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Complex lanthanide chromate(VI)-phosphates $K_2R(CrO_4)(PO_4)$ (R = Dy—Lu, Y)

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The conditions of formation of complex lanthanide chromate(VI)-phosphates $K_2R(CrO_4)(PO_4)$ were found and these compounds were synthesized by solid-state synthesis with variation of the starting compounds, the temperature of synthesis (500—800 °C), and the annealing time (6—200 h). These salts are typical of late lanthanides, R = Dy—Lu, Y. Using lutetium derivatives as examples, it was shown that no similar compounds with lithium or sodium are formed. All the complex chromate(VI)-phosphates obtained decompose under static conditions at temperatures above 550 °C. They are isostructural and crystallize in the monoclinic system. The unit cell parameters for thulium, ytterbium, and lutetium compounds were calculated. It is shown by IR spectroscopy that PO_4 tetrahedra in the crystal lattice of potassium lanthanide chromate(VI)-phosphates are substantially distorted, whereas the CrO_4 tetrahedra retain the regular tetrahedron symmetry (T_d).

Key words: chromates, phosphates, tetrahedral anions, lutetium, ytterbium, thulium, holmium, erbium, dysprosium, synthesis, unit cell parameters, IR spectroscopy.

Complex lanthanide chromate(VI)-phosphates $K_2R(CrO_4)(PO_4)$ represent a new group of compounds. Their investigation is of interest for both fundamental and applied purposes.

Examples of complex compositions based on AO_4 tetrahedra with variation of the anionic moiety have been reported; both individual compounds and solid solutions can be formed. For example, heterovalent replacement of the PO_4^{3-} anions by MoO_4^{2-} and $S_2O_3^{2-}$ was found to yield the $Na_2Y(PO_4)(MoO_4)$ [1] and $Na_2La(PO_4)(S_2O_3)$[2] phases, whereas isovalent replacement of the PO_4^{3-} anion in $K_3R^{III}(PO_4)_2$ and $R(PO_4)$ (R^{III} = Y, La, Eu, Gd, Yb) by VO_4^{3-} affords infinite or finite solid solutions based on the structural types characteristic of unsubstituted double phosphates or vanadates $K_3R^{III}(AO_4)_2$, $R(AO_4)$ (A = P, V).[3] Data on the chromates with a complex anionic part are quite scarce;[4—6] they have not been studied systematically, and the compounds $M^IR^{III}(CrO_4)(PO_4)$ have not been described at all.

The purpose of this study is to investigate the formation of individual compounds upon combination of two heterovalent anions in double lanthanide and alkali metal chromates at a $PO_4^{3-} : CrO_4^{2-}$ ratio of 1 : 1. This study is useful for extending the data on the poorly studied group of compounds $M^IM^{III}(AO_4)(PO_4)$ and for elucidating the effect of the nature of the AO_4 anions on the structure and properties of the compounds.

Experimental

The compounds $K_2R(CrO_4)(PO_4)$ were prepared by solid-state synthesis. The starting compounds used were R_2O_3 with R = Nd, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu, Y (chemically pure grade), $Lu_2(CO_3)_3 \cdot 3H_2O$ (chemically pure grade), M_2CrO_4 with M = Li, Na, K (chemically pure grade), and $NH_4H_2PO_4$ (analytical grade). Lanthanide oxides and chromates M_2CrO_4 were preannealed at 800 and 600 °C, respectively, for 24 h to remove the sorbed water. The phase composition of the reaction products was checked by powder X-ray diffraction using the PDF-2 database (Set 1-85). The samples were studied on a STOE diffractometer (Cu-Kα_1 radiation, λ = 1.54060 Å, SiO_2 monochromator, transmission geometry, the range of angles 2θ = 5—70° with a 0.02° step; effective recording time in one point 1—5 min).

IR spectra were obtained at room temperature on a PE 1600 FTIR spectrometer in the 400—4000 cm^{-1} range with a 4 cm^{-1} resolution. The samples were prepared as KBr pellets (1 mg of the substance per 100 mg of KBr).

Results and Discussion

The first series of experiments considered the possibility of formation of a new $K_2R(CrO_4)(PO_4)$ phase in the

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lanthanide series in relation to neodymium and lutetium. The reactants were mixed in stoichiometric amounts according to the reaction equation

$$R_2O_3 + 2\,(NH_4)H_2PO_4 + 2\,K_2CrO_4 \longrightarrow 2\,K_2R(CrO_4)(PO_4) + 2\,NH_3 + 2\,H_2O. \quad (1)$$

The resulting mixtures were triturated with acetone, dried under a lamp, and annealed at 550 °C for 100, 150, or 200 h.

In the case of lutetium compound, a new phase was detected after annealing of the initial mixtures for 100 h at 550 °C. An increase in the annealing duration resulted in decomposition of $K_2Lu(CrO_4)(PO_4)$ into $LuPO_4$ and K_2CrO_4. For the neodymium compound, the formation of $NdPO_4$ and K_2CrO_4 without formation of a new phase was observed.

The difficulty of performing the solid-state synthesis of double chromates $K_2R(CrO_4)(PO_4)$ is due to their relatively low thermal stability and low degree of crystallinity. The effect of a number of factors (reactant nature, temperature, and annealing time) on the formation of $K_2R(CrO_4)(PO_4)$ was studied for the lutetium compound.

When $Lu_2(CO_3)_3$ was used instead of the lutetium oxide, $K_2Lu(CrO_4)(PO_4)$ was also formed. However, the product yield and degree of crystallinity were much lower than with Lu_2O_3, all other factors (temperature, annealing time) being the same. The half-widths of the 100% reflection characteristic of the new phase differ almost twofold: ~0.63 and ~0.37 in the case of $Lu_2(CO_3)_3$ and Lu_2O_3, respectively.

The use of $LuPO_4 \cdot 3H_2O$ as the starting component instead Lu_2O_3 does not give a new phase, which is probably due to the high stability of the phosphate, formed upon dehydration during annealing.

The role of the temperature of synthesis of $K_2Lu(CrO_4)(PO_4)$ by reaction (1) was studied in the temperature range of 600—800 °C with a 100 °C step. The reaction time varied from 6 to 120 h. If annealing was carried out at 600 °C for 6 h, no new phase was formed, the reaction mixture containing the starting lutetium oxide and potassium chromate. An increase in the annealing time to 8.5 h at the same temperature gave rise to a complex potassium lutetium chromate(VI)-phosphate. In addition, the X-ray diffraction pattern showed reflections corresponding to potassium chromate and lutetium phosphate. At 700 °C and annealing time of 2 h, the reaction mixture contained $K_2Lu(CrO_4)(PO_4)$, K_2CrO_4, and $LuPO_4$, the decomposition products being the predominant components. After annealing at 800 °C for 2 h, only K_2CrO_4 and $LuPO_4$ were detected. Thus, the use of higher temperatures for the synthesis of $K_2Lu(CrO_4)(PO_4)$ is impossible due to its low thermal stability.

In other series of experiments, we attempted to reduce the temperature of synthesis to 500 °C. The annealing time varied from 50 to 200 h. The formation of the $K_2Lu(CrO_4)(PO_4)$ phase was detected after annealing for 180 h. The half-width of the reflections corresponding to the reaction product was ~0.18. Thus, the synthesis is possible on reducing the temperature to 500 °C but then the annealing time should be markedly increased.

The influence of the conditions of pre-annealing of the reactant mixtures on the degree of crystallinity (half-width of reflections) of the resulting samples was studied in the 150—450 °C temperature range with a temperature step of 50 °C with annealing for 36 h at each step and trituration every 18 h. The selection of the temperature conditions was due to the thermal stability of $(NH_4)H_2PO_4$, which decomposes at temperatures of ≥150 °C. The final annealing was conducted at the synthesis temperature (550 °C). This showed that to prepare potassium lanthanide chromate(VI)-phosphates with a reflection half-width sufficient for calculating the parameters (~0.18), annealing of the reaction mixture should be carried out with gradual raising of the temperature from 150 to 550 °C with a step of 50 °C. The annealing of samples at the synthesis temperature (550 °C) as pellets and keeping the complex chromate(VI)-phosphate under hydrothermal conditions at 170 °C did not decrease the half-width of reflections.

Thus, the conditions of choice for the synthesis include the use of lanthanide oxide as the starting compound and long-term pre-annealing of the reaction mixture according to a multistage temperature pattern with trituration at the intermediate steps; the temperature of the final annealing stage should not exceed 550 °C.

Under the optimal conditions, the syntheses of analogous derivatives of lithium and sodium in combination with lutetium was carried out according to Eq. (1). Instead of K_2CrO_4, lithium or sodium chromate was used. The samples obtained after annealing at 550 °C represented a mixture of $LuPO_4$ and alkali metal chromate M_2CrO_4 (M = Li, Na).

Using the developed optimal procedure, compounds $K_2R(CrO_4)(PO_4)$ were prepared for the following lanthanides: R = Eu, Gd, Dy, Ho, Er, Tm, Yb, and Y. Potassium chromates and lanthanide oxides were used as the starting compounds.

In the case of synthesis of europium, gadolinium, and terbium compounds, as for neodymium, the final products were potassium chromate and lanthanide phosphate. The reaction products obtained for dysprosium, holmium, erbium, and yttrium compounds were found to exhibit reflections corresponding to not only a complex chromate(VI)-phosphate phase but also to potassium chromate. For thulium, ytterbium, and lutetium compounds, single-phase $K_2R(CrO_4)(PO_4)$ samples were obtained.

Table 1. Results of indexing for $K_2Lu(CrO_4)(PO_4)$

N	h	k	l	I/I_0	d/Å	
					Experiment	Calculations
1	1	0	0	100.0	13.1236	13.0863
2	2	0	0	2.0	6.5436	6.5431
3	−1	0	1	6.8	5.8532	5.8515
4	−1	1	1	8.6	4.9441	4.9455
5	3	0	0	19.6	4.3607	4.3621
6	3	1	0	6.2	3.9438	3.9456
7	0	2	1	12.0	3.7001	3.7015
8	3	0	1	14.3	3.3813	3.3806
9	4	0	0	93.1	3.2725	3.2716
10	2	2	1	3.1	3.1268	3.1291
11	1	1	2	4.1	2.7916	2.7912
12	3	2	1	28.8	2.7265	2.7295
	−1	3	1	—	—	2.7284
13	2	0	2	13.1	2.6724	2.6728
	1	3	1	—	—	2.6714
	4	2	0	—	—	2.6711
	−3	0	2	—	—	2.6704
14	5	0	0	7.7	2.6165	2.6173
15	−5	2	1	16.4	2.2115	2.2114
16	−2	4	1	6.6	2.0831	2.0819
	−6	1	1	—	—	2.0816
17	4	1	2	5.1	2.0705	2.0703
	5	2	1	—	—	2.0697
	−1	0	3	—	—	2.0694
18	0	1	3	4.4	2.0073	2.0079
19	1	0	3	7.6	1.9952	1.9965
20	7	0	0	6.1	1.8689	1.8695
21	−3	2	3	11.4	1.7979	1.7973
22	6	0	2	6.2	1.6904	1.6903
23	5	4	1	9.4	1.6368	1.6360
	8	0	0	—	—	1.6358
24	7	2	1	5.9	1.6236	1.6235
	3	5	1	—	—	1.6232

Table 2. Results of indexing for $K_2Yb(CrO_4)(PO_4)$

N	h	k	l	I/I_0	d/Å	
					Experiment	Calculations
1	1	0	0	100.0	13.1113	13.1142
2	2	0	0	2.8	6.5539	6.5571
3	−1	0	1	5.9	5.8625	5.8652
4	−1	1	1	6.8	4.9533	4.9562
5	3	0	0	20.9	4.3682	4.3714
6	2	0	1	7.6	4.2646	4.2583
7	3	1	0	5.1	3.9530	3.9537
8	0	2	1	8.6	3.7076	3.7089
9	3	0	1	10.1	3.3907	3.3884
10	4	0	0	94.3	3.2785	3.2786
11	3	2	1	24.8	2.7339	2.7352
	−1	3	1	—	—	2.7334
12	2	0	2	10.8	2.6777	2.6793
	1	3	1	—	—	2.6765
	−3	0	2	—	—	2.6765
	4	2	0	—	—	2.6765
13	5	0	0	6.0	2.6221	2.6228
14	1	2	2	4.4	2.4782	2.4794
15	−5	2	1	12.3	2.2163	2.2158
16	−6	1	1	4.6	2.0862	2.0859
	−2	4	1	—	—	2.0856
17	4	1	2	4.2	2.0729	2.0751
	−1	0	3	—	—	2.0744
	5	2	1	—	—	2.0741
18	1	0	3	4.8	2.0028	2.0014
19	2	0	3	3.4	1.9026	1.9044
20	7	0	0	6.2	1.8731	1.8735
21	−3	2	3	8.1	1.8016	1.8013
22	6	0	2	5.1	1.6937	1.6942
23	8	0	0	7.8	1.6396	1.6393
	5	4	1	—	—	1.6393
24	7	2	1	4.1	1.6272	1.6270
	3	5	1	—	—	1.6262

This is confirmed by the fact that all lines in the X-ray diffraction patterns have been indexed (Tables 1—3).

The obtained complex chromate(VI)-phosphates $K_2R(CrO_4)(PO_4)$ (R = Dy—Lu, Y) are isostructural. Their X-ray diffraction patterns are wholly identical: the reflection positions and intensities are the same. Using the STOE WinXPOW program package, the X-ray diffraction patterns of the thulium, ytterbium, and lutetium compounds were indexed (see Tables 1—3) in the monoclinic system. The unit cell parameters are summarized in Table 4.

The IR spectra of chromate(VI)-phosphates were studied for the single-phase thulium, ytterbium, and lutetium compounds. The spectra (Table 5) exhibit bands due to the PO_4 vibrations (triply degenerate antisymmetric stretching vibration ν_3F_2 at 1130—900 cm^{-1}, triply degenerate antisymmetric bending vibration ν_4F_2 at 500—680 cm^{-1}, and the symmetric stretching vibration ν_1A_1 at 891 cm^{-1}) and bands due to the CrO_4 vibrations (triply degenerate antisymmetric stretching vibration ν_3F_2 at 855—840 cm^{-1}).

Each of the degenerate vibration bands for the PO_4 group (ν_3F_2 and ν_4F_2) is highly split into four components. The ν_3F_2 band of the CrO_4 group is not split and occurs as a sharp symmetric peak with a maximum at 840 cm^{-1}.

This pattern of band splitting attests to a pronounced distortion of the PO_4 tetrahedron in the crystal lattice and strong dipole—dipole interaction; the CrO_4 tetrahedra in the structure retain T_d symmetry.

The complex chromate-phosphates $K_2R(CrO_4)(PO_4)$ are not hygroscopic and are insoluble in water, but soluble in concentrated acids. These compounds are thermally unstable; they exist up to 550 °C under static conditions

Table 3. Results of indexing for $K_2Tm(CrO_4)(PO_4)$

N	*h*	*k*	*l*	I/I_0	*d*/Å	
					Experiment	Calcu-lations
1	1	0	0	100.0	13.1296	13.1327
2	2	0	0	2.5	6.5677	6.5663
3	−1	0	1	5.5	5.8806	5.8678
4	−1	1	1	6.7	4.9656	4.9648
5	3	0	0	19.1	4.3718	4.3776
6	3	1	0	4.8	3.9634	3.9618
7	0	2	1	8.5	3.7186	3.7247
8	3	0	1	12.4	3.4045	3.4028
9	4	0	0	78.0	3.2858	3.2832
10	−1	3	1	27.5	2.7423	2.7444
11	1	3	1	12.3	2.6864	2.6895
12	5	0	0	6.2	2.6256	2.6265
13	−5	2	1	13.7	2.2200	2.2175
14	−2	4	1	5.5	2.0957	2.0937
15	−1	0	3	4.2	2.0786	2.0788
16	0	1	3	3.3	2.0197	2.0189
17	1	0	3	5.9	2.0036	2.0053
18	7	0	0	5.6	1.8759	1.8761
19	−4	1	3	10.5	1.8088	1.8098
20	5	4	1	7.8	1.6412	1.6420
	8	0	0	—	—	1.6416
21	3	5	1	4.7	1.6319	1.6326
	7	2	1	—	—	1.6323

Table 4. Unit cell parameters for $K_2R(CrO_4)(PO_4)$ (R = Tm, Yb, Lu)

R	*a*	*b*	*c*	β/deg	*V*/Å^3
	Å				
Tm	13.215(5)	9.315(5)	6.243(3)	96.39(4)	763.7(5)
Yb	13.205(6)	9.268(2)	6.229(3)	96.70(4)	757.1(1)
Lu	13.177(3)	9.252(4)	6.213(2)	96.71(3)	752.3(3)

Table 5. Wave numbers of the absorption maxima (ν) in the IR spectra of compounds $K_2R(CrO_4)(PO_4)$ (R = Tm, Yb, Lu)

ν/cm^{-1}			Assignment[7,8]
R = Tm	R = Yb	R = Lu	
3439 w	3424 w	3424 w	$\nu_1 + \nu_3$ (H_2O)
1635 vw	1635 vw	1624 vw	ν_2 (H_2O)
1110 s	1113 s	1116 s	ν_3F_2 (PO_4)
1058 m	1063 m	1063 m	
1005 s	1007 s	1009 s	
973 s	971 s	973 s	
899 s	901 s	901 s	ν_1A_1 (PO_4)
837 s	837 s	838 s	ν_3F_2 (CrO_4)
671 w	673 w	673 w	ν_4F_2 (PO_4)
639 s	639 s	642 s	
576 m	576 m	578 m	
528 m	526 m	528 m	

and up to 600 °C under dynamic conditions (heating rate 10 °C min^{-1}).

In this study we established for the first time the formation of potassium lanthanide chromate(VI)-phosphates $K_2R(CrO_4)(PO_4)$, where R = Dy, Ho, Er, Tm, Yb, Lu, and Y. These compounds are formed upon combination of an alkali metal and a late lanthanide having an atomic radius greater than those of lithium or sodium.

The specific features of the solid-state synthesis of new lanthanide compounds are due to their low thermal stability, in particular, long-term annealing at ≥550 °C results in their decomposition into lanthanide phosphate and potassium chromate. The yield and the degree of crystallinity of the new phase is much higher when lanthanide oxide is used as the starting compound than with lanthanide carbonate, all other factors (annealing temperature and time) being the same. When R_2O_3 and $NH_4H_2PO_4$ are used, the amount of lanthanide phosphate resulting from decomposition of the complex chromate-phosphate markedly decreases. The formation of the new phase is probably preceded by the formation of X-ray amorphous lanthanide polyphosphate upon decomposition of $NH_4H_2PO_4$ at relatively low temperature (195—440 °C).[9] Further annealing at higher temperature gives the phase $K_2R(CrO_4)(PO_4)$. In the case of lanthanide carbonates, this intermediate stage is missing, as decomposition involves the intermediate formation of oxocarbonates, which are less reactive than lanthanide oxides, and complete decomposition is attained at higher temperature.[10] Under these conditions, lanthanide phosphate rather than potassium lanthanide chromate(VI)-phosphate is stable.

It is worth noting that the resulting compounds $K_2R(CrO_4)(PO_4)$ (R = Dy—Lu, Y) are less thermally stable than double chromates or phosphates. No data on CrO_4^{2-} and PO_4^{3-}anions both present in compounds with a complex cationic part involving other M^{III} cations have been reported. However, the formation of complex chromate(VI)-molybdate $M_2R(CrO_4)_{0.5}(MoO_4)_{1.5}$ (M = Cs, Rb) with 1 : 3 ratio of the anions has been described.[4,5] This may underlie the synthesis of complex chromate-phosphates other than $K_2R(CrO_4)(PO_4)$. There is a probability of formation of compounds with a higher or lower content of the CrO_4^{2-} anions, apparently, having higher stabilities, $KR_2(CrO_4)_2(PO_4)$, $K_3R_2(CrO_4)_3(PO_4)$ or $KR_2(CrO_4)(PO_4)_2$, and $KR_3(CrO_4)(PO_4)_3$.

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References

1. M. Ben Amara and M. Dabbabi, *Acta Crystallogr., Sect. C*, 1987, **43**, 616.
2. L. N. Komissarova, M. G. Zhizhin, and A. A. Filaretov, *Usp. Khim.*, 2002, **71**, 707 [*Russ. Chem. Rev.*, 2002, **71** (Engl. Transl.)].
3. A. N. Kirichenko, Ph.D. (Chem.) Thesis, Moscow State Univ.—Institute of General and Inorganic Chemistry, Moscow, 1999, 154 pp. (in Russian).
4. A. A. Evdokimov, E. V. Proskuryakova, and V. V. Fomichev, *Zh. Neorg. Khim.*, 1983, **28**, 2424 [*J. Inorg. Chem. USSR*, 1983, **28** (Engl. Transl.)].
5. V. L. Butukhanov, M. V. Mokhosoev, and S. R. Sambueva, *Zh. Neorg. Khim.*, 1979, **24**, 2978 [*J. Inorg. Chem. USSR*, 1979, **24** (Engl. Transl.)].
6. Y. Aoki and H. Konno, *J. Solid State Chem.*, 2001, **156**, 370.
7. *Atlas infrakrasnykh spektrov fosfatov. Ortofosfaty* [*Atlas of the Infrared Spectra of Phosphates. Orthophosphates*], Ed. I. V. Tananaev, Nauka, Moscow, 1981, 248 pp. (in Russian).
8. R. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley and Sons, Inc., New York, 1986, p. 536.
9. Z. P. Rogova and P. I. Kuznetsov-Fetisov, *Zh. Prikl. Khim.*, 1975, **48**, 875 [*J. Appl. Chem. USSR*, 1975, **48** (Engl. Transl.)].
10. L. N. Komissarova, V. M. Shatskii, G. Ya. Pushkina, L. G. Shcherbakova, L. G. Mamsurova, and G. E. Sukhanova, *Soedineniya redkozemel´nykh elementov. Karbonaty, oksalaty, nitraty, titanaty* [*Rare Earth Element Compounds. Carbonates, Oxalates, Nitrates, Titanates*], Nauka, Moscow, 1984, 235 pp. (in Russian).

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