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Double Molybdates and Tungstates of the Rare Earth and Alkali Metals

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Data on the preparation, structure, and various properties of the double tungstates and molybdates (EO_4) of the alkali (M) and rare earth (R) metals with the composition $RM(EO_4)_2$ have been summarised and systematised. The regular features of the change in the symmetry, polymorphism, and nature of the fusion with change in the nature of the alkali and reare earth metals have been examined. The bibliography contains 82 references.

CONTENTS

I. Introduction 822
II. Preparation of double molybdates and tungstates $R^{3+}M^{+}(EO_4)_2$ 823
III. Polymorphism 825
IV. Fusion 830

I. INTRODUCTION

Double molybdates and tungstates of the type $R^{3+}M^{+}(EO_4)_2$, where R represents a rare earth element (REE) or any other tervalent element, M represents an alkali metal, and E represents molybdenum or tungsten, are of considerable interest in connection with their possible use as laser matrices. Up to the present, lasing has been achieved in single crystals of $LaNa(WO_4)_2$,[1] $LaNa(MoO_4)_2$,[2-8] $PrNa(MoO_4)_2$, $TbNa(MoO_4)_2$,[8] $GdNa(MoO_4)_2$,[7] $GdLi(MoO_4)_2$,[9] and $YK(MoO_4)_2$,[10,11] containing Nd^{3+}. The transparency of these crystals over a wide range of wavelengths of the spectrum (0.4–5.0 μ), the high thermal conductivity [22 mW cm^{-1} deg^{-1} for $LaNa(MoO_4)_2$], low lasing threshold [5.5 J for $LaNa(MoO_4)_2$–Nd^{3+}], and the possibility, in principle, of obtaining single crystals with any concentration of active ion, have been noted.

The crystals of many double tungstates and molybdates are characterised by structural disorder, involving the random distribution of R^{3+} and M^{+} in the lattice[12]; the disorder is apparently greater, the closer the radii of these two ions[13,14]; it is revealed in the indistinct nature of the birefringence pattern and in the broadening of the bands in the vibrational absorption, luminescence, and paramagnetic resonance (PMR) spectra[2,3,7,12,15,16]. Two important possible applications of these disordered crystalline systems have been noted: the production of extremely short ($<10^{-11}$ s) giant pulses of coherent radiation in optical quantum generators (OQG) with phasing of the modes; and high-temperature lasing[17].

Almost all double molybdates and tungstates $RM(EO_4)_2$ have now been prepared, their structures and polymorphism have been studied, and their melting points and other physicochemical properties have been determined. Most of these compounds have been obtained in the form of small single crystals suitable for the study of their structures and optical, magnetic, and various other properties. Large single crystals for lasers have been grown for only a few of these compounds, however. The lack of a well-developed technology for the growth of large crystals is retarding the further study of this interesting class of laser material.

The wide variety of properties shown by this group of compounds on the one hand provides the possibility, in principle, of an extensive selection of methods for the preparation of active solids with desirable properties, and on the other hand complicates this selection. In this connection, we have attempted to analyse and systematise the available (in many instances contradictory) data.

As compounds derived from scheelite (by replacing two calcium atoms by R and M atoms), the double compounds $RM(EO_4)_2$ can be classified naturally according to the extent to which the dimensions of the ions R^{3+} and M^{+} differ from those of the calcium ion. This replacement, in addition to the scheelite-like structure, produces a whole set of new structural types. Thus the properties of the double compounds must be related not only to the disordered character of the structure, but also to the actual structures and structural types.

According to Goldschmidt's rule[18], the crystal structure of a compound depends chiefly on the polarisation properties, geometric parameters, and relative numbers of the ions present. The polarisation properties (the nature of the hybridisation) of the ion in complex compounds (to which class the double molybdates and tungstates belong) are suppressed by the large total energy of the lattice[19]. It may therefore be assumed that the structure of $R^{3+}M^{+}(EO_4)_2$ is determined chiefly by the ratio of the dimensions of the ions, which in turn may change with change in temperature, so that it also determines the polymorphism. In the series of normal double molybdates and tungstates $R^{3+}M^{+}(EO_4)_2$, the variable species are R^{3+} and M^{+}, so that the structure and also the degree of disorder will depend on the values of the ionic radii $r_{R^{3+}}$ and $r_{M^{+}}$ (naturally, within the approximation indicated).

Existing systems[20] of ionic radii characterise the values at room temperature, so that it is justifiable to examine the dependence of the symmetry of the structures on $r_{R^{3+}}$ and $r_{M^{+}}$ only for the low-temperature phases. We cannot however reach completely reliable conclusions regarding the crystal system of the low-temperature phase in those cases where some authors have established a polymorphic transition, and others have not detected it, and the problem of whether the crystal systems which they have established correspond to the high-temperature or low-temperature modifications remains open. This ambiguity can be resolved on the basis of the working hypothesis that there is a certain probability of quenching or stabilisation of high-temperature phases at low temperatures either as a consequence of the presence of impurities or as a result of

insufficiently slow cooling in the region of the temperature of the phase transformation.

Comparison of the results obtained by different authors leads to the conclusion that the ability of the high-temperature phases to undergo quenching or stabilisation is a characteristic feature of double tungstates and molybdates, so that the production of a particular modification depends on the method of preparation and subsequent thermal treatment.

II. PREPARATION OF DOUBLE MOLYBDATES AND TUNGSTATES $R^{3+}M^{+}(EO_4)_2$

A bibliography of various methods for the preparation of the double molybdates and tungstates formed by the alkali metals with the REE and Y is given in Tables 1 and 2. The compounds are prepared by precipitation from aqueous solutions (O), by the hydrothermal method (Г), by crystallisation from solutions in melts (P), and by heating mechanical mixtures of the oxides and salts (T). (The preparation of large single crystals by the Czochralski method is denoted by the letter C in the Tables.)

Table 1. Methods for the preparation and the growth of single crystals of double molybdates of the REE (R) and alkali metals (M) $RM(MoO_4)_2$.

R	M				
	Li	Na	K	Rb	Cs
Y	T[21,22] P[23,24]	T[21,22,25] P[16,23,24,26]	T[27] P[16,28]	T[29]	T[30,31] P[23,31]
La	T[21,32] P[16,33]	O[34,35,36]P[16] T[21,25,37,38] C[8,37,38,39]	T[21,32] P[16,21]	T[29,31] P[40]	T[21,30,31,32] P[29]
Ce	T[21] P[33]	O[36] T[21]	T[21] P[41]		
Pr	T[21] P[33]	O[35]T[21,25] P[42]C[8]	T[21,27] T[41]	T[21,29,31,43] P[44]	T[30,31] P[31]
Nd	T[21,45] P[33]	O[35]T[21,25,46] P[42,47],C[8]	T[21,27,48] P[41]	T[21,29,31,44]	T[30,31]
Sm	T[21,45] P[39]	T[21,25] P[42,47]	T[21,48] P[41]	T[21,29,31,13]	T[30,31]
Eu	T[21] P[23,24,33]	T[21,25] P[23,42,47]	T[21,48] P[22,41]	T[21,29,31,43] P[23]	T[30,31] P[23,49]
Gd	T[21,45] P[33]	O[50]T[21,25] P[42,47]	T[48,51] P[41]	T[21,29,31,49]	T[30,21]
Tb	T[21,52] P[22,24,33]	T[21,52] P[23,42,47]C[8]	T[21,48,52] P[23,41]	T[21,43] P[23]	T[30,31]
Dy	T[21,45,53] P[33,54]	T[21,25,55] T[42,47]	T[21,48,51] P[41]	T[21,29,41,43]	T[30,31]
Ho	T[21,53] P[33]	O[50]T[21,25,55] P[42,47]	T[21,48,51]	T[21,29,41,43]	T[30,31]
Er	T[21,53] P[33]	O[56]T[21,24,55] P[42,47]	T[21,27,48,51] P[41]	T[21,29,41,43]	T[30,31] O[56]
Tm	T[21,52] P[33]	T[21,25,52] P[42, 7]	T[21,48,52] P[41]	T[21,29,41,43]	T[30,31]
Yb	T[21,52] P[33]	T[21,25,52] P[42,47]	T[19,25,83] P[21,48,52]	T[21,29,41,43]	T[21,30,31]
Lu	T [21,45,52] P[33]	T[21,52] P[42]	T[21,48,52] P[41]	T[21,29,41,43]	T[21,30,31]

1. Precipitation from Aqueous Solutions

The double compounds $RM(EO_4)_2$ are precipitated by mixing aqueous solutions of M_2EO_4 and a salt of the tervalent element. Both the direct (addition of M_2EO_4 solution to a solution of the REE salt) and the reverse order of mixing are used. The second alternative appears less reliable, as a consequence of the hydrolysis of the salt of the tervalent element when it is added to the MEO_4 solution, which has an alkaline reaction [61].

It has not been possible to obtain the sodium double tungstates with the REE from La to Sm, or any of the lithium double tungstates, by simply mixing the solutions [61]. $RNa(WO_4)_2$ (R = La, Ce, Pr, or Nd) have been obtained only in neutral medium; for this purpose, nitric acid was added to Na_2WO_4 solution to pH 8, so that on mixing with $R(NO_3)_3$ solution the mother-liquor had pH 7. [35] The corresponding double molybdates are formed by simply mixing the solutions.

Table 2. Methods for the preparation and the growth of single crystals of double tungstates of the REE (R) and alkali metals (M) $RM(WO_4)_2$.

R	M				
	Li	Na	K	Rb	Cs
Y	T[57] P[23,58]	O[61]T[25,59,60] P[12,23,62,63] C[63]	O[61]T[61,64] P[65]	O[61]T[54,61] P[23]	O[61]T[54,61] P[23]
La	P[58]	O[36]T[25,59,60] P[63,66]C[39,62,63]	O[61]T[15,61] P[23,65,66] Г[68]	O[61]T[54,61]	O[61]T[54,61]
Ce	T[68-70] Г[68,69]P[23]	O[35]Г[68] P[66]	T[15]Г[67,68] P[65,66]		
Pr	T[68-70] Г[68,69]P[58]	O[36]T[25,59] Г[68]C[72]	T[15]Г[67,68] P[65]	T[54]	T[54]
Nd	T[68,69] Г[68,69]P[58]	O[35]T[25,59,60] Г[69,71]P[73]	O[61]T[15] Г[67,68,71] P[61,65]	O[61]T[54,61]	O[61]T[54,61]
Sm	P[58]	O[61]T[25,59,60] P[62]	O[61]T[15,61] P[65]	O[61]T[54,61]	O[61]T[54,61]
Eu	P[23,58]	O[61]T[25,60] P[23,62]	O[61]T[15,61] P[23,65]	O[61]T[54,61] P[23,75]	O[61]T[54,61] P[23,75]
Gd	P[58]	O[61]T[25,59,60] P[23,62,72] C[7,72]	O[61]T[15,61] P[65]	O[61]T[54,61]	O[61]T[54,61]
Tb	P[23,58]	O[61]P[23,62]	O[61]T[15,61] P[65]	O[61]T[54,61] P[23]	O[61]T[54,61]
Dy	P[58]	O[61]T[25, 60] P[62]	O[61]T[15,61] P[65]	O[61]T[54,61] P[76]	O[61]T[54,61] P[23]
Ho	P[58]	O[61]T[25,60] P[62]	O[61]T[15,61] P[65]	O[61]T[54,61]	O[61]T[54,61]
Er	P[58]	O[61]T[25,60] P[62]	O[61]T[15,61] P[65]	O[61]T[54,61]	O[61]T[54,61]
Tm	P[58]	T[25,60] P[62]	T[15] P[65]	T[54]	T[54]
Yb	T[76] P[58,76]	O[61]P[25,60] P[62]	O[61]T[15,61] P[65]	O[61]T[54,61] P[74]	O[61]T[54,61] P[74]
Lu	T[58]P[63] C[63]	P[60,62]	T[15] P[65]	T[54]	T[54]

In all cases the normal tungstate or molybdate is precipitated first; on standing, this reacts with the excess of M_2EO_4 in the solution to form the double salt [36,61]. The double molybdates with sodium and potassium (unlike those with rubidium and caesium) are readily decomposed by water. Since departures from stoichiometry take place when these precipitates are washed with water, the removal of mother-liquor in a press has been proposed [61]. At low concentrations of the REE salt (≤ 0.01 M), the sodium and potassium double molybdates (unlike the

rubidium and caesium compounds) are not formed[61].

The data given show that the stability of the double tungstates, under the conditions of preparation from solution, increases from Li to Cs. In view of the similarity in the chemical properties of molybdates and tungstates, it may be assumed that the same regular features are observed for the double molybdates

The precipitated double molybdates formed by sodium with the REE from La to Nd contain one molecule of water of crystallisation[34-36]. The removal of water and the crystallisation of anhydrous $NdNa(MoO_4)_2$ begin at 540°.[34]

The compositions of the hydrated tungstates, and the temperatures of their dehydration and crystallisation with the formation of the anhydrous double compounds are given in Table 3.

Table 3. Characteristics of double tungstates $RM(WO_4)_2$ obtained by precipitation from aqueous solutions.

Composition of the air-dry precipitate	Temp. of complete dehydration, °C	Temp. of crystallisation of the anhydrous compound, °C	References
$NdNa(WO_4)_2 \cdot 5H_2O$.	>300	540	35
$RNa(WO_4)_2 \cdot 2.5H_2O$, R=Sm — Er, Yb, Y.	155—190	460—570	61
$RK(WO_4)_2 \cdot 2.5H_2O$, R = La, Nd, Sm.	250—260	540—610	61
$RK(WO_4)_2 \cdot 1.5H_2O$, R = Sm — Er, Yb, Y.	100—150	615—830	61
$RRb(WO_4)_2 \cdot 1.5H_2O$, R = La, Nd.	190—230	560÷730	61
$RRb(WO_4)_2 \cdot 1.5H_2O$, R=Sm — Er, Yb, Y.	120—130		61
R = Er, Tm, Y, Lu	360		29
$LaCs(WO_4)_2 \cdot 1.5H_2O$,	210	550	61
$RCs(WO_4)_2 \cdot H_2O$, R=Nd — Er, Yb, Y.	140—180		61

2. Hydrothermal Preparation of $RM(EO_4)_2$

This method has been used for the preparation of the double compounds $RM(EO_4)_2$ only by Klevtsov and Kharchenko[71] (Table 2). They prepared crystals of $RLi(WO_4)_2$, $RNa(WO_4)_2$, and $RK(WO_4)_2$ (where R = Ce, Pr, or Nd), and also $LaK(WO_4)_2$, by spontaneous nucleation under isothermal conditions in 8—12 cm^3 capacity autoclaves with titanium linings.

For the lithium—REE double tungstates, the best results from the viewpoint of yield (70%) and crystal size (up to 3 mm) were obtained with a charge consisting of a heated mixture of the oxides R_2O_3 and WO_3 with molar ratio 1 : 2, and 20—30% LiCl solution as solvent, at 525—550° with a filling factor of 50—60%.

The compounds $RNa(WO_4)_2$ were obtained under hydrothermal conditions in the form of fine crystals with dimensions up to 0.3 mm. The optimal conditions of crystallisation were the same as those for $RLi(WO_4)_2$.

The potassium double compounds were prepared under hydrothermal conditions at 500—600° in 50% KCl solution. At lower concentrations, non-stoichiometric crystals with variable composition $R_{1-x}K_{1-3x}(WO_4)_2$ are formed.

At the comparatively low temperatures characteristic of the hydrothermal method of preparation, the lithium double molybdates crystallise in the triclinic modification, and the potassium compounds in the monoclinic form. When heated above 800°, these phases undergo monotropic conversion into the tetragonal (scheelite) and monoclinic [analogous to $Nd_2(WO_4)_3$] modifications respectively, which are obtained when other methods of preparation are used (Table 2). The sodium REE tungstates are tetragonal for all methods of preparation. The similarity in the ionic radii of Na^+, R^{3+}, and Ca^{2+} evidently facilitates the preservation of the $CaWO_4$ structure[68].

3. Crystallisation of $RM(EO_4)_2$ from Molten Solutions

This method was used to prepare the first double compounds of the type $R^{3+}M^+(EO_4)_2$[66] (if we exclude the work of Carobbi[36], who precipitated $LaNa(MoO_4)_2$ from aqueous solutions). Several versions of the method are now employed, and in most cases spontaneous crystallisation is used.

Alkali metal chlorides or tungstates (or molybdates) are used as solvents. The latter are more convenient, since they undergo little volatilisation[63] under the crystallisation conditions, have lower melting points, and do not contaminate the crystals with foreign ions.

The high volatility of chlorides can be used to grow crystals by evaporation of the solvent (chloride) from the corresponding molten salts at a constant temperature (700—750°, 10 h).[29,31,40,54] Most frequently, after being heated for 3—20 h in the superheated (1100—1250°) state, the solution is cooled slowly (2—3 deg h^{-1}) to a temperature below the melting point of the eutectic (~700°). The subsequent cooling is carried out more rapidly (~25 deg h^{-1}).

The charge is introduced into the solvent in all possible forms: the oxide R_2O_3, mixtures of the oxides R_2O_3 + $3EO_3$, R_2EO_4, $RM(EO_4)_2$, etc. The only condition is that the ratio of the components of the molten mixture should ensure the formation of the double compound and the solvent in the optimal proportions.

Sometimes, in order to obtain large crystals of $RM(EO_4)_2$, sufficient EO_3 is added to the solvent M_2EO_4 to form $M_2E_2O_7$, which has a higher "capacity" as solvent, as a consequence of the decrease in the EO_4^{2-} concentration with the formation of $E_2O_7^{2-}$.[26] This also explains the existence, on the ternary diagram of the $Na_2O—Gd_2O_3—Mo_2O_6$ system[77], of optimal composition ranges for the production of relatively large crystals. The solidified $M_2E_2O_7$ solvent, however, can be washed from the crystal only with concentrated MOH solution[26], whereas M_2EO_4 is readily removed with water. Moreover, the crystallisation from highly concentrated solutions takes place at a high rate, a large number of crystallisation centres are produced, and entrainment of the solvent by the rapidly growing faces of the crystals takes place. Transparent crystals without inclusions have been obtained only at a molar ratio $R_2(WO_4)_2 : Na_2WO_4 \leq 1 : 9$ (R = Y, La, Lu), at a rate of growth equal to 0.020—0.025 mm h^{-1}.[63] Reverse rotation (60 r.p.m.) of the crucible, beginning at a temperature 10—15 deg below the temperature of the start of crystallisation, made it possible to reduce by an order of magnitude the quantity of crystals of these compounds forming spontaneously.

Individual attempts to grow single crystals on seed crystals and by pulling (Czochralski method) from the melt solutions have been made. $EuCs(MoO_4)_2$[49] and $RNa(WO_4)_2$, where R = Y, La, and Lu,[63] have been prepared in this way. In the last cases, growth took place in the upper part of a cylindrical quartz vessel containing the melt under conditions of a temperature gradient or a temperature drop (with the use of a diaphragm).

4. Preparation by Heating a Mechanical Mixture

The phase composition of the original mixture can represent any stoichiometric combination of thermally unstable salts of the rare earth and alkali metals and the products of their reaction with one another. It determines the chemistry of the process and hence the minimal temperature of heating.

It has been suggested [25,46] that the preparation of $RNa(EO_4)_2$, where R = La or Nd, by the action of heat on $R_2O_3 + 4EO_3 + Na_2CO_3$ and $R_2O_3 + EO_3 + Na_2EO_4$ mixtures involves the formation of amorphous sodium molybdates and tungstates $Na_2E_4O_{13}$ with their subsequent active reaction with R_2O_3, and that the preparation by the action of heat on an $Nd_2(MoO_4)_3 + Na_2MoO_4$ mixture involves the formation of the intermediate compound $NdNa_5(MoO_4)_4$. The formation of the molybdate $NdNa(MoO_4)_2$ is complete at 500° in the first case and at 600° in the second case. It has also been noted that the formation of the double tungstates takes place at higher temperatures (~750° for the ternary mixture). Other authors (see bibliography in Tables 1 and 2) prepared double molybdates and tungstates by heating at 500–900° and 600–1100° respectively for periods of 8–100 h. The possibility of carrying out the preparation over a wide range of temperatures makes it possible in some cases to obtain various polymorphic modifications immediately [21,43,57].

III. POLYMORPHISM

Comparison of the results obtained by different authors in the thermographic study of polymorphism with the methods of preparation of the compounds which they studied reveals a curious feature. In some cases, transformations which could not be detected in the study of compounds obtained from solutions in a melt have been clearly revealed when the same compounds were prepared by the sintering of solid mixtures.

For sodium and lithium double molybdates it has been possible to establish the existence of transitions (Tables 4 and 5) only after they had been prepared by heating mechanical mixtures with subsequent fusion and slow cooling of the melt. Crystals of the same compounds grown from molten solutions do not show any effects. It may therefore be assumed that in the first case a low-temperature form is obtained, and in the second case a high-temperature form. Both were found to be tetragonal (scheelite type). The weak reversible effects observed on the DTA curves when these compounds are heated indicate only slight rearrangement of the structure [52].

Table 4. Structures and polymorphism of double molybdates of the REE (R) and alkali metals (M) $RM(MoO_4)_2$ (1).

	M	Li	Na	K	Rb	Cs
R	r (2)	0.68	0.98	1.33	1.49	1.65
Y	0.97	T [21,33] 0.82 0.29	T [21,23,25] 0.98 0.01	550 [28,51] (3) T [28] 1.15 0.36	P [29] 1.23 0.60	M [31] 1.31 0.68
La	1.04	T [21,33] 0.86 0.36	T [21,25,34,35,38] 1.01 0.06	T [21,41] (4) 1.18 0.29	T [21,29,40,43] 740 [31] (5.6) M [74]500 [74] M [29,43,51] 1.26 0.45	T [30,31] (4) 950 [31] (7) 1.34 0.61
Ce	1.02	T [21,33] 0.85 0.34	T [21,35] 1.00 0.04	T [21,41] (4) 1.18 0.31	1.26 0.47	(7) 1.34 0.63
Pr	1.00	T [21,33] 0.84 0.32	T [21,25,35,42] 0.99 0.02	T [21,41] (4) 810 [41] 685 [27] 1.16 0.33	T [29] 680 [21,31,43,44] (8) P[74]450 [44] 500 [31] P [29,44] 1.24 0.49	M [31] 1.32 0.65
Nd	0.99	T [21,33] 0.84 0.31	T [21,25,35,42] 0.98 0.01	T [21,41] (9) 780 [27] 680 [27] M [48] 1.16 0.34	T [21,29] 730 [31,43] P [74]510 [31] P [29] (10) 1.23 0.50	M [31] 1.32 0.66
Sm	0.97	T [21,33] 0.82 0.29	T [21,25,42] 0.98 0.01	M [21,48] 1.15 0.36	T [29]860 [31] P [74]510 [31] P [29] (10) 1.23 0.52	M [31]505 [31] M [31] 1.31 0.68
Eu	0.97	T [21,33] 0.82 0.29	T [21,25,42] 0.98 0.01	M [48] M [21]Tp [48] 1.15 0.36	T [29]920 [31] P [74]505 [31] P [29] 1.23 0.52	M [31] 500 [31] M [31] 1.31 0.68
Gd	0.94	T [21,33] 0.81 0.26	T [21,25,42] 0.96 0.94	885 [51] 545 [51] Tp [48] 1.14 0.39	T [74] P [74]520 [31] P [29] (10) 1.22 0.55	M [31] 505 [31] M[31] 1.30 0.71
Tb	0.89	T [21,23,33] 490 [52] T(11) 450 [52] T [52] 0.78 0.21	T [21,42] T [52] 0.94 0.09	P [41,52] (12) 540 [52] (13) Tp [48] 1.11 0.44	T (15) P (12) 520 (14) P (10) 1.19 0.60	M (14) 500 (14) M (14) 1.27 0.76
Dy	0.88	T [21,33,54] 530 [55] T [53] 0.78 0.20	T [21,25,47] T (11) 0.93 0.10	P (12) 530 [51] (13) P [41,48,52] 1.10 0.45	T (15) P [74] 520 [31] P [29] (10) 1.18 0.61	M (14) 500 (14) M [31] 1.26 0.77
Ho	0.86	T [21,33] 520 [53] T [53] 0.77 0.18	T [21,25,47] T (11) 0.92 0.12	P (12) 545 [51] (13) P [41,48,51] 1.10 0.47	T (15) P [74] 520[31] P [29] (10) 1.18 0.63	Γ [31] 980 [31] M [31] 500 [31] M [31] 1.26 0.79

(continued).

Table 4 (continued).

	M	Li		Na		K		Rb		Cs	
R	r (2)	0.68		0.98		1.33		1.49		1.65	
Er	0.85	T [21,33] 515 [53] T [53]	0.76 0.17	T [21,25,47] T (11)	0.92 0.13	Γ [21] P (12) 550 [51] (13) P [41,48,51]	1.09 0.48	Γ [29] 910 [31] P [74] 530 [31] (16) P [21] (10)	1.17 0.64	Γ [31] 905 [31] M [31] 520 [31] M [31]	1.25 0.80
Tm	0.85	T [21,33] 515 [52] T (11) 450 [52] T [52]	0.76 0.17	T [21,25,47] 580 [52] T [52]	0.92 0.13	Γ [21] P (12) 640 [41] (17) P (18) 515 [41,52] P [41,48,52]	1.09 0.48	Γ [29] 850 [31] M [74] 530 [31] M [29] (19)	1.17 0.64	Γ [31] 820 [31] M [31] 510 [31] M [31]	1.25 0.80
Yb	0.81	T [21,33] 510 [52] T (11) 419 [42] T [52]	0.74 0.13	T [21,25,47] 575 [52] T (11) 505 [52] T [52]	0.90 0.17	Γ [21] 875 [41,52] P [41,48,52]	1.07 0.52	Γ [21,29,43] 750 [31,43] M [74] 530 [31] M [29] (19)	1.15 0.68	Γ [21,30,31] 750 [31] M [31] 530 [31] M [31]	1.23 0.84
Lu	0.80	T [21,33] 500 [52] T (11) 450 [52] T [52]	0.74 0.12	T [21,47] 575 [19] T [52]	0.89 0.18	Γ [21] 825 [41,52] P (12) 535 [52] P [41,48]	1.06 0.53	Γ [21,29,43] 720 [31,43] M [74] 540 [31] M [29] (19)	1.14 0.69	Γ [21,30,31] 700 [31] M [31] 520 [31] M [31]	1.22 0.85

*See footnotes to Tables 4 and 5.

Table 5. Structures and polymorphism of double tungstates of the REE (R) and alkali metals (M) $RM(WO_4)_2$ (1).

	M	Li		Na		K		Rb		Cs	
R	r (2)	0.68		0.98		1.33		1.49		1.65	
Y	0.97	T [57,58] 910 [57] (20) M [58] 715 [42] M (14)	0.82 0.29	T [12,25,60,62]	0.98 0.01	1009 [28,64] (21) M [28,79]	1.15 0.36	M [54]	1.23 0.60	Γ [54] M [54]	1.31 0.68
La	1.04	T [58]	0.86 0.36	T [25,35,60,62,80]	1.01 0.06	M [15,23] (22,23)	1.18 0.29	T [54] 815 [54] M [54]	1.26 0.45	T [54] 910 [54]	1.34 0.61
Ge	1.02	T [23,68,69] (24)	0.84 0.32	T [35,62]	1.00 0.04	M [15] (22,23) 740 [15] M (20)	1.18 0.31		1.26 0.41		1.34 0.63
Pr	1.00	T [32,68,69] (24)	0.84 0.32	T [25,35,59]	0.99 0.02	T [54] 950 [54] P [54] 825 [54] M [15,68,71] (22,23) M (23)	1.16 0.33	M [54]	1.24 0.49	M [74] 350 [74] M [74]	1.32 0.65
Nd	0.99	T [32,68,69] 665 [82] T [32,48,68,69] (24)	0.84 0.31	T [25,35,59,60]	0.98 0.01	T [54] 830 [54] M [15,68,71] (22,23) 870 [61] M (23)	1.16 0.34	M [54]	1.24 0.50	M [74] 380 [54] M [74] (25)	1.32 0.66
Sm	0.97	T [48,58]	0.82 0.29	T [25,59,60,62]	0.98 0.01	T [74] 800 [54] M [15] (22,23) 1010 [65] M [15,65] (25)	1.15 0.36	M [54]	1.23 0.52	M [74] 400 [54] M [74] (26)	1.31 0.68
Eu	0.97	T [32,48,75]	0.82 0.29	T [25,60,62]	0.98 0.01	M [74] 800 [54] M [15] (25) 1000 [15] (25) M [15,65,79] (27)	1.15 0.36	M [23,54]	1.23 0.52	M [74] 400 [54] M [74] (26)	1.31 0.68
Gd	0.94	T [48,58]	0.81 0.26	T [25,60,62,80]	0.96 0.04	M [74] 860 [54] M [15] (25) 1005 [65] M [65,79] (27)	1.14 0.39	M [54]	1.22 0.55	M [74] 400 [54] M [74] (26)	1.30 0.71
Tb	0.89	T [48,58] 744 [58] M [48] M [48,58]	0.78 0.21	T [62]	0.94 0.09	M (25) 1080 [65] M [15,65] (27,28)	1.11 0.44	M [74] 800 [55] M [23,54]	1.19 0.60	M [74] 400 [54] M [74] (26)	1.27 0.76
Dy	0.88	T [48,58] 840 [58] M [48,58]	0.78 0.20	T [25,60,62]	0.93 0.10	M [25] 1025 [65] 1040 [61] M [15,65] (27)	1.10 0.45	M [74] 800 [54] M [54]	1.18 0.61	M [74] 400 [54] M [74]	1.26 0.77
Ho	0.86	T [48,58] 882 [58] M [48,58]	0.77 0.18	T [25,60,62]	0.92 0.12	M (25) 1025 [65] 1010 [61] M [15,65] (27)	1.10 0.47	M [74] 800 [54] M [54]	1.18 0.63	Γ [74] 1100 [54] M [74] 400 [54] M [74] (29)	1.26 0.79
Er	0.85	T [48,58] 983 [58] M [48] M [48,58]	0.76 0.17	T [25,60,62]	0.92 0.13	M (25) 1040 [65] 1055 [61] M [15,65] (27)	1.10 0.48	M [74] 830 [54] M [54]	1.17 0.64	Γ [54] 1000 [54] M [74] 400 [54] M [74] (29)	1.25 0.80
Tm	0.85	T [48,58] 976 [58] M [48] M [48,58]	0.76 0.17	T [25,60,62]	0.92 0.13	M (25) 1030 [65] 1060 [61] M [15,65] (27)	1.09 0.48	Γ [54] 1020 [54,74] M [74] 830 [54] M [54]	1.17 0.64	Γ [54] 970 [54] M [74] 440 [54] M [74]	1.25 0.80
Yb	0.81	M [48,58,76,81] (30)	0.74 0.13	T [25,60,62]	0.90 0.17	M (25) 1030 [65] 1060 [61] M [15,65] (27)	1.07 0.52	Γ [54] 920 [54] M [74] 850 [54] M [54]	1.15 0.68	Γ [54] 900 [54] M [74] 400 [54] M [74] (31)	1.23 0.84
Lu	0.80	M [48,58] (30)	0.74 0.12	T [60,62]	0.89 0.18	M (25) 1060 [65] M [15,65] (27)	1.06 0.53	Γ [54] 900 [54] M [74] 870 [54] M [54]	1.14 0.69	Γ [54] 850 [54] M [74] 500 [54] M [74] (31)	1.22 0.85

Footnotes to Tables 4 and 5.

(1) The following symbols are used in Tables 4 and 5: T—tetragonal, P—orthorhombic, M—monoclinic, Tp.—triclinic, Г—hexagonal.
The Tables are divided into blocks, each of which corresponds to a particular double compound. The lower part of each block contains the low-temperature modification, the upper part the high-temperature modification, and the central part the intermediate phase; the temperature (°C) of the phase transformations are given on the right. The values of Δr and r_{av} are given in the lower right-hand corner of the block.
(2) The ionic radii are taken from Ref. 18.
(3) According to Ref. 27, there is no polymorphic transformation.
(4) In our opinion, polymorphism is observed here, and the authors cited obtained the quenched high-temperature forms.
(5) According to Ref. 39, there is no polymorphic transformation.
(6) According to Ref. 43, the temperature of the transformation is 690°.
(7) According to our ideas, the low-temperature phase should have monoclinic or orthorhombic symmetry.
(8) In Ref. 21, a single polymorphic transformation was observed at 700°.
(9) In Ref. 48 it is reported that the high-temperature phase is isostructural with the high-temperature modification of $NdK(WO_4)_2$.
(10) In Refs. 21 and 43 the symmetry was not determined, but it was established that the compound is isostructural with PrRb molybdate, which has orthorhombic symmetry.
(11) We assume tetragonal symmetry here.
(12) Examination of the diagram in Fig. 1 indicates that this is apparently an orthorhombic phase.
(13) According to Ref. 41 there is no polymorphic transformation.
(14) The authors' suggestion.
(15) Quenching of the specimens from temperatures close to the melting points[74] gave a mixture of a tetragonal phase (isostructural with the high-temperature phases of $RRb(MoO_4)_2$ with R = La–Gd) and an orthorhombic phase.
(16) In Ref. 43, a single polymorphic transformation was established at 730° (the measurements were made up to 800°). The low-temperature phase was found to be tetragonal, and the high-temperature phase was found to be isostructural with $PrPb(MoO_4)_2$, orthorhombic[44]. Quenching of $ErRb(MoO_4)_2$ from 650–700° into liquid nitrogen gives a monoclinic modification of the same type as the low-temperature modifications of the rubidium molybdates formed by thulium, ytterbium, and lutetium.
(17) The second polymorphic transformation at 640° in Ref. 52 was not established.
(18) If the orthorhombic structure is stable above 640° [see (12)], then the phase between 515° and 640° is also orthorhombic, since it cannot have a lower symmetry than the low-temperature phase, which has been found to be orthorhombic[41,48,52].
(19) In Refs. 21 and 43, the compound was found to have a tetragonal low-temperature modification, and a low-temperature polymorphic transformation was not detected.
(20) In Ref. 58 the temperature of the phase transformation was found to be 904°.
(21) In Ref. 28 it was suggested that the high-temperature modification has a tetragonal structure.
(22) In Ref. 8 the high-temperature phase was found to have a tetragonal structure with monoclinic distortion.
(23) According to Refs. 65 and 79, polymorphic transformations are not observed.
(24) Hydrothermal preparation[68,69] gave monoclinic crystals.
(25) According to Refs. 43 and 71, the low-temperature form of $RK(WO_4)_2$, where R = La–Nd, has a monoclinic structure. According to Ref. 8, these phases are isostructural with the high-temperature modifications of $RK(WO_4)_2$, where R = Sm–Lu. They are therefore monoclinic, since the symmetry of the high-temperature modification is never lower than that of the low-temperature phase, and the latter, for $RK(WO_4)_2$, where R = Sm–Lu, are monoclinic[15,65,79]. In the case of Lu, the high-temperature modification is apparently hexagonal (see section headed "Fusion").
(26) The low-temperature phase is isostructural with the low-temperature modification of $PrCs(WO_4)_2$.[54]
(27) This phase is isostructural with the low-temperature modification of $YK(WO_4)_2$.[15,65]
(28) In Ref. 76, the structure was found to be triclinic.
(29) The low-temperature phase is isostructural with the low-temperature modification of $YCs(WO_4)_2$.[54]
(30) In Ref. 58 it is suggested that the temperature of the phase transformation is so close to the melting point that the low-temperature monoclinic modification crystallises immediately.
(31) The low-temperature phase is isostructural with the low-temperature modification of $YCs(WO_4)_2$.[54]

It is probable that almost all other $RLi(MoO_4)_2$ and $RNa(MoO_4)_2$ have been obtained in the form of stabilised or quenched high-temperature phases.

The RK molybdates are characterised by a large number of clearly defined polymorphic transitions. The isostructural tetragonal phases $RK(MoO_4)_2$, where R = La–Nd,

prepared from solution in a melt[41] and by sintering mechanical mixtures[21], are probably high-temperature phases, since $NdK(MoO_4)_2$, prepared by the methods of ceramic technology[48], was obtained in two forms: a high-temperature monoclinic distorted scheelite form, corresponding to the tetragonal form[41], and a low-temperature monoclinic form.

$YK(MoO_4)_2$ crystals, obtained from solution in a melt, were found to be orthorhombic[41]. When heated, they underwent a polymorphic transformation[28]. The orthorhombic structure can therefore be regarded as the low-temperature form, although there is still some doubt regarding this conclusion, since the X-ray diffraction pattern for this compound, obtained by sintering mechanical mixtures, contains a large number of lines, the splitting of which indicates a low-symmetry, apparently triclinic, structure[21].

The RK molybdates from Dy to Lu [41,48] and the high-temperature (orthorhombic) modification of $TbK(MoO_4)_2$ [48] are isostructural with the double molybdate $YK(MoO_4)_2$. Crystallisation from solution in a melt[41] gave only this structure of $TbK(MoO_4)_2$, which does not exhibit polymorphism. In this case, therefore, stabilisation of the orthorhombic phase takes place under the conditions of growth. This phenomenon is of undoubted importance for the growth of single crystals.

The crystals obtained from solutions in a melt[41] for the most part undergo high-temperature polymorphic transformations (Table 3). Low-temperature transformations have been detected in the study of the equilibrium diagrams[51] of compounds obtained by sintering mechanical mixtures with subsequent fusion of the sinter and slow cooling[51,52]. The low-temperature transitions in all cases are accompanied by weak thermal effects.

Mokhosoev and coworkers[21] assumed for the potassium molybdates from Er to Lu not the orthorhombic structure, as all other authors have done (Table 4), but a hexagonal structure. At the same time, X-ray diffraction studies[78] of the orthorhombic crystals of $YK(MoO_4)_2$ have shown that their structure is close to hexagonal. From the analogy between the rubidium and caesium double molybdates, we have classified the hexagonal phases as high-temperature phases (Table 3).

Most rubidium and caesium REE molybdates show low-temperature phase transformations (Table 3), which give weak endothermic effects on the thermograms obtained by heating[31], and which do not lead to marked changes in structure.

At high temperatures, the rubidium and caesium double molybdates of the heavy REE become hexagonal (Table 4). In the three-dimensional diagram of phase transformations (Fig. 1), which we constructed from published data, the right-hand upper corner shows the range of existence of the high-temperature hexagonal phase, bounded below by the surface *1*, *2*, *3*, *4*, *5*, *6*, *7*. It can thus be seen that the high-temperature phases of the potassium molybdates of Lu and Yb (and possibly also Tm and Er) should be similar to the high-temperature phases of the caesium and rubidium double molybdates with the heavy REE, that is they should be hexagonal.

A noteworthy feature is that the temperatures of the low-temperature transformations for almost all double molybdates are approximately the same (the surface *14*, *15*, *16*, *17*, *18*, *19*, *20*, *21*, *22*, *23*, *24*, *25*, *26* in Fig. 1). In the diagram, a single overall surface has been drawn through the points corresponding to these transitions (in some regions it is "split" into two surfaces close together). In fact, these transformations have much in common: they are difficult to detect, apparently as a consequence of stabilisation of the high-temperature phase; they give weak thermal effects; and they do not lead to a change in symmetry. Their nature has not yet been established. It is quite possible that this surface has a "gap" in the region of the lithium and sodium double molybdates of the light REE, and their low-temperature transformations are even more difficult to detect.

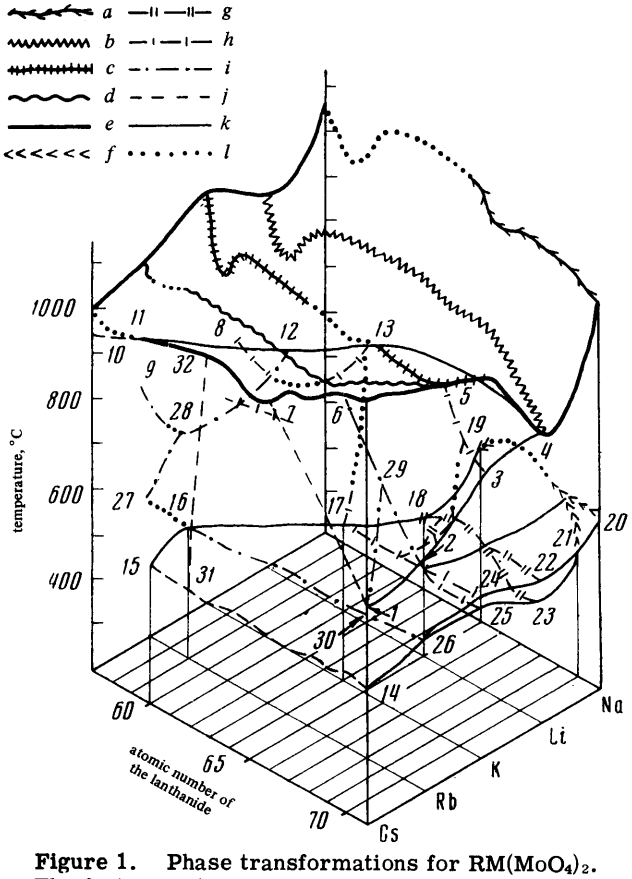


Figure 1. Phase transformations for $RM(MoO_4)_2$. The fusion surface is indicated by the lines: *a*) Na, *b*) Li, *c*) K, *d*) Rb, *e*) Cs. The surfaces of the other phase transformations are shown by the lines: *f*) Na, *g*) Li, *h*) K, *i*) Rb, *j*) Cs. *k*) Guide lines; *l*) assumed lines.

The range of existence of the phases with a tetragonal structure is occupied by all the lithium and sodium double molybdates. On going to the potassium, rubidium, and caesium compounds, this range (which is bounded below by the surface *8*, *9*, *10*, *11*, *12*, *13*) becomes narrower towards lanthanum and becomes the high-temperature region.

The dependence of the type of structure at low temperatures on $r_{R^{3+}}$ and r_{M^+} can be characterised by the extent to which these radii differ from one another ($\Delta r = |r_{M^+} - r_{R^{3+}}|$) and from the radius of the calcium ion in the scheelite structure [$r_{av} = (r_{M^+} + r_{R^{3+}})/2$]. The greater

this difference, the lower the symmetry of the low-temperature modification (Table 3).

For the potassium, rubidium, and caesium double compounds, the parameter Δr increases towards Lu, whereas r_{av} decreases, that is the two factors act in opposite directions. If the low-temperature potassium and rubidium double molybdates with the $YK(MoO_4)_2$ structure did in fact have orthorhombic symmetry, and not a lower symmetry, r_{av} would obviously have a greater influence on the structure than Δr, since on going towards Lu the symmetry increases to orthorhombic. The fairly large values of Δr, however, have a stronger influence than r_{av}: the heavy rubidium and all the caesium REE molybdates have monoclinic symmetry.

It should also be noted that with increase in the deviation from the "scheelite" radius ratio ($r_{R^{3+}} \simeq r_{M^+} \simeq r_{Ca^{2+}}$) there is an increase in the variety of structural types and in the tendency for polymorphism to be observed (Table 3). As a rule, the symmetry of the high-temperature phase is higher than that of the low-temperature phase. This suggests that with increase in temperature, equalisation of the ion dimensions takes place. Thus it has been shown [49] that the large difference in the ionic radii of Pr and Rb causes these cations to be distributed in separate layers on transformation of the high-temperature modification of $PrRb(MoO_4)_2$ into the low-temperature form.

The high-temperature phase of $LaCs(MoO_4)_2$ has not been identified, and the low-temperature phase is assumed to be tetragonal [31]. It is not excluded, however, that this tetragonal phase is in fact the high-temperature phase, and that the effect on the thermograms at 950° [31] is due merely to partial phase transformation. In this case, $LaCs(MoO_4)_2$ would not be an exception in the diagram (Fig. 1) and would complete the range of tetragonal phases in regular fashion. If this is the case, the low-temperature form of $LaCs(MoO_4)_2$ should have either a monoclinic or an orthorhombic structure, depending on whether it completes the monoclinic range, bounded below by the surface *13*, *17*, *27*, *28*, or the orthorhombic range, bounded on the left by the same surface, and on the right by the surface *29*, *30*, *31*, *32*.

The monoclinic low-temperature modifications of $RRb(MoO_4)_2$, where R = Tm–Lu, and $RCs(MoO_4)_2$, where R = Pr–Lu, have been assigned to the $PrCs(MoO_4)_2$ structural type [31,74]. The X-ray powder diagrams of the caesium molybdates from Pr to Sm can be indexed satisfactorily in the orthorhombic system. The heavier REE show appreciable splitting of some of the lines, which increases with increase in the atomic number of R.

The double tungstates $RM(WO_4)_2$ are characterised by the same regular features as were noted above for the molybdates, but reveal them much more sharply (Table 4).

In fact, the crystals of the NaREE tungstates, as a consequence of the similarity in $r_{R^{3+}}$, r_{M^+}, and $r_{Ca^{2+}}$, have the tetragonal (scheelite) structure and do not exhibit polymorphism, whereas the low-temperature modifications of the lithium double molybdates of the heavy REE have monoclinic symmetry. When heated, they undergo reversible transformations into high-temperature tetragonal phases.

In the case of the scheelite-like lithium double molybdates of the light REE, a polymorphic transformation has been established only for $NdLi(WO_4)_2$ (Table 4). At 665° it gives a weak thermal effect, which is not accompanied by a change in symmetry. Similar transformations can apparently be detected for the other light RLi tungstates.

The decrease in symmetry towards Lu can be attributed to the large contribution of the influence of change in r_{av} compared with Δr. The low-temperature phases of the other double tungstates are monoclinic.

The diagram for the phase transformations of the double tungstates (Fig. 2) is approximately the same as that for the molybdates. Instead of the horizontal surface corresponding to the low-temperature transformations, however, it has a steep sloping surface (*3*, *7*, *8*, *14*, *15*, *16*). In the region where this surface approaches the melting point surface (RK molybdates), the polymorphic transformations are accompanied by marked thermal effects [65] and mechanical stresses leading to breakdown [79]. In the low-temperature region of the surface (RCs tungstates) the transformations correspond to weak effects on the thermograms and do not lead to significant changes in structure.

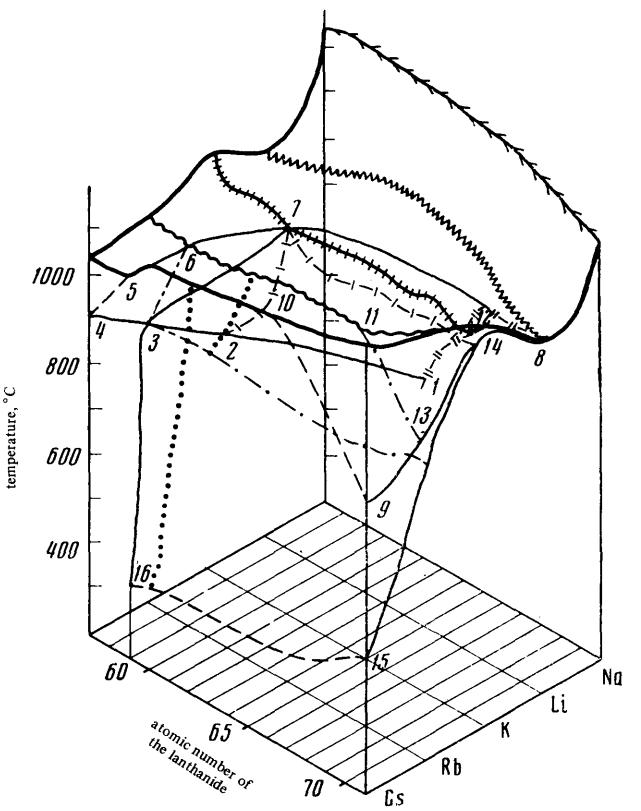


Figure 2. Phase transformations for $RM(WO_4)_2$. For symbols see Fig. 1.

This relationship between the "strength" of a transformation and its proximity to the melting point can be readily followed for other double compounds from all those papers which give DTA curves. On the other hand, it makes it possible to estimate the disruptive tendencies of the phase transformation in the selection of compounds and procedures for the growth of single crystals.

The ranges of existence of the tetragonal and hexagonal modifications are bounded below by the surfaces *1*, *2*, *3*, *4*,

5, *6*, *7*, *8*, and *9*, *10*, *11*, *12*, *13* respectively, and are bounded above by the fusion surface. The reverse order of the positions of Li and Na in Fig. 2 was chosen for the sake of clarity in the representation of the actual diagram as a whole, and also to set off the regular increase in the width of the range corresponding to the tetragonal phases from the caesium double tungstates to the sodium compounds. Although this last feature is not of importance for the double molybdates (since all the phases $RLi(MoO_4)_2$ and $RNa(MoO_4)_2$ are tetragonal), the positions of Li and Na are also represented in Fig. 1, for convenience in comparing the two diagrams. The monoclinic phases lying above and below the sloping surface *3*, *7*, *8*, *14*, *15*, *16* correspond to at least six structural types [15,54,65,74]. Thus as in the case of the molybdates, increase in Δr and r_{av} is accompanied by an increase in the variety of tungstate structures. The symmetry of the high-temperature structure is always higher than that of the low-temperature structure.

It should also be noted that the crystals of the low-temperature forms of the potassium, rubidium, and caesium double tungstates and molybdates exhibit perfect cleavage, and this creates additional difficulties in the growth of large crystals and their use in lasers. The anisotropy of the mechanical properties can be attributed to the tendency for R and M with a large value of Δr to distribute themselves in layers. This increases the degree of order in the structure, however, and hence decreases the width of the luminescence lines, as noted above for the $YK(MoO_4)_2$–Nd^{3+} system.

The existence of "smooth" surfaces on the three-dimensional diagrams giving the phase transformations of $RM(MoO_4)_2$ and $RM(WO_4)_2$, bounding the ranges of existence of related structures, means that we are dealing not with a simple set of compounds, but with systems. This feature makes it possible to represent regularities, to estimate the reliability of published data in those cases where they are contradictory, and to predict various properties which have not yet been established.

IV. FUSION

The "smooth" form of the fusion surfaces on the diagrams (Figs. 1 and 2) makes it possible in many cases to estimate melting points which have not yet been determined: $RNa(MoO_4)_2$ from Nd to Gd ~1160°; $CeNa(MoO_4)_2$ and $PrNa(MoO_4)_2$, apparently, ~1080°; $SmK(MoO_4)_2$ ~ 990°; $GdK(MoO_4)_2$ ~ 960°; $TbRb(MoO_4)_2$ ~ 980°; $TbCs(MoO_4)_2$ ~ 1010°; $CeNa(WO_4)_2$ ~ 1270°; $CeLi(WO_4)_2$ ~ 1060°; and $CeRb(WO_4)_2$ and $CeCs(WO_4)_2$ ~ 1040°.

The melting points of the double tungstates are always higher than those of the corresponding molybdates, so that the high melting points found by Heindl and coworkers [8] for the sodium molybdates of La, Pr, and Nd (Table 5) contradict the values found by other workers [38,58,80].

Data on the fusion of double molybdates and tungstates are contradictory (Tables 6 and 7). It has been suggested [60,61,74] that there exists a boundary of congruent fusion, separating the congruently melting double molybdates and tungstates of the light REE from the incongruently melting double compounds of the heavy REE. For molybdates containing sodium, potassium, and rubidium, this boundary passes through gadolinium or terbium and is then displaced towards the end of the REE series in the case of caesium. For the tungstates it passes through $ErNa(WO_4)_2$, $LaK(WO_4)_2$, $HoRb(WO_4)_2$, and $DyCs(WO_4)_2$. According to other sources [41,65], however, all the compounds $RK(EO_4)_2$ (obtained from solution in a melt) melt congruently.

The suggestion that there is a relationship between the position of the boundary of congruent fusion and the fairly sharp decrease in melting point on going into the range of incongruent fusion, put forward for the rubidium and caesium double tungstates [61], is apparently justified in individual cases. The fusion surface for the double molybdates (Fig. 1) in fact shows a curvature due to a decrease in the melting points along the REE series, beginning at Tb for the rubidium and caesium compounds, at Gd for the potassium compounds, and at Dy for the lithium and sodium compounds, corresponding approximately to the boundary of incongruent fusion (Table 6). The fusion surface of the double tungstates also shows corresponding curvatures in the region of $HoCs(WO_4)_2$, $ErRb(WO_4)_2$, $HoK(WO_4)_2$, $HoLi(WO_4)_2$, and $ErNa(WO_4)_2$. These compounds apparently also form the boundary of incongruent fusion for the tungstates.

Table 6. Temperatures and nature of the fusion of the double molybdates of the REE (R) and alkali metals (M) $RM(MoO_4)_2$*.

R	M				
	Li	Na	K	Rb	Cs
Y	975^{33} 950^{22}	$1110+^{22}$	$980^{22,27}$		
La	930^{33} 1075^{26}	1163^{38} 1140^{58} 1425^{8}	$1070-^{41}$ 1140^{32}	1040^{32} 1020^{31}	980^{32} 1000^{31}
Ce	900^{33}		$930-^{41}$		
Pr	975^{33}	1435^{8}	$1000-^{41}$ 1030^{27}	1015^{44} 1025^{31}	1000^{31}
Nd	1010^{33}	1460^{8}	$990^{-27,41}$	1030^{31}	1010^{31}
Sm	1020^{33}			1015^{31}	1040^{31}
Eu	1025^{33}			1015^{31}	1040^{31}
Gd	1035^{33}		$+51$	1000^{31}	1050^{31-74}
Tb	1020^{33} $1030+^{52}$	$1160+^{52}$	975^{-41+41} $1000+^{52}$		
Dy	1010^{33} 980^{53}	$1090+^{55}$	$975-^{41}$ $+51$	980^{31}	1025^{31}
Ho	1005^{33} $990+^{53}$	$1110+^{55}$	$965-^{41}$ $+51$	1000^{31}	1070^{31}
Er	990^{33+53}	$1100+^{55}$	$955-^{41}$ 990^{27}	1040^{31}	1085^{31}
Tm	950^{33+53}	$1095+^{52}$	$935-^{41}$ $1000+^{52}$	1060^{31}	1115^{31}
Yb	900^{33} $925+^{52}$	$1080+^{52}$	$990-^{41}$ 1025^{52}	1075^{31}	1145^{31}
Lu	835^{33} $863+^{52}$	$1050+^{52}$	$1030-^{41}$ $1050+^{52}$	1100^{31}	1150^{31}

*In Tables 6 and 7, the minus sign denotes congruent fusion, the plus sign denotes incongruent fusion, and the absence of a sign denotes that the nature of the fusion has not been established.

The very sharp decrease in the melting points of the double molybdates formed by cerium with lithium and potassium apparently cannot be related to the nature of the fusion until more information is obtained. The increase in the melting points of the hexagonal high-temperature phases for both the double tungstates and the double molybdates of the heavy REE (Figs. 1 and 2) is evidently not accidental.

The high-temperature modification of $LuK(MoO_4)_2$ should be hexagonal.

In the other cases, the relationship between the melting points and the structures of the high-temperature phases is not so clear.

Table 7. Temperatures and nature of the fusion of the double tungstates of the REE (R) and the alkali metals (M) $RM(WO_4)_2$.*

R	M				
	Li	Na	K	Rb	Cs
Y	1050^{58}	1200^{-60}	$1046^{28,62}$ 1060^{+61}	1070^{+61}	1145^{+61}
La	1040^{58}	$1250^{-60,80}$	1120^{-65} 1160^{-61}	$1050^{54,71}$ 1070^{-61}	$1040^{54,74}$ 1090^{-61}
Ce			1060^{-65}		
Pr	1070^{58}		$1080^{-62,65}$	1020^{54} 1040^{-74}	1050^{57-74}
Nd	1075^{58} 1045^{62}	$1263^{-60,80}$	1075^{-65} 1070^{+61}	1030^{54} 1045^{74} 1055^{-61}	1080^{54} 1100^{74} 1055^{-61}
Sm	1120^{58}	1250^{-60}	1060^{-65} 1030^{+61}	$1050^{54,74}$ 1080^{-61}	1100^{54} 1060^{74} 1100^{-61}
Eu	1130^{58}	1248^{-60}	1065^{-65} 1052^{+61}	$1070^{54,74}$ 1095^{-61}	1100^{54} 1065^{74} 1135^{-61}
Gd	1135^{58}	1260^{-80} 1253^{-60}	1075^{-65} 1060^{+61}	1070^{54} 1075^{74} 1105^{-61}	1100^{54} 1075^{74} 1162^{-61}
Tb	1120^{58}		1080^{-65} 1070^{+61}	1070^{54} 1075^{74} 1105^{-61}	1100^{54} 1080^{74} 1165^{-61}
Dy	1108^{58}	1230^{-60}	1075^{-65} 1070^{+61}	1070^{54} 1080^{74} 1120^{-61}	1100^{54} 1075^{74} 1140^{-61}
Ho	1086^{58}	1215^{-60}	1070^{-65} 1075^{+61}	1070^{54} 1075^{74} 1085^{-61}	1080^{54} 1090^{74} 1155^{+61}
Er	1069^{58}	1200^{-60}	1080^{-65} 1070^{+61}	1060^{54} 1070^{+74} 1075^{+61}	1100^{54} 1110^{+74} 1145^{+61}
Tm	1008^{58}	1175^{+60}	1055^{-65}	1080^{54} 1090^{74}	1120^{54} 1120^{74}
Yb	982^{58+76}	1160^{+60}	1045^{-65} 1090^{+61}	1100^{54} 1105^{74} 1130^{+61}	1150^{54} 1140^{74} 1260^{+61}
Lu	975^{58}	1134^{+60}	1090^{-65}	1130^{54} 1150^{74}	1180^{54} 1150^{74}

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Almost all compounds of the type $RM(EO_4)_2$, where R = the REE and Y, M = an alkali metal, and E = Mo or W, have been prepared, but only a few of them have been obtained in the form of large crystals.

Single crystals of double tungstates and molybdates containing REE exhibit valuable laser properties. Their luminescence characteristics depend on the ratio of the dimensions of the R^{3+} and M^+ ions and on the structure. The low-temperature structure of $RM(EO_4)_2$ is determined chiefly by the quantities $\Delta r = |r_{M^+} - r_{R^{3+}}|$ and $r_{av} = (r_{M^+} + r_{R^{3+}})/2$, which characterise the extent of the departure from the scheelite radius ratio of the ions $r_{M^+} \simeq r_{R^{3+}} \simeq r_{Ca^{2+}}$. With increase in Δr and r_{av}, the symmetry of the low-temperature modification decreases, the number of structural types increases, the tendency to exhibit polymorphism becomes greater, and the R and M atoms tend to distribute themselves in individual layers, leading to the production of perfect cleavage in the crystals. At the same time, increase in these two parameters leads to a decrease in the disorder of the low-temperature structure and a corresponding decrease in the width of the luminescence line.

Δr and r_{av} change in opposite directions along the REE series, so that in some cases the symmetry of the low-temperature phase increases towards lutetium.

The symmetry of the high-temperature modification is never lower than that of the low-temperature phase.

The formation of a given modification depends on the method of preparation and the subsequent thermal treatment. This constitutes the chief difficulty in the deduction of the above regular features from an analysis of published material.

The construction of phase transformation diagrams on the basis of published data has made it possible to compile a fairly complete picture of the polymorphism and fusion of the rare earth metal double tungstates and molybdates, to reveal the regions with identical symmetries, and in some cases to estimate the structures, melting points, and polymorphic transitions where these have not yet been established.

A relationship evidently exists between the nature of the fusion and the form of the fusion surface; the boundary of incongruent fusion passes in "steps" over this surface.

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