ISSN 1070-3632, Russian Journal of General Chemistry, 2006, Vol. 76, No. 5, pp. 677–681. © Pleiades Publishing, Inc., 2006.
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An IR and Raman Study of Trigonal Triple Molybdates $\mathbf{M^{I}_{5}M^{II}_{0.5}Hf_{1.5}(MoO_4)_6}$ ($\mathbf{M^{I}}$ = K, Tl; $\mathbf{M^{II}}$ = Ca, Sr, Ba, Pb)

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Received March 15, 2005

Abstract — The vibration spectra of triple molybdates $M^{I}_{5}M^{II}_{0.5}Hf_{1.5}(MoO_4)_6$ (M^{I} = K, Tl; M^{II} = Ca, Sr, Ba, Pb) were examined. The internal vibration frequencies of molybdate groups were assigned. The double-charged cations affect the symmetric stretching (ν_1), bending, and translation vibration frequencies in the Raman spectra. In the IR spectra, the triply degenerate stretching vibration of the MoO_4 group (~890–720 cm^{-1}) is split, and the splitting increases with an increase in the radius of the double-charged cation.

DOI: 10.1134/S1070363206050021

In the systems $M^{I}_{2}MoO_4$–$M^{II}MoO_4$–$Hf(MoO_4)_2$ (M^{I} = K, Tl; M^{II} = Ca, Sr, Ba, Pb), we revealed formation of triple molybdates $M^{I}_{5}M^{II}_{0.5}Hf_{1.5}(MoO_4)_6$ in the subsolidus region (550–600°C). We performed a single crystal X-ray diffraction study of $K_5Pb_{0.5}\cdot Hf_{1.5}(MoO_4)_6$ in collaboration with the Institute of Inorganic Chemistry, Siberian Division, Russian Academy of Sciences [1]. The trigonal unit cell parameters refined with an APEX-X8 diffractometer (MoK_α radiation, graphite monochromator, $2\theta_{max}$ 65°) are as follows: $a = b = 10.739(2)$, $c = 37.933(9)$ Å; $V = 3789(1)$ Å^3, $Z = 6$, $\rho_{calc} = 4.014$ g cm^{-3}. The choice of the space group, $R\bar{3}$, was based on analysis of systematic absences in the intensity set, supported by the statistical test.

The crystal structure of the molybdate is a three-dimensional mixed framework formed by alternating Mo tetrahedra (two kinds) and Pb and Hf octahedra, sharing common O vertices. Three kinds of potassium cations are accommodated in large voids of the framework. The molybdenum atoms occupy two crystallographically independent general positions of the C_1 symmetry. The Pb atoms are located in a singular point of inversion axis $\bar{3}$ inside the octahedron, with the Pb–O distances of 6 × 2.405(9) Å. One of the Hf atoms, Hf(1), is located in the similar point of inversion axis $\bar{3}$ [Hf–O 6 × 2.074(6) Å], and the other atom, Hf(2), on rotation axis 3 [Hf–O 3 × 2.068(6) + 3 × 2.093(5) Å]. Both hafnium atoms are located inside slightly deformed octahedra. The potassium cations of three kinds are located inside large polyhedra. The K(1) atoms are located on 3-axes inside nine-vertex polyhedra with K–O distances of 3 × 2.817(7), 3 × 3.104(9), and 3 × 3.105(7) Å. The K(2) atoms in the nearest coordination surrounding have six O atoms at distances of 2.761 and 2.949 Å, forming a very flattened octahedron. To obtain a more isometric polyhedron, the coordination sphere is supplemented with six remote O atoms (3 × 3.676 and 3 × 3.851 Å) to obtain a 12-vertex polyhedron. The K(3) atom in the general position forms a relatively isometric ten-vertex polyhedron with the K–O distances varying from 2.738 to 3.402 Å.

In contrast to the previously studied structure of $K_5Mg_{0.5}Zr_{1.5}(MoO_4)_6$ (*R*3*c*) [2–4], in the structure of $K_5Pb_{0.5}Hf_{1.5}(MoO_4)_6$ the Pb and Hf atoms are arranged in different crystallographic positions because of their essentially different ionic radii; as a result, the space group of this compound is different.

In this study we consider series of compounds isostructural with $K_5Pb_{0.5}Hf_{1.5}(MoO_4)_6$ and containing Ca, Sr, Ba, or Pb as a bivalent element and K or Tl as a univalent element. Our goal was to reveal structural features and correlations between the structure and vibrational spectra in this series of compounds.

The vibration frequencies in the IR and Raman spectra of the triple molybdates are given with the assignments in Tables 1 and 2.

In the spectra of the triple molybdates, we can distinguish the frequencies of internal vibrations of MoO_4 groups and of external vibrations (of cationic sublattices and MoO_4 tetrahedra as a whole). This pattern is primarily determined by the structural features of the compounds: presence of discrete tetrahedral groups with relatively strong Mo–O bonds. The

Table 1. Vibration frequencies in the IR spectra of triple molybdates $M^I_5M^{II}_{0.5}Hf_{1.5}(MoO_4)_6$, cm^{-1}

M^I, M^{II}							Assignment
K, Ca	K, Sr	K, Pb	Tl, Ca	Tl, Sr	Tl, Pb	Tl, Ba	
942	947	945	934	939	945	941	$\nu_1(MoO_4)$
921		920					
905	910			906	907	909	
886	882	881	884	886	887	886	$\nu_3(MoO_4)$
853	845		849	845	847	843	
		824	829	828	826		
814	807	804	800	792	805	791	
739	744	744			737	741	
	729	724	731	727	727	723	

Table 2. Vibration frequencies in the Raman spectra of triple molybdates $M^I_5M^{II}_{0.5}Hf_{1.5}(MoO_4)_6$, cm^{-1}

M^I, M^{II}							Assignment
K, Ca	K, Sr	K, Pb	Tl, Ca	Tl, Sr	Tl, Pb	Tl, Ba	
	953						$\nu_1(MoO_4)$
941	945	945	932	934	935	940	
925	921	912	902	905	900	903	
	885		893	884			$\nu_3(MoO_4)$
877		868	877		877		
851	847	838		832	836	836	
830	827			809	810	808	
728	728	727					
354	346	343	354	352	339	338	$\nu_4(MoO_4)$
322	320	318	320	317	314	323	$\nu_2(MoO_4)$
297	295	295	292	289	288	288	
	202	199					Libration of MoO_4
	159	159	158	154	155	155	
111			110	112	113	113	Translation of MoO_4
90	95	94		96	96		

vibration bands of the cationic sublattices can be assigned taking into account trends in their variation in the series Ca–Ba.

In the internal field of the crystal of the $R\bar{3}$ symmetry, the local symmetry of the complex ion MoO_4 decreases to C_1 [5]. If a molecule or ion is located in the crystal in a general position, i.e., not on a symmetry element of the crystal (C_1), all the degenerate vibrations should split under the action of the crystal field. Relatively low symmetry of the Mo–O tetrahedra also suggests the IR activity of components of the fully symmetric stretching vibration. Thus, the ν_3 and ν_4 modes are split into three bands (3*A*); the ν_2 mode is split into two bands (2*A*); and the ν_1 mode becomes IR-active.

Another factor complicating the spectra of crystalline substances is coupling of vibrations of several molecules or ions in a unit cell of a crystal [5]. This coupling often causes splitting of even nondegenerate internal modes of molecules in the spectra of crystals. The vibration coupling of particles is associated with changes in the dipole moment at vibration and therefore is termed dipole–dipole interaction. The strongest splitting is observed for IR-active modes involving large changes in the dipole moment. Consideration of the resonance interaction of several polyatomic ions in a unit cell results in the transition from the representations of the local group of the MoO_4 tetrahedron to the representations of factor group C_{3i} of the crystal space group:

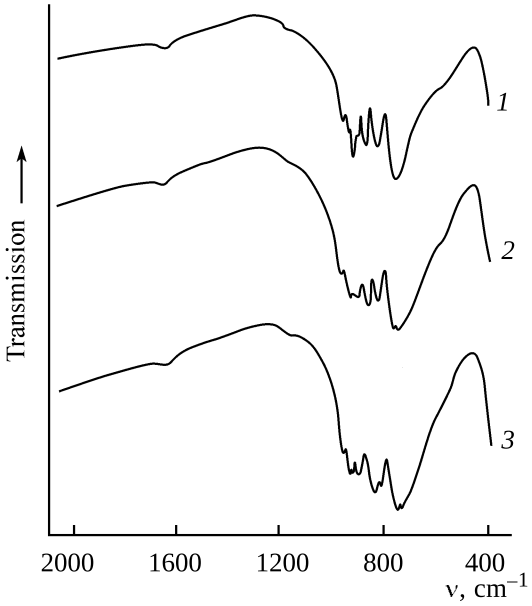

Fig. 1. IR spectra of triple molybdates (*1*) $K_5Ca_{0.5}Hf_{1.5}\cdot(MoO_4)_6$, (*2*) $K_5Sr_{0.5}Hf_{1.5}(MoO_4)_6$, and (*3*) $K_5Pb_{0.5}\cdot Hf_{1.5}(MoO_4)_6$.

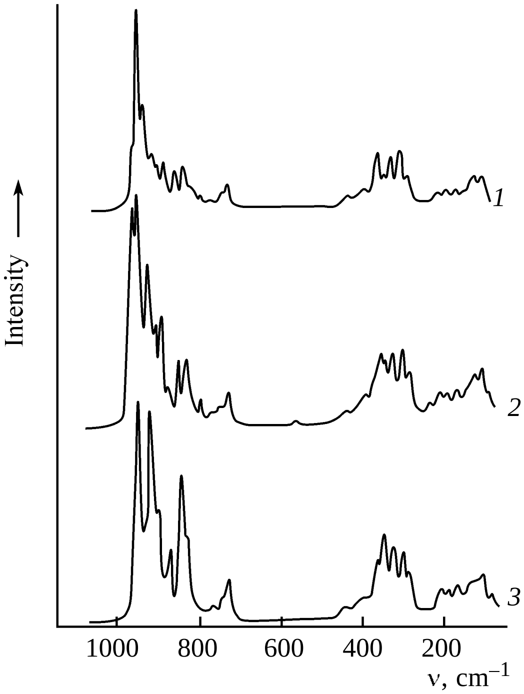

Fig. 2. Raman spectra of triple molybdates (*1*) $K_5Ca_{0.5}\cdot Hf_{1.5}(MoO_4)_6$, (*2*) $K_5Sr_{0.5}Hf_{1.5}(MoO_4)_6$, and (*3*) $K_5Pb_{0.5}Hf_{1.5}(MoO_4)_6$.

$$\nu_1\text{: } A_1(\mathrm{Td}) \rightarrow A(C_1) \rightarrow A_g + E_g + A_u + E_u \ (C_{3i}),$$

$$\nu_2\text{: } E(T_d) \rightarrow 2A(C_1) \rightarrow 2A_g + 2E_g + 2A_u + 2E_u \ (C_{3i}),$$

$$\nu_3 \text{ and } \nu_4\text{: } F_2(T_d) \rightarrow 3A(C_1) \rightarrow 3A_g + 3E_g + 3A_u + 3E_u \ (C_{3i}).$$

In a centrosymmetrical crystal, the mutual exclusion principle for vibrations of a polyatomic ion is preserved: The modes symmetric with respect to the inversion center (*g* modes) are Raman-active and IR-inactive.

The group-theory analysis in the approximation of factor group C_{3i} of crystals of space group $R\bar{3}$, $\Gamma_{\mathrm{int}} = 9A_g(\mathrm{Raman}) + 9E_g(\mathrm{Raman}) + 9A_u(\mathrm{IR}) + 9E_u(\mathrm{IR})$, suggests the presence of 18 IR-active and 18 Raman-active frequencies.

In the experimental spectra we observe 6–8 IR absorption bands in the range 1000–400 cm^{-1} and 9–13 Raman bands in the range 1000–90 cm^{-1} (Figs. 1–4). The bands at 980–700 (stretching) and 410–300 cm^{-1} (bending) are assigned to internal vibrations of MoO_4 groups, taking into account the relationships found previously [6].

The inconsistency between the theoretically predicted and actually observed numbers of Raman and IR bands, the low symmetry of the positions of the Mo atoms, and the large unit cell volume allow the spectra to be analyzed in the site group approximation. To a first approximation, the vibration spectra are consistent with the results of the site analysis. However, strong bands at ~950–900 cm^{-1} in the IR and Raman spectra are split into two or three components (Figs. 1–4). The factor-group splitting of the ν_1 mode does not exceed 38 cm^{-1}. As expected, the IR bands are split to a greater extent.

In the Raman spectrum, the double-charged cations affect the vibrations that are close in energy to the fundamental vibrations of the cationic sublattice, namely, the bending vibrations. The ν_4 frequencies decrease in going from Ca to Ba by 11–16 cm^{-1} (Table 2). Consideration of the spectra of neutral alkaline-earth molybdates and tungstates (scheelites) shows that the ν_1 frequency (fully symmetric mode) increases in the series Ca–Sr–Ba to the greatest extent [7]. It should be noted that, whereas the higher-frequency line of the Raman spectrum is sensitive only to isotope substitution of calcium, the two low-frequency lines are sensitive to isotope substitution of both calcium and molybdenum. This fact indicates that the subdivision of translation modes into those involving calcium and molybdenum atoms, based on consideration of the symmetry coordinates, is largely conventional, especially at lower ratios of the atomic weights of cations in the compounds. For the double-

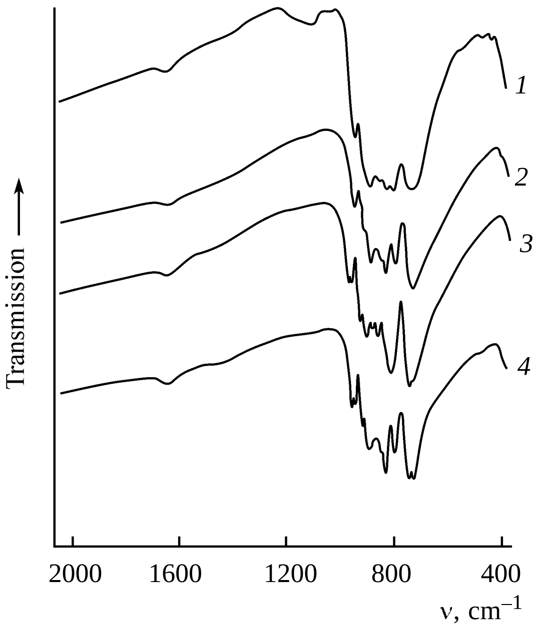

Fig. 3. IR spectra of triple molybdates (*1*) $Tl_5Ca_{0.5}Hf_{1.5}\cdot(MoO_4)_6$, (*2*) $Tl_5Sr_{0.5}Hf_{1.5}(MoO_4)_6$, (*3*) $Tl_5Pb_{0.5}Hf_{1.5}\cdot(MoO_4)_6$, and (*4*) $Tl_5Ba_{0.5}Hf_{1.5}(MoO_4)_6$.

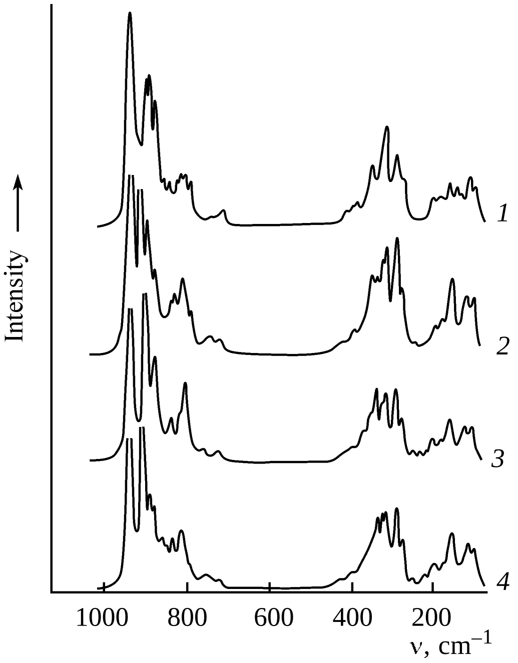

Fig. 4. Raman spectra of triple molybdates (*1*) $Tl_5Ca_{0.5}\cdot Hf_{1.5}(MoO_4)_6$, (*2*) $Tl_5Sr_{0.5}Hf_{1.5}(MoO_4)_6$, (*3*) $Tl_5Pb_{0.5}\cdot Hf_{1.5}(MoO_4)_6$, and (*4*) $Tl_5Ba_{0.5}Hf_{1.5}(MoO_4)_6$.

charged cations that are heavier than Mo (Ba, Pb), this subdivision is not sufficiently correcrt, and the low-frequency modes correspond to collective vibrations of all the cations. In the Raman spectra of the compounds considered in this study, the ν_1 frequency is also the most sensitive to the kind of the double-charged cation, increasing by 8–12 cm^{-1} in going from Ca to Ba; the frequency of the translation mode (~110 cm^{-1}) also increases in going from Ca to Ba (by 1–2 cm^{-1}). Also, the spectra contain lines corresponding to the translation and libration modes of MoO_4 tetrahedra (159, 155, 96 cm^{-1}); these frequencies should not vary in the series studied [8].

It should be noted that the vibrations of the K (or Tl) sublattice are inactive in the Raman spectrum [9].

The range of the experimental IR spectra covers the stretching modes only. A decrease in the symmetry of the local position of the molybdate groups to C_1 led to splitting of the $\nu_3(F_2)$ mode into three components (~890–720 cm^{-1}). The factor-group splitting of each degenerate mode increases with an increase in the radius of the double-charged cation (Figs. 1, 3).

In addition, in going from Tl to K, the stretching frequencies in the IR and Raman spectra show a long-wave shift.

Analysis of the ν_1 and ν_3 stretching frequencies allows certain assumptions concerning the structure of triple molybdates $M^I_5M^{II}_{0.5}Hf_{1.5}(MoO_4)_6$. Being located between the Mo–O tetrahedra, the double-charged cations exert a perturbing effect primarily on the vibrations that are close in the energy to the fundamental vibrations of the cationic sublattice, namely, on the bending vibrations. The effect of double-charged cations in the series Ca–Sr–Pb–Ba on the electrophysical properties of the compounds will be the subject of further studies.

EXPERIMENTAL

The IR spectra of polycrystalline samples were recorded on a Scimitar FTS-2000 Fourier IR spectrometer in the range 1000 – 400 cm^{-1}. Samples were prepared as KBr pellets. The Raman spectra were recorded on a Triplemate-Spex spectrometer. The excitation wavelength was 488 nm.

ACKNOWLEDGMENTS

The authors are grateful to L.A. Sheludyakova for recording the IR spectra and to R.F. Klevtsova and L.A. Glinskaya for a single crystal X-ray diffraction study of $K_5Pb_{0.5}Hf_{1.5}(MoO_4)_6$.

The study was supported by the Russian Foundation for Basic Research (project no. 04-03-32714) and by the basic research program of the Presidium of the Russian Academy of Sciences (no. 9.5).

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