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Synthesis and Crystal Structure of New Complex Sodium Lanthanide Phosphate Molybdates $Na_2M^{III}(MoO_4)(PO_4)$ (M^{III} = Tb, Dy, Ho, Er, Tm, Lu)

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Abstract—New complex sodium lanthanide phosphate molybdates $Na_2M^{III}(MoO_4)(PO_4)$ (M^{III} = Tb, Dy, Ho, Er, Tm, Lu) have been synthesized by the ceramic method (T = 600°C, τ = 48 h), and their unit cell parameters have been determined. The structures of $Na_2M^{III}(MoO_4)(PO_4)$ (M^{III} = Dy, Ho, Er, Lu) were refined by the Rietveld method. The compounds are isostructural: they are orthorhombic (space group *Ibca*, $Z = 8$) and have layered structures. In the structures of phosphate molybdates, chains of $M^{III}O_8$ polyhedra and MoO_4 tetrahedra are linked by PO_4 tetrahedra to form layers. The MoO_4^{2-} anions are involved in dipole–dipole interaction. The sodium ions are arranged in the interlayer space. The compounds melt incongruently at 850–870°C.

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New materials based on inorganic phosphates have been sought for many years. Information on individual compounds containing, in addition to PO_4 tetrahedra, other differently charged tetrahedral groups with two cations is rather scanty and only concerns compounds of three compositions. Phosphate sulfates $KM_3(SO_4)_2(PO_4)$ (M = Sr, Ba, Pb) [1] have a cubic eulitine-type structure. The compound $Na_3Ba(MoO_4)(PO_4)$ [2], as well as double phosphates of singly and triply charged cations, have a glaserite-type structure. Compounds $M^I_2M^{III}(EO_4)(PO_4)$ (M^I = Na, M^{III} = La, $EO^4 = S_2O_3$; M^I = Na, M^{III} = Y or Yb, $EO_4 = MoO_4$; M^I = K, M^{III} = Yb, $EO_4 = MoO_4$; M^I = Li, M^{III} = Fe, $EO_4 = SO_4$) [3–6] form original layered structures, all phosphate molybdates being isostructural. Only $Li_2Fe(SO_4)(PO_4)$ has a NASICON structure. A combination of two triply charged anions leads to the formation of solid solutions $K_3M^{III}(PO_4)_x(VO_4)_{2-x}$ (M^{III} = Y, La, Eu, Gd, Yb) [7].

In the present paper, we report the results of studying sodium lanthanide phosphate molybdates $Na_2M^{III}(MoO_4)(PO_4)$ (M^{III} = Tb–Lu), their synthesis, structure, and thermal stability.

EXPERIMENTAL

Sodium lanthanide phosphate molybdates were synthesized by the temperature-programmed solid-phase reaction of stoichiometric amounts of $Na_2MoO_4 \cdot 2H_2O$ (chemically pure, Russian State Standard), $M_2^{III}O_3$ (chemically pure), and $NH_4H_2PO_4$ (pure for analysis) or by the reaction of sodium molybdate with $M^{III}PO_4 \cdot xH_2O$ precipitated from aqueous solutions. Samples were ground every 24 h to ensure homogenization. The completeness of the reaction was monitored by X-ray powder diffraction. The highest synthesis temperature was 750°C. New compounds as polycrystalline samples were identified by X-ray diffraction even at the stage of annealing at 600°C.

X-ray powder diffraction analysis was carried out on a Siemens D500 diffractometer ($CuK_{\alpha1}$ radiation, λ = 1.5406 Å, reflection geometry, scintillation detector, SiO_2 monochromator, scan step 0.02° (2θ), 2θ range 5°–60° with a counting time of 1 s per step). The TREOR-90 program and the STOE WinXPOW software were used for analysis and primary processing of experimental data. Phase analysis was performed with the use of the JCPDS PDF-2 database.

A set of experimental data for X-ray crystallography was collected on the same diffractometer in the 2θ range 5°–100° with the scan step 0.02° and the counting time 10 s per step. Corundum (Al_2O_3) was used as the external reference.

Crystal structures were refined by the full-profile Rietveld method [8] using the JANA 2000 program package [9].

Table 1. Unit cell parameters and the results of refinement of some structures of sodium lanthanide phosphate molybdates ($Na_2M^{III}(MoO_4)(PO_4)$) (M^{III} = Tb–Lu)

Parameter	Tb	Dy	Ho	Er	Tm	Lu
2θ range, deg	5–120	5–105	5–105	5–105	5–60	5–125
scan step, deg	0.02	0.02	0.02	0.02	0.02	0.02
I_{max}, counts	44474	37740	34634	31657	2255	36804
Unit cell parameters:						
a, Å	17.9849(2)	17.9927(2)	18.0010(2)	18.0104(1)	18.012(2)	18.0186(2)
b, Å	12.1989(2)	12.1553(1)	12.1162(1)	12.0825(1)	12.053(1)	11.9973(1)
c, Å	6.9129(1)	6.8775(1)	6.8543(1)	6.8256(1)	6.803(1)	6.7537(1)
V, Å^3	1516.70(3)	1504.17(3)	1494.97(3)	1485.34(2)	1476.8(3)	1459.99(2)
Number of Bragg reflections	479	392	388	386	108	549
Reliability factors:						
R_p, R_{wp}, %	6.95, 9.25	5.43, 7.45	6.06, 8.13	4.48, 5.77		7.03, 9.20
F_{20}					175	

The IR spectra were recorded as mineral oil or hexachlorobutadiene mulls on a Perkin Elmer 1600 FTIR spectrophotometer in the range 400–4000 cm^{-1}.

Thermogravimetric (TGA) and differential thermal analyses (DTA) were carried out on a Q-1500 derivatograph and a Setaram DSC 2000K differential scanning calorimeter. Sample weights were 100–150 mg (Q-1500) and 10–20 mg (DSC 2000K). Samples were heated in alundum crucibles under an inert gas flow at a rate 20 K/min in the range 20–500°C and 10 K/min in the range 500–900°C.

RESULTS AND DISCUSSION

Analysis of the X-ray diffraction patterns of all synthesized sodium lanthanide phosphate molybdates shows that they are isostructural and have a structure similar to that of the first representative of this family $Na_2Yb(MoO_4)(PO_4)$ [5]. The orthorhombic unit cell parameters were determined in the course of primary data collection (Table 1). The following trends in the change in the crystal parameters of isostructural compounds were observed: as the radius of the triply charged cation decreases, the *a* parameter slightly increases while the *b* and *c* parameters and, especially, the unit cell volume linearly decrease to a significant extent (Fig. 1). In X-ray diffraction patterns of the series of the Tb–Lu derivatives, the reflections are slightly shifted toward larger angles (Fig. 2).

Based on systematic absences ($h + k + l = 2n$; $hk0$: $h, k = 2n$; $h0l$: $h, l = 2n$; $h00$: $h = 2n$; $00l$: $l = 2n$), the structures of the compounds $Na_2M^{III}(MoO_4)(PO_4)$ (M^{III} = Tb, Dy, Ho, Er, Lu) were refined in space group *Ibca* (no. 73) (Table 1). The atomic coordinates in sodium ytterbium phosphate molybdate [5] were used as the initial positional parameters in the refinement.

The refined atomic coordinates and isotropic thermal parameters for the structures of some representatives of this family are listed in Table 2, and the interatomic distances are presented in Table 3.

The lanthanide atoms in the structures of $Na_2M^{III}(MoO_4)(PO_4)$ are located in special positions (Fig. 3) and are bound to eight-vertex arrays of oxygen atoms. The $M^{III}O_8$ polyhedra share an edge (along the *c* axis) to form zigzag chains, their convex and concave parts alternating. Neighboring chains of $M^{III}O_8$ polyhedra are linked through PO_4 tetrahedra by edge sharing to form layers in the *bc* plane. In the layer, a convex part of one chain is linked to a concave part of a neighboring chain. With a decrease in the ionic radius of $M^{III,}$ the average M^{III}–O distance somewhat increases in the range 2.38–2.45 Å, the average P–O distance (1.495–1.51 Å) remaining virtually unaltered.

The molybdenum atoms, like the phosphorus and lanthanide atoms, are located in special positions. Two neighboring polyhedra in lanthanide chains are linked by edges of two MoO_4 tetrahedra. The MoO_4 tetrahedra are linked only to $M^{III}O_8$ polyhedra and are not connected with each other. The other two vertices point to the interlayer space and do not link two layers. The change in the ionic radius of the triply charged cation has no effect on the average Mo–O distance in tetrahedra. The Mo–O distances, as well as the P–O distances, are pairwise identical; correspondingly, the M^{III}–O distances are also pairwise identical since the $M^{III}O_8$ polyhedra are formed by six oxygen atoms from PO_4 tetrahedra and two oxygen atoms from MoO_4 tetrahedra.

Sodium cations in the structures occupy the interlayer space and are located in the general position. The average Na–O distance in NaO_6 polyhedra decreases

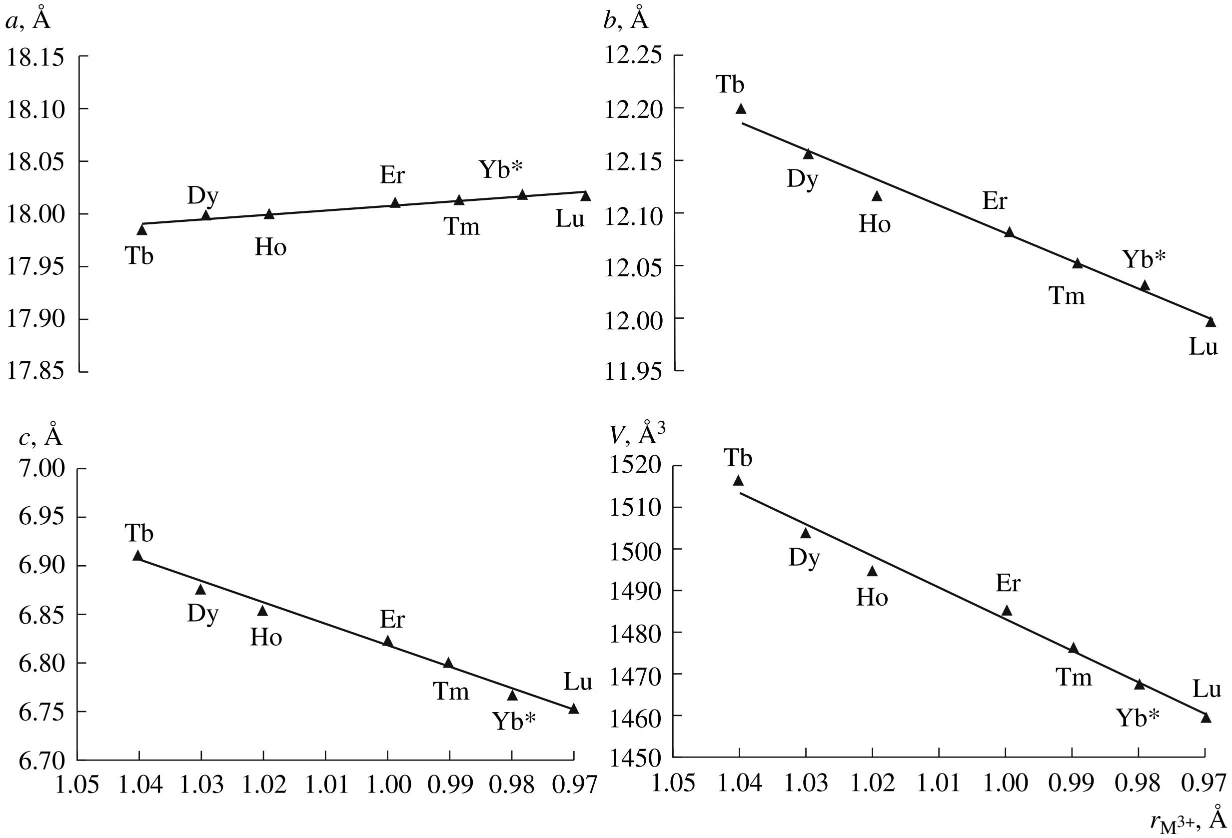

Fig. 1. Unit cell parameters of $Na_2M^{III}(MoO_4)(PO_4)$ vs. the radius of the M^{III} cation (CN = 8). * Parameters were taken from [5].

with a decrease in the radius of a triply charged cation. This change is contributed by the distances to the oxygen atoms from MoO_4 tetrahedra (O(1) and O(2)). The sodium polyhedron is formed by three oxygen atoms from two PO_4 tetrahedra and three oxygen atoms from three MoO_4 tetrahedra (Fig. 4). In the structures of $Na_2M^{III}(MoO_4)(PO_4)$, the NaO_6 polyhedra are combined into two parallel chains (along the *c* axis) by edge sharing.

The structure of sodium lanthanide phosphate molybdates is a derivative of the xenotime (YPO_4) structure [10], typical of late lanthanide orthophosphates.

In the xenotime framework structure, layers can be discerned that are made of chains of $M^{III}O_8$ polyhedra in the *ac* and *bc* planes, the chains being connected to one another by edges of PO_4 tetrahedra. This type of layer is typical of the framework structures of the minerals zircon $ZrSiO_4$ [11] and anhydrite $CaSO_4$ [12] and sodium perchlorate $NaClO_4$ [13]. The complication of the cationic component of the xenotime structure by the introduction of alkali-metal cations leads to loosening of the initial framework and formation of layered structures with discrete $M^{III}O_{8\pm1}$ polyhedra. Such a structure is typical of glaserite- and arcanite-type compounds $M^I_3M^{III}(PO_4)_2$ [14]. Changing the anionic part by combination of the PO_4^3 anion with differently charged tetrahedral anions makes it possible to obtain compounds with a layered structure. This structure contains the chains of $M^{III}O_8$ polyhedra linked by PO_4 tetrahedra to form layers as in xenotime. In the structures of $Na_2M^{III}(MoO_4)(PO_4)$, sodium ions loosen the initial xenotime framework and occupy the interlayer space. Hence, the complication of the composition by the introduction of differently charged anions into the xenotime structure leads to the formation of layered phases in which chains of lanthanide polyhedra persist. This results in lowering of the unit cell symmetry (tetragonal–orthorhombic) while *I* centering is retained. In these phases, the *a* (17.98–18.02 Å) and *b* (11.99–12.19 Å) unit cell parameters are multiples of those in xenotime phosphates, while the *c* parameter (6.75–6.91 Å) is retained (Table 2), again as in xenotime phosphates (*a* = 6.79–6.94 Å, *c* = 5.95–6.07 Å).

The IR spectra of the synthesized compounds show absorption bands due to internal vibrations of PO_4^{3-} and MoO_4^{2-} ions (Table 4) [15–17]. The splitting of absorption bands of tetrahedral anions corresponds to

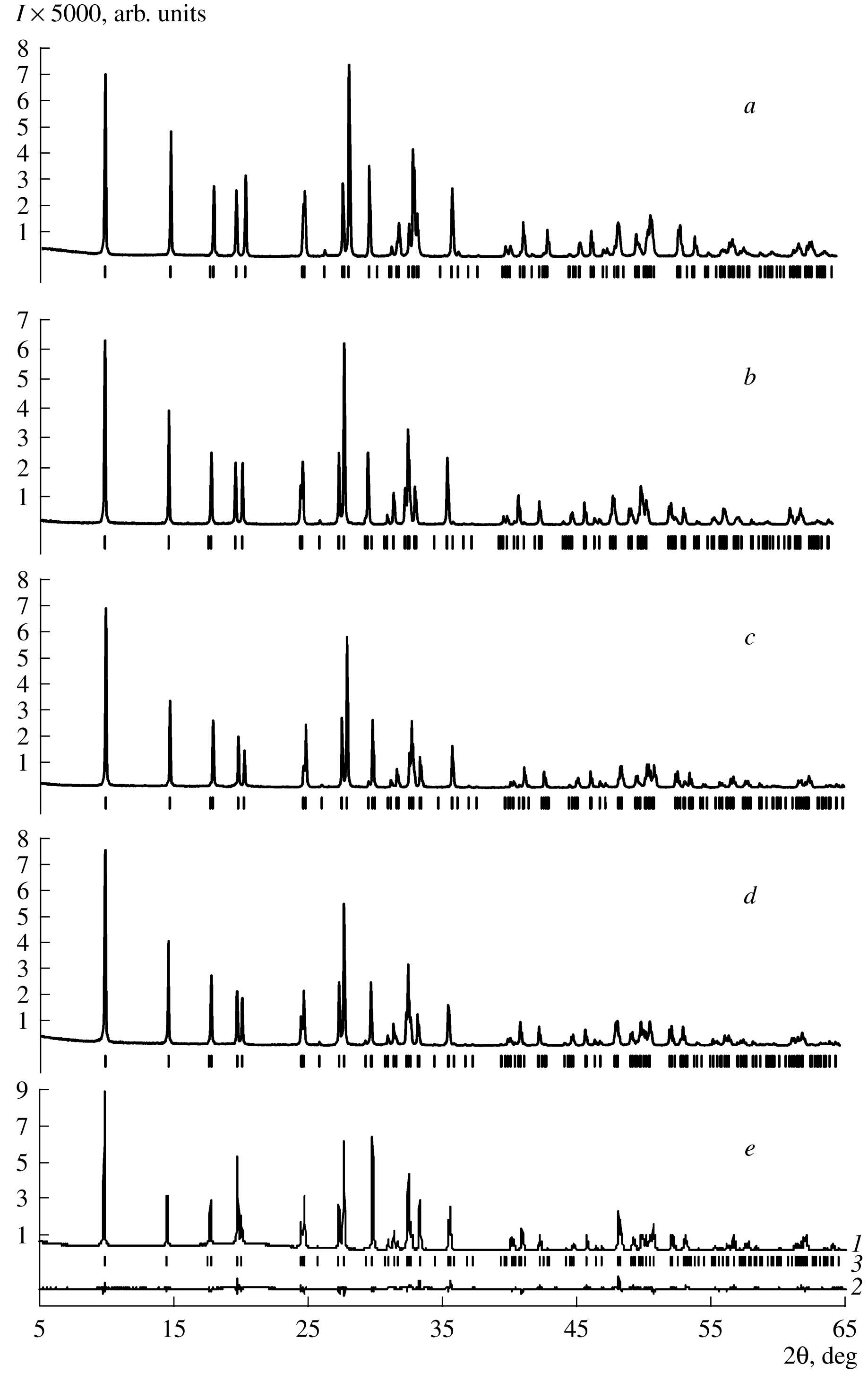

Fig. 2. Portions of the experimental X-ray diffraction spectra and positions of Bragg reflections of $Na_2M^{III}(MoO_4)(PO_4)$ for M^{III} = (*a*) Lu, (*b*) Er, (*c*) Ho, and (*d*) Dy and (*e*) a portion of the (*1*) experimental and (*2*) difference X-ray diffraction spectrum and (*3*) positions of Bragg reflections of $Na_2Tb(PO_4)(MoO_4)$.

symmetry C_2 of the position occupied by the PO_4^{3-} and MoO_4^{2-} anions in the unit cell. For this site symmetry, each of the bands of triply degenerate vibrations should be split into five components and the bands of doubly degenerate vibrations should be split into two components.

The band of the triply degenerate antisymmetric stretching vibration (ν_3 F_2) of the tetrahedral PO_4^{3-}

Table 2. Atomic coordinates and thermal parameters in the structures of $Na_2M^{III}(MoO_4)(PO_4)$ (M^{III} = Tb, Dy, Ho, Er, Lu)

Atom		Tb	Dy	Ho	Er	Lu
Na	x	0.5963(2)	0.5992(3)	0.5972(2)	0.5948(2)	0.5904(3)
	y	0.1884(5)	0.1886(5)	0.1905(5)	0.1910(5)	0.1904(6)
	z	0.272(1)	0.2719(9)	0.265(1)	0.2612(9)	0.262(1)
	U_{iso}	0.029(2)	0.043(2)	0.030(2)	0.030(2)	0.031(2)
M^{III}	x	0.75	0.75	0.75	0.75	0.75
	y	0.0716(1)	0.0719(1)	0.0719(1)	0.0721(1)	0.0715(1)
	z	0	0	0	0	0
	U_{iso}	0.0054(8)	0.0096(4)	0.0116(5)	0.0065(4)	0.0063(4)
Mo	x	0.4292(1)	0.4290(1)	0.4296(1)	0.4295(1)	0.4290(1)
	y	0	0	0	0	0
	z	0.25	0.25	0.25	0.25	0.25
	U_{iso}	0.0145(9)	0.0176(7)	0.0199(7)	0.0119(6)	0.0112(6)
P	x	0.25	0.25	0.25	0.25	0.25
	y	0.1727(5)	0.1771(5)	0.1839(5)	0.1856(5)	0.1898(6)
	z	0	0	0	0	0
	U_{iso}	0.011(1)	0.008(1)	0.013(2)	0.008(1)	0.008(2)
O(1)	x	0.3773(5)	0.3759(3)	0.3770(3)	0.3803(3)	0.3845(4)
	y	0.0257(6)	0.0256(5)	0.0263(6)	0.0255(5)	0.0247(7)
	z	0.473(1)	0.4605(8)	0.4583(8)	0.4658(7)	0.4732(9)
	U_{iso}	0.030(2)	0.013(2)	0.011(2)	0.006(1)	0.017(2)
O(2)	x	0.4895(4)	0.4805(4)	0.4841(4)	0.4844(3)	0.4827(4)
	y	0.1202(9)	0.1195(5)	0.1196(5)	0.1190(5)	0.1210(6)
	z	0.195(2)	0.198(1)	0.207(2)	0.203(1)	0.212(2)
	U_{iso}	0.030(2)	0.013(2)	0.011(2)	0.006(1)	0.017(2)
O(3)	x	0.1844(4)	0.1851(3)	0.1812(4)	0.1793(2)	0.1754(3)
	y	0.2553(5)	0.2540(4)	0.2531(4)	0.2475(4)	0.2510(5)
	z	–0.009(2)	–0.004(2)	–0.011(2)	–0.010(2)	–0.007(4)
	U_{iso}	0.008(2)	0.013(2)	0.011(2)	0.006(1)	0.012(2)
O(4)	x	0.2476(4)	0.2424(5)	0.2386(6)	0.2610(5)	0.2351(5)
	y	0.1087(6)	0.1057(5)	0.1073(5)	0.1077(5)	0.1089(6)
	z	0.183(1)	0.1775(9)	0.170(1)	0.1661(9)	0.162(1)
	U_{iso}	0.008(2)	0.013(2)	0.011(2)	0.006(1)	0.012(2)

anion is split into three components (978–985, 1082–1084, 1092–1099 cm^{-1}), whereas, for the MoO_4^{2-} tetrahedron in the IR spectra of $Na_2M^{III}(PO_4)(MoO_4)$, this band is split into four components and is observed in the range 780–860 cm^{-1}.

The spectra show absorption bands due to the symmetric stretching vibrations of PO_4 tetrahedra (1006–1020 cm^{-1}) and MoO_4 tetrahedra (913–916 cm^{-1}). The band splitting pattern allows us to draw the conclusion that the MoO_4^{2-} anions are involved in dipole–dipole interaction with one another.

Sodium lanthanide phosphate molybdates are rather thermally stable. The temperature range of their incongruent melting is 790–918°C with a maximum at 850–870°C. Their cooling curves show several exotherms, none of which corresponds to the formation of the solid phase $Na_2M^{III}(MoO_4)(PO_4)$. Comparison of the temperatures of the peaks with the data of the database "Thermal Constants of Substances" [18] showed that they correspond to the phase transitions of sodium molybdate. Hence, the decomposition of phosphate molybdates proceeds according to the scheme

$$Na_2M^{III}(MoO_4)(PO_4) \longrightarrow Na_2MoO_4 + M^{III}PO_4.$$

Table 3. Interatomic distances in the structures of $Na_2M^{III}(MoO_4)(PO_4)$ (M^{III} = Tb, Dy, Ho, Er, Lu)

Bond (Å), angle (deg)	$Na_2Tb(MoO_4)(PO_4)$	$Na_2Dy(MoO_4)(PO_4)$	$Na_2Ho(MoO_4)(PO_4)$	$Na_2Er(MoO_4)(PO_4)$	$Na_2Lu(MoO_4)(PO_4)$
Na–O(1)	2.91(1)	2.95(1)	2.93(1)	2.87(1)	2.82(1)
Na–O(2)	2.16(1)	2.35(1)	2.25(1)	2.21(1)	2.14(1)
Na–O(2')	2.85(1)	2.78(1)	2.76(1)	2.73(1)	2.64(1)
Na–O(3)	2.60(1)	2.35(1)	2.39(1)	2.40(1)	2.36(2)
Na–O(3')	2.34(1)	2.51(1)	2.40(1)	2.39(1)	2.41(2)
Na–O(4)	2.91(1)	2.78(1)	2.77(1)	2.83(1)	2.83(1)
⟨Na– O⟩	2.63	2.62	2.58	2.57	2.53
M^{III}–O(1) × 2	2.37(1)	2.35(1)	2.37(1)	2.42(1)	2.50(1)
M^{III}–O(3) × 2	2.42(1)	2.42(1)	2.45(1)	2.47(1)	2.52(1)
M^{III}–O(4) × 2	2.54(1)	2.48(1)	2.47(1)	2.46(1)	2.44(1)
M^{III}–O(4') × 2	2.24(1)	2.26(1)	2.31(1)	2.33(1)	2.34(1)
⟨M^{III}–O⟩	2.39	2.38	2.40	2.42	2.45
Mo–O(1)	1.79(1)	1.76(1)	1.74(1)	1.75(1)	1.73(1)
Mo–O(2)	1.76(1)	1.76(1)	1.78(1)	1.77(1)	1.76(1)
⟨Mo–O⟩	1.775	1.76	1.76	1.76	1.745
O(1)MoO(1)	117.7(4)	114.3(3)	114.2(3)	119.0(3)	124.9(4)
O(1)MoO(2)	107.1(5)	107.9(4)	106.7(4)	106.9(4)	103.9(5)
O(1)MoO(2)	109.1(4)	105.3(4)	108.2(4)	105.9(4)	105.5(5)
O(2)MoO(2)	106.1(3)	116.4(4)	112.9(4)	112.2(3)	113.4(4)
P–O(3)	1.49(1)	1.49(1)	1.50(1)	1.51(1)	1.53(1)
P–O(4)	1.55(1)	1.50(1)	1.51(1)	1.49(1)	1.49(1)
⟨P–O⟩	1.52	1.495	1.505	1.50	1.51
O(4)PO(4)	116.7(7)	102.7(5)	103.9(6)	101.5(5)	98.6(6)
O(4)PO(3)	106.5(6)	107.5(6)	105.9(6)	105.2(6)	100.1(9)
O(4)PO(3)	113.3(6)	114.9(7)	114.7(7)	115.3(5)	116.7(9)
O(3)PO(3)	99.1(6)	109.5(5)	111.8(6)	114.5(6)	122.7(6)

Table 4. Maximum absorption frequencies in the IR spectra of $Na_2M^{III}(MoO_4)(PO_4)$

Tb	Dy	Ho	Er	Tm	Lu	Assignment
530 s	530 s	529 s	527 s	526 s	526 s	ν_4 F_2 PO_4
537 sh	537 sh	538 sh		538 sh	538 sh	ν M^{III}–O
559 sh	555 sh	556 sh		556 sh		
574 s	575 s	575 s	573 s	572 s	574 s	ν_4 F_2 PO_4
614 s	616 s	617 s	618 s	616 s	621 s	ν_4 F_2 PO_4
783 s	780 s	782 s	783 s	782 s	782 s	ν_3 F_2 MoO_4
809 w	809 w	809 w	806 w	806 w	811 sh	ν_3 F_2 MoO_4
			829 sh		827 sh	ν_3 F_2 MoO_4
846 sh	846 sh	848 sh				
860 s	857 s	860 s	862 s	858 s	861 s	
916 m	915 s	914 s	915 s	914 s	915 s	$\nu_1 A_1$ MoO_4
978 s	981 s	980 s	983 s	980 s	985 s	ν_3 F_2 PO_4
	1006 sh		1015 sh		1020 sh	$\nu_1 A_1$ PO_4
1082 s	1084 s	1082 s	1082 s	1082 s		ν_3 F_2 PO_4
1094 sh	1099 s			1092 s	1094 s	

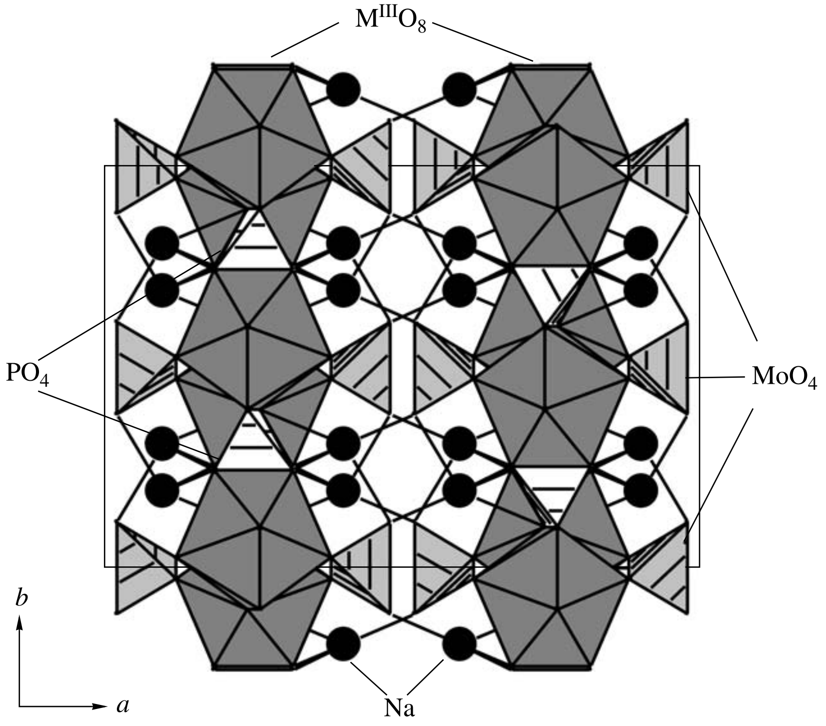

Fig. 3. General view of the structure of $Na_2M^{III}(MoO_4)(PO_4)$.

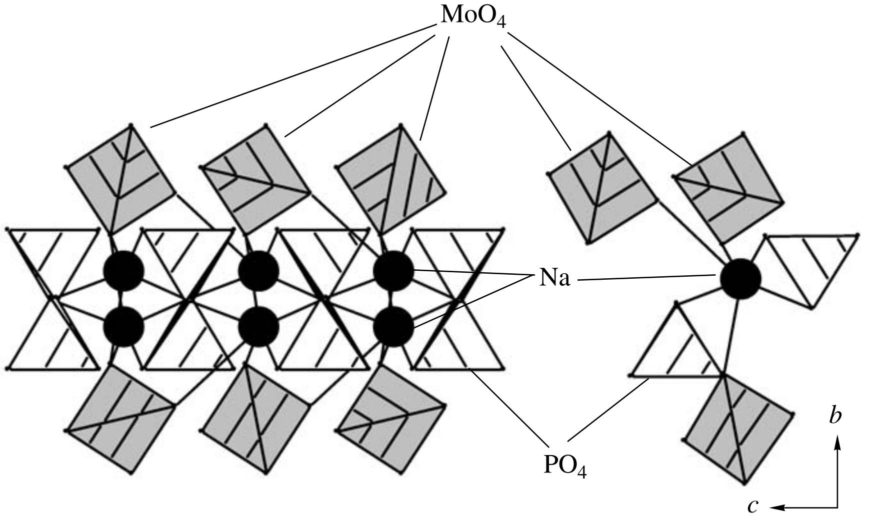

Fig. 4. Sodium ions surrounded by MoO_4 and PO_4 tetrahedra.

The formation of Na_2MoO_4 and $M^{III}PO_4$ is supported by X-ray powder diffraction analysis of the samples after thermal analysis. Complication of the composition impairs the thermal stability of the compounds. The melting point of framework lanthanide orthophosphates is as high as 2000°C, whereas the thermal stability range of $Na_2M^{III}(MoO_4)(PO_4)$ with a layered structure extends no higher than 900°C.

Thus, representatives of a new family of complex phosphates—sodium lanthanide phosphate molybdates $Na_2M^{III}(MoO_4)(PO_4)$ (M^{III} = Tb, Lu)—were synthesized. They were found to be isostructural with the previously obtained $Na_2Yb(MoO_4)(PO_4)$. They are orthorhombic crystalline compounds with a layered structure. The structure of the new sodium lanthanide phosphate molybdates turned out to be a derivative of the xenotime structure. Complication of the composition of the initial structure leads to a reduction in symmetry and a multiple increase in crystallographic parameters.

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REFERENCES

1. C. Jouber, A. Durif, and C. Martin, Bull. Soc. Fr. Miner. Crist. **89**, 523 (1966).
2. M. Quarton and W. Freundlich, J. Solid State Chem. **56**, 355 (1985).
3. M. G. Zhizhin, H. A. Pounds, F. M. Spiridonov, et al., J. Alloys Comp. **418**, 90 (2006).
4. M. Ben Amara and M. Dabbabi, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. **43**, 616 (1987).
5. L. N. Komissarova, M. A. Ryumin, A. P. Bobylev, et al., Zh. Neorg. Khim. **51** (3), 350 (2006) [Russ. J. Inorg. Chem. **51** (3), 350 (2006)].
6. A. K. Padhi, V. Manivannan, and J. B. Goodenough, J. Electrochem. Soc. **145**, 1518 (1998).
7. A. N. Kirichenko, Extended Abstract of Candidate's Dissertation in Chemistry (Moscow, 1999).
8. H. M. Rietveld, J. Appl. Crystallogr. **2**, 65 (1969).
9. V. Petricek and M. Dusek, Z. Kristallogr. **219**, 692 (2004).
10. I. Krstanovic, Z. Kristallogr. **121**, 315 (1965).
11. K. Robinson, G. V. Gibbs, and P. H. Ribbe, Am. Mineral. **64**, 196 (1979).
12. P. Hartman, Eur. J. Miner. **1**, 721 (1989).
13. R. Wartchow and H. J. Berthold, Z. Kristallogr. **147**, 307 (1978).
14. L. N. Komissarova, M. G. Zhizhin, and A. A. Filaretov, Usp. Khim. **71**, 705 (2002).
15. A. N. Lazarev, A. N. Mazhenov, and A. P. Mirgorodskii, Izv. Akad. Nauk SSSR, Neorg. Mater. **14**, 2107 (1978).
16. V. V. Vakulyuk, V. V. Fomichev, and A. A. Evdokimov, Zh. Neorg. Khim. **28** (3), 650 (1983).
17. F. M. Clark and W. P. Doule, Spektrochim. Acta, Part A **22**, 1441 (1966).
18. V. S. Iorish and P. I. Tolmach, http://www.chem.msu.su/sgi-bin/tkv.