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On rubidium lanthanide double chromates

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Abstract

Synthesis and crystallographic data are reported for a family of double rubidium–rare earth chromates $RbLn(CrO_4)_2$, where Ln ≡ La–Lu, Y and Sc. The compounds are closely related to the potassium chromates $KLn(CrO_4)_2$ but with a slightly different distribution of structural types: those of La, Pr and Nd are monoclinic, Sm, Eu, Gd are orthorhombic and those of Tb–Lu are also monoclinic but with another unit cell. $RbSc(CrO_4)_2$ has high and low temperature forms: hexagonal and monoclinic respectively. Lattice parameters of all the above compounds are given. Thermal decomposition takes place over 450 °C leading to the rare earth chromites and Cr_2O_3.

1. Introduction

Studies of the potassium rare earth chromates have produced several compounds with the formula $KLn(CrO_4)_2$, where Ln ≡ La–Lu, Y and Sc. Their structure is characterized by the infinite layers or tunnels formed by $|Ln(CrO_4)_2|_\infty$ groups with potassium atoms inside [1–4]. These structures can also be related to the wide family of the corresponding phosphates, arsenates and vanadates containing alkali and rare earth cations in the inner spaces [5]. These solids may present a certain technological interest due to the possibility of substituting the alkaline cations by other positive ions, *e.g.* H_3O^+. In this way new materials were devised having the necessary electrophysical properties for thermistors [6] and humidity sensors working in aggressive media [7].

2. Experimental details

The double chromates $RbLn(CrO_4)_2$ where Ln ≡ La–Lu, Y and Sc were prepared from stoichiometric mixtures of Rb_2CO_3, Ln_2O_3 and CrO_3. The initial reactants were ground under hexane in order to inhibit the reaction between Rb_2CO_3 and CrO_3 in the early stages. After the evaporation of hexane the syntheses were carried out by successive thermal treatments at 200 (72 h), 350 (96 h), 400 (96 h) and 650 °C (168 h). Such a prolonged heating is necessary in order to obtain samples suitable for X-ray investigations.

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X-ray patterns were recorded using a Siemens Kristalloflex (Ni-filtered CuKα radiation) provided with a graphite monochromator. Tungsten and silver were used as internal standards.

3. Results

X-ray investigation shows the formation of new compounds in the samples heated over 400 °C. No reflexions due to the initial rare earth oxides or rubidium chromates are detected in the X-ray patterns. In the case of scandium, however, an additional low temperature form is found at 250 °C.

New phases were identified by comparison with the corresponding potassium–lanthanide double chromates recently obtained and investigated [1–4]. Tables 1–5 contain the results of indexing the X-ray powder data for those representatives of each individual group of compounds that showed the highest crystallinity, both forms of scandium chromates included. In any case the number of reflexions is remarkably reduced in com-

TABLE 1. Powder X-ray diffraction data for $RbLa(CrO_4)_2$

I/I_0	$h\ k\ l$	d_{obs}	d_{calc}	I/I_0	$h\ k\ l$	d_{obs}	d_{calc}
7	$\bar{1}\ 1\ 2$	4.064	4.062	3	0 0 4	2.788	2.792
10	0 2 0	3.756	3.753	12	3 1 1	2.678	2.669
70	$\bar{2}\ 0\ 2$	3.591	3.568	11	0 1 4	2.614	2.617
100	$\bar{1}\ 2\ 1$	3.316	3.322	8	1 2 3	2.516	2.515
15	$\bar{2}\ 1\ 2$	3.227	3.222	10	2 0 4	2.329	2.327
80	2 1 2	3.116	3.116	3	$\bar{4}\ 1\ 3$	1.891	1.892
10	3 0 0	2.969	2.986				

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TABLE 2. Powder X-ray diffraction data for $RbSm(CrO_4)_2$

I/I_0	$h\ k\ l$	d_{obs}	d_{calc}	I/I_0	$h\ k\ l$	d_{obs}	d_{calc}
20	2 0 2	3.826	3.861	7	3 2 0	2.485	2.465
80	4 0 0	2.526	3.534	3	0 2 2	2.445	2.449
10	3 0 2	3.278	3.295	5	2 2 2	2.308	2.314
100	2 1 2	3.201	3.211	7	1 0 4	2.265	2.274
7	1 0 3	3.028	3.003	8	1 1 4	2.117	2.117
10	3 1 2	2.888	2.864	5	2 1 4	2.045	2.049
5	2 0 3	2.853	2.818	3	4 2 2	2.008	2.013
6	0 1 3	2.710	2.714	5	2 3 0	1.859	1.859

TABLE 3. Powder X-ray diffraction data for $RbLu(CrO_4)_2$

I/I_0	$h\ k\ l$	d_{obs}	d_{calc}	I/I_0	$h\ k\ l$	d_{obs}	d_{calc}
10	0 2 1	5.539	5.513	14	0 4 2	2.769	2.756
10	$\bar{1}$ 0 1	4.840	4.835	3	$\bar{2}$ 0 1	2.726	2.721
5	$\bar{1}$ 2 0	4.410	4.407	7	1 0 3	2.650	2.639
4	1 2 0	4.390	4.407	3	1 2 3	2.468	2.468
5	$\bar{1}$ 2 1	3.962	3.943	5	2 0 2	2.400	2.389
3	0 2 2	3.791	3.781	18	2 2 2	2.243	2.263
45	$\bar{1}$ 1 2	3.459	3.441	10	$\bar{1}$ 0 4	2.091	2.101
70	1 1 2	3.394	3.401	5	2 2 3	1.970	1.967
30	0 4 1	3.238	3.252	5	$\bar{1}$ 5 3	1.925	1.928
100	1 2 2	3.119	3.133	5	$\bar{2}$ 3 3	1.901	1.896
20	1 4 0	2.976	2.973	4	2 4 3	1.770	1.768
15	1 4 1	2.820	2.817	15	3 4 1	1.632	1.634

TABLE 4. Powder X-ray diffraction data for $RbSc(CrO_4)_2$, h. t.

I/I_0	$h\ k\ l$	d_{obs}	d_{calc}	I/I_0	$h\ k\ l$	d_{obs}	d_{calc}
5	0 0 2	3.995	3.966	15	2 0 0	2.166	2.160
100	1 0 1	3.793	3.794	9	1 1 3	1.822	1.814
50	1 0 2	2.891	2.921	42	2 0 3	1.675	1.672
70	0 0 3	2.658	2.644	8	1 0 5	1.485	1.489
30	1 1 0	2.496	2.494	35	3 0 0	1.440	1.440
20	1 1 1	2.364	2.379				

TABLE 5. Powder X-ray diffraction data for $RbSc(CrO_4)_2$, l. t.

I/I_0	$h\ k\ l$	d_{obs}	d_{calc}	I/I_0	$h\ k\ l$	d_{obs}	d_{calc}
3	2 0 0	4.170	4.178	5	1 0 3	2.458	2.458
5	$\bar{1}$ 1 1	3.920	3.928	10	0 1 3	2.361	2.366
100	1 1 1	3.731	3.721	7	$\bar{1}$ 1 1	2.341	2.345
70	$\bar{1}$ 1 2	3.092	3.047	15	$\bar{2}$ 1 3	2.160	2.164
8	2 1 1	2.925	2.900	5	4 0 0	2.090	2.089
100	1 1 2	2.844	2.856	5	$\bar{4}$ 0 2	1.950	1.955
15	2 0 2	2.736	2.728	3	$\bar{2}$ 1 4	1.787	1.782
70	0 0 3	2.659	2.672	8	3 2 2	1.646	1.649
12	0 2 0	2.538	2.544				

parison with the corresponding potassium group. Lattice parameters refined by the usual least-square technique are summarized in Table 6.

The thermal stability of rubidium compounds is much less than that of potassium analogues. Their decomposition starts at over 450 °C and, according to X-ray patterns, leads to the formation of rare earth chromites which are always found as final products. During heating in closed crucibles single crystals of Cr_2O_3 are formed on the colder areas. Lutecium and scandium compounds are still stable at 850 °C.

4. Discussion

Regarding the distribution of structural types in the rare earth series, the $RbLn(CrO_4)_2$ family seems to be different from the corresponding $KLn(CrO_4)_2$ family and in exact accordance with 'classical' La–Nd, Eu–Gd and Tb–Lu subdivisions. We also looked for dimorphism in Eu and Tb compounds but no traces of a low temperature modification were found. Hence we can consider the structural types of the obtained chromates as derived from the well-known potassium compounds $KLa(CrO_4)_2$ (monoclinic I, mica-like La–Nd group), $KTb(CrO_4)_2$ (orthorhombic tunnels containing Eu–Gd group) and $KLu(CrO_4)_2$ (monoclinic II, Tb–Lu group, also with tunnels but of different shape and size). A deviation from the initial $KLn(CrO_4)_2$ series is evident from these data.

On the other hand it could be assumed that they are related to the monoclinic ternary phosphates containing, together with lanthanide, two different alkali metal cations, *e.g.* $K_2CsLn(PO_4)_2$ [5]. Cell transformation for the monoclinic II type would be quite simple:

$$a_{Ch}=b_{Ph};\ b_{Ch}=3^{1/2}b_{Ph} \text{ and } c_{Ch}=a_{Ph}$$

where Ch and Ph subindexes mean chromates and phospates respectively.

In addition, we should perhaps reconsider the conclusions of an earlier study [8] of $RbLn(CrO_4)_2$, in which all compounds are classified as monoclinic, being derived from $PbCrO_4$ with double a and c parameters.

As is frequently the case for other scandium compounds [9], the corresponding double chromates are completely different from the above La–Lu derivatives. They have been identified on the basis of the well-known similarities and close isomorphism between chromate and sulphate groups and related to glaserite, double potassium–sodium sulphate $K_3Na(SO_4)_2$. In the structure, layers are formed by both SO_4-tetrahedra and sodium atoms while potassium is situated in the interlamellar spaces [5]. That is why the glaserite-related monoclinic $KFe(SO_4)_2$ and trigonal $RbFe(SO_4)_2$ proved to be the appropriate archetypes for the low and high temperature modifications of $RbSc(CrO_4)_2$. It is quite obvious that in these iron sulphates the framework is determined by the relationship of K and Rb ionic radii;

TABLE 6. Lattice parameters for $RbLn(CrO_4)_2$ (Ln = La–Lu, Y and Sc) with e.s.d. in parentheses

Compound	Unit cell	Parameters			
		a (Å)	*b* (Å)	*c* (Å)	*β* (grad)
$RbLa(CrO_4)_2$	monoclinic I	8.966(7)	7.507(1)	11.179(2)	92.39(4)
$RbPr(CrO_4)_2$	monoclinic I	8.957(4)	7.460(4)	11.085(5)	91.48(1)
$RbNd(CrO_4)_2$	monoclinic I	8.914(6)	7.430(1)	11.050(1)	91.61(8)
$RbSm(CrO_4)_2$	orthorhombic	14.140(4)	5.783(2)	9.219(3)	–
$RbEu(CrO_4)_2$	orthorhombic	13.927(6)	5.765(9)	9.217(2)	–
$RbGd(CrO_4)_2$	orthorhombic	13.743(6)	5.693(6)	9.209(4)	–
$RbTb(CrO_4)_2$	monoclinic II	5.589(6)	14.201(1)	9.125(4)	91.18(1)
$RbDy(CrO_4)_2$	monoclinic II	5.881(8)	14.099(4)	9.069(7)	90.61(4)
$RbHo(CrO_4)_2$	monoclinic II	5.743(4)	14.073(7)	9.166(9)	91.40(3)
$RbEr(CrO_4)_2$	monoclinic II	5.721(1)	14.021(1)	9.035(8)	90.46(2)
$RbTm(CrO_4)_2$	monoclinic II	5.795(8)	13.997(2)	9.078(6)	90.93(2)
$RbYb(CrO_4)_2$	monoclinic II	5.703(2)	13.994(7)	9.041(6)	90.70(7)
$RbLu(CrO_4)_2$	monoclinic II	5.687(1)	13.952(3)	9.002(1)	90.74(1)
$RbY(CrO_4)_2$	monoclinic II	5.773(9)	14.017(2)	9.104(1)	90.97(6)
$RbSc(CrO_4)_2$ h.t.	hexagonal	4.988(1)	–	7.931(1)	–
$RbSc(CrO_4)_2$ l.t.	monoclinic	8.422(4)	5.088(4)	8.080(2)	97.17(7)

in the case of $RbSc(CrO_4)_2$ both tendencies are reflected within the same compound resulting in its dimorphism. The corresponding transition seems to be irreversible.

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