			241		
		197	191			197	193			216	209			217	213	
										197	189					
						152	160?			160	153			157	154	
										147	145			146	143	
128	120			130	118			115	118			110	110			T
												103				
100	89			90	90			92	84			87	87			
		125	123			123	124							85	88	R
							120									

sible for the possibility of the existence of inverted forms.

The general patterns of the spectra of $Sr_2LnB''O_6$ and $Ba_2LnB''O_6$ indicate that the structure of all of these compounds has some deviations from that peculiar to the ordered cubic perovskite. Two Raman lines (components of a symmetrical stretching vibration) in the spectra of lanthanum compounds indicate the presence of two dissimilar types of the $B''O_6$ octahedra. The regular profile of the only line at ν_5 attests that highly symmetrical octahedra predominate in the structure. With the assumption of a statistical distribution of strontium and lanthanum cations, the low-frequency line (175 cm^{-1} for the niobate and 163 cm^{-1} for the tantalate) in the long-wavelength region of the spectrum was assigned to the translational vibration T_1 of the strontium cations, and a more high-frequency line (251 cm^{-1} for the niobate and 248 cm^{-1} for the tantalate)

was attributed to the translational vibrations of lanthanum cations in the cubo-octahedral positions.

The Raman spectra of Sr_2LuNbO_6 and Sr_2LuTaO_6 are substantially different. In fact, in the spectrum of the niobate, one line at ν_1 was recorded, while in the case of the tantalate, five components were measured in this region, despite the fact that, according to the X-ray diffraction studies,[30] these compounds are isostructural. The high multiplicity (up to six components) of the deformation bands may result from both a low symmetry of the octahedra and a substantial Davydov splitting. The frequencies of the vibrations of strontium and lutetium cations in the cubo-octahedral positions are similar to those measured for lanthanum compounds. This similarity is due to the counterbalancing of two factors, the variation of the mass of the cations and the effect of the lanthanide contraction.

In the region of stretching vibrations of the spectra of $Ba_2LnB''O_6$, which covers a substantial frequency range, two to five lines are recorded indicating a diversity of types of the $B''O_6$ octahedra. The unusually high frequencies of these vibrations suggest that the structure contains fused systems of the $B''O_6$ octahedra, including those with common faces. The translations of barium cations in cubo-octahedral positions are manifested as narrow intense lines at 90—142 cm^{-1}. Since no lines corresponding to the $T_1(Ln)$ vibrations are recorded in the range 200—300 cm^{-1} (except for Ba_2LnTaO_6, the spectrum of which exhibits a weak band at 238 cm^{-1}), the assumption that lanthanide ions virtually do not occupy cubo-octahedral positions in compounds with barium is well founded.

The positions and intensities of the bands in the IR absorption spectra of $M_2^{II}LnB''O_6$ (M^{II} = Sr, Ba) correspond to the model of the ordered cubic perovskite, the use of which is quite substantiated. Four main absorption bands can be distinguished for all of the compounds. A distinctive feature of the spectra of these compounds is that the ν_3 frequency of the asymmetrical stretching vibration of $B''O_6$ in tantalates is higher than that in niobates, and the deformation (ν_4) and translational (T_2 and T_3) vibration frequencies are higher in the case of niobates.

Based on the foregoing, the following conclusions may be drawn. The translations of the lanthanide atoms occupying the octahedral positions are manifested in the frequency region 175—215 cm^{-1}. The T_2 vibration frequencies depend slightly on the presence of either barium or strontium alkaline earth cations occupying the cubo-octahedral positions. The nature of the atoms located at the octahedral positions exerts a great effect on the vibration frequencies. For lutetium and niobium compounds, the frequencies are higher than for lanthanum and tantalum compounds. Of the two major determining factors (the mass of the vibrating ions and the character of the interaction between them), the frequency of the T_2 vibration in the series of lanthanides is mostly governed by the dynamic factor. The data available imply that the T_3 translational vibrations predominantly involve cations occupying cubo-octahedral positions. The T_3 frequencies are 110—122 cm^{-1} for barium compounds and 130—135 cm^{-1} for strontium compounds.

A study of phase ratios in the $SrO—La_2O_3—Nb_2O_5$ system showed the presence of an extended homogeneity region based on the $Sr_6Nb_2O_{11}$ double oxide. This is accounted for by the fact that strontium can be replaced by lanthanum and the vacancies in the oxygen sublattice of the cryolite-type structure of the double oxide can be filled. Depending on the conditions of the synthesis, the corresponding specimens can be prepared as the phase of either a cubic or a tetragonal system.

The vibrational spectrum of the $Sr_4Nb_2O_9$ phase corresponding to the solid solution with the completely filled oxygen sublattice (the composition can be represented as $Sr_4(Sr_{4/3}Nb_{2/3})Nb_2O_{12}$) has been described.[31] Unfortunately, the Raman spectra of the cubic and tetragonal modifications of the solid solutions[32] have only been studied in the frequency region above 200 cm^{-1}. The frequencies corresponding to the vibrations of strontium cations in octahedral and cubo-octahedral positions could not be detected due to strong Rayleigh scattering of the exciting line.

The character of the spectrum as a whole for all of the compositions in the homogeneity region remains the same; the spectra undergo monotonic variations when a part of the strontium is replaced by lanthanum. For phases of the cubic modification, the frequency of the symmetrical stretching vibration of the NbO_6 octahedra noticeably decreases initially, as the proportion of lanthanum increases, and then starts to increase. This behavior is explained by the redistribution of the electron density and weakening of the Nb—O bond due to the disposition of lanthanum atoms in the octahedral positions followed by strengthening of these bonds, which is due to the redistribution of the cations and filling of the cubo-octahedral positions with lanthanum atoms. Transition of the cubic modification into the low-temperature tetragonal modification results in equalization of the intensities of the two bands of the symmetrical stretching vibrations (evidence for the ordering of the arrangement of the cations and oxygen vacancies in the crystal lattice) accompanied by some decrease in their frequencies.

The presence of the general perovskite motive as well as the similarity of the dimensional parameters of the crystal lattice and the ion radii of the cations predetermined the possibility of the formation of solid solutions in the $Ba_2LaTaO_6—M_3^{II}WO_6$ systems (M^{II} is Sr, Ba).[33] The general patterns of the Raman spectra indicate that the perovskite motive of the structure is retained in these phases. However, despite the fact that the unit cell parameters of the starting components differ insignificantly, the spectra are characterized by essential distinctions, which allow one to follow structural variations as a function of the concentrations.

In the region of symmetrical stretching vibrations, variation of the number of lines (from one to four) and their displacement occurs. The lines corresponding to the deformations of the $B''O_6$ octahedra (350—450 cm^{-1}) were found to shift to the high-frequency region as the content of tungsten increases. This may be due to the gradual replacement of lanthanum in octahedral positions by strontium or barium, which should result in a higher localization of the electron density and the vibrations at the $B''O_6$ octahedra. Most stable are the frequencies (~100 cm^{-1}) of the vibrations of strontium and barium cations in cubo-octahedral positions. On the basis of the variations observed in the spectra, it has been shown that these systems do not form a continuous succession of solid solutions, and the phases containing 100, 80—40, and 20—0 mol. % of Ba_2LaTaO_6 for the Ba_2LaTaO_6—Ba_3WO_6 system and 100—80, 60—20, and 0 mol. % for Ba_2LaTaO_6—Sr_3WO_6 fall in different homogeneity regions.

By substituting magnesium for half of the alkaline earth metal cations in niobates and tantalates $M_2^{II}LnB''O_6$ (M^{II} is Ca, Sr, Ba), compounds of a more complex composition, $M_2^{II}LnMgB''O_6$, were prepared. Magnesium cations having small ion radii, comparable with those of niobium and tantalum cations, do not leave an alternative for other cations, and on the isomorphous substitution, they must be disposed in the oxygen octahedra either in a statistical or in an ordered fashion. The latter case is apparently realized in $BaLaMgNbO_6$ and $BaLaMgTaO_6$, since their spectra[34] coincide to the greatest extent with those allowed by the selection rules for the ordered cubic perovskite. The Raman spectra of all of the niobates each exhibit one line corresponding to the symmetrical stretching vibration of the oxygen octahedra. For tantalates, the second component of this vibration has been recorded at a lower frequency, which decreases with an increase in the size of the alkali earth metal cation.

The $T_1(F_{2g})$ vibrations of barium cations occupying the A positions account for the lines at 122 and 124 cm^{-1} in the Raman spectra of Ba-containing compounds; these lines transform into multiplets in the case of the strontium (170—200 cm^{-1}) and calcium (150—260 cm^{-1}) phases. These frequencies as a whole are sensitive to the calcium (^{40}Ca—^{44}Ca) and magnesium (^{24}Mg—^{26}Mg) isotope substitution. The manifestation of the isotope effect with respect to magnesium has been attributed to the decrease in the symmetry of the crystal lattice or the possibility that vibrations of relatively light magnesium cations would be excited by the vibrations of other sublattices. Whereas the positions of the bands corresponding to the $T_2(F_{1u})$ vibrations virtually do not vary in the spectra of all of the compounds, the $T_3(F_{1u})$ vibration frequencies grow on going from tantalates to niobates and in the series of alkaline earth metals, from barium to calcium, which is unambiguously determined by masses of the cations. This implies that the T_3 vibration involves cations located both in A and in B positions. However, it turned out that this vibration does not undergo an isotopic shift with respect to magnesium. It has been suggested that the mass of the vibrating cationic system is too great to be sensitive to the isotope substitution of a light cation.

* * *

All of the compounds with the perovskite structure considered exhibit a common trend for a decrease in the symmetry when alkali metal cations in the octahedral positions are replaced by alkaline earth metal or lanthanide cations. As this takes place, the vibrations become less characteristic, their interaction increases, and the conditions for the occurrence of various types of oxygen coordination octahedra arise. Nevertheless, the spectra of almost all of the phases considered can be advantageously interpreted based on irreducible representations of the vibrations of crystals with the ordered cubic perovskite structure, $A_2B'B''O_6$. The vibration frequencies of the cations in octahedral and cubo-octahedral positions are generally sufficiently characteristic, and the regularities of their behavior identified make it possible to reveal the manner in which the cations are distributed throughout the crystallographic positions of a perovskite-type structure, specifically, after an isomorphous substitution. Analysis of the behavior of vibrations of the $B''O_6$ octahedra allows one to determine the limits of the homogeneity regions of solid solutions, in some cases, more accurately than is done relying only on the data of the X-ray phase analysis, and to study characteristic features of their structure and the character of the effect of various components on the system as a whole.

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