SYNTHESIS, X-RAY, AND THERMOGRAPHIC STUDY OF POTASSIUM-RARE-EARTH TUNGSTATES

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SYNTHESIS, X-RAY, AND THERMOGRAPHIC STUDY OF POTASSIUM-RARE-EARTH TUNGSTATES

$KLn(WO_4)_2$, Ln—R.E.E.

(Presented by Academician N. V. Belov, July 25, 1968)

Among the double tungstates of alkali and rare-earth metals of the type $M^{1+}Ln^{3+}(WO_4)_2$, the sodium compounds, $M^{1+} = Na^{1+}$, have been synthesized and studied most extensively. These compounds are usually obtained either by sintering the oxides of the initial components in stoichiometric ratio, or by crystallization from a solution in a melt. Double sodium tungstates for the entire series of rare-earth elements crystallize in the structural type of scheelite. In works ([1]), the fluorescence spectra of many double tungstates $M^{1+}Ln^{3+}(WO_4)_2$ were studied, in which the R.E.E. Ln^{3+} is partially replaced by Eu^{3+}.

Potassium–rare-earth tungstates have been synthesized and studied less completely. In ([2]), potassium tungstates of lanthanum and cerium were obtained by melting a mixture Ln_2O_3 (Ln—La, Ce)—$3WO_3$ with an excess of K_2WO_4. According to X-ray analysis, both compounds possess a tetragonal scheelite structure. Van Uitert and Soden ([1]) obtained crystals of double potassium tungstates of yttrium, europium, and terbium from a solution in a $K_2W_2O_7$ melt. It was established that potassium–yttrium tungstate belongs to the monoclinic system ([3]).

Under hydrothermal conditions, potassium tungstates of cerium, praseodymium, and neodymium are formed as phases of variable composition $K_{1-3x}Ln_{n,1+x}(WO_4)_2$ in a new monoclinic modification ([4]).

Thus, depending on the atomic number of the rare-earth element and on the physicochemical conditions, double potassium tungstates may possess different crystalline structures. In the present work, potassium tungstates $KLn(WO_4)_2$ for the entire series of rare-earth elements from lanthanum to lutetium have been synthesized and studied by X-ray and differential thermographic analyses.

Single crystals of $KLn(WO_4)_2$ (Ln–R.E.E.) were obtained by crystallization from a solution in a $K_2WO_4 + WO_3$ melt, taken in equimolar ratio. As the charge, a powder of the normal tungstate $Ln_2(WO_4)_3$ was used, prepared by sintering the oxides Ln_2O_3 and WO_3 in stoichiometric ratio, or the oxide of the rare-earth element. The synthesis of the normal tungstates by sintering was carried out in the temperature range 500-900° at intervals of 100°, with repeated thorough grinding of the sinter. Annealing at the specified temperature was carried out for 2-3 h. The molar ratio of charge to solvent was 1:2, and, when oxides were used, 1:3. The initial mixture of charge and solvent was heated in a platinum crucible to 1000-1200° and held for several hours. It was then cooled to 700° at a rate of 3 deg/h. From 700° to room temperature, cooling was carried out at a high rate–about 25 deg/h. The crystals were extracted by boiling the contents of the crucible in water. Crystals are leached out more rapidly when the oxide of the R.E.E. is used as the charge, for in this case during the process of synthesis, the composition of the solvent changes to the more readily water-soluble K_2WO_4. When the normal tungstate is used, after synthesis the initial solvent contains tungsten trioxide.

The crystals of KLn tungstates synthesized in this way are transparent and have colors characteristic of many analogous compounds of rare-earth elements Ln: for Ce–with a greenish tint, Pr–green, Nd–violet, Sm–yellow, Tb–light brown, Dy–light green, Ho–with a greenish-yellow tint, Er–pink; for La, Eu, Gd, Yb, and Lu the crystals are practically colorless. Individual crystals have well-developed faces. For the first four elements from La to Nd, the double potassium tungstates crystallize in the form of a tetragonal dipyramid or combinations of a tetragonal dipyramid and relatively weakly developed faces of a tetragonal prism and pinacoid. For the remaining rare-earth elements the crystals have a different, prismatic habit. Optico-goniometric measurements carried out for

Table 1

Unit-cell dimensions of $KLn(WO_4)_2$

Ln	*a*, Å, ±0.02	*b*, Å, ±0.02	*c*, Å, ±0.02	Ln	*a*, Å, ±0.02	*b*, Å, ±0.02	*c*, Å, ±0.02
La	5.42	–	12.08	Tb	8.07	10.38	7.54
Ce	5.41	–	12.05	Dy	8.05	10.32	7.52
Pr	5.39	–	12.01	Ho	8.04	10.30	7.51
Nd	5.38	–	11.91	Er	8.03	10.29	7.51
Sm	8.10	10.42	7.58	Tu	8.02	10.26	7.49
Eu	8.08	10.41	7.58	Yb	8.01	10.24	7.47
Gd	8.07	10.40	7.57	Lu	7.99	10.21	7.45

crystals of $KLn(WO_4)_2$, Ln–Sm, Dy, and Er, indicate that the latter belong to the monoclinic system. The angle of monoclinicity, found by direct measure-

Fig. 1. Differential heating curves of potassium–rare-earth tungstates $KLn(WO_4)_2$, where Ln : 1—Eu, 2—Tu, 3—Yb, 4—Lu

Figure 1: Fig. 1. Differential heating curves of potassium–rare-earth tungstates $KLn(WO_4)_2$, where Ln : 1—Eu, 2—Tu, 3—Yb, 4—Lu

ments on an optical goniometer, is equal to $94°05'$, $94°13'$, $94°13'$, $94°13' \pm 8'$, respectively.

X-ray data were obtained by indexing powder X-ray diffraction patterns recorded on a URS-50I instrument using filtered copper radiation. Analysis of the diffraction patterns made it possible to distinguish, among the potassium–rare-earth tungstates, two groups with different crystal structures: 1) tungstates of La, Ce, Pr, and Nd, which crystallize in the tetragonal scheelite structure, and 2) tungstates of rare-earth elements from Sm to Lu, which crystallize in the monoclinic structure of $KY(WO_4)_2$.

From the powder diffraction patterns, the unit-cell parameters were determined for all KLn tungstates. On the basis of optico-goniometric measurements for the monoclinic crystals, the angle β was taken as $94°$. Subsequently the linear parameters were refined on a computer by the least-squares method using a program compiled by F. A. Brusentsev and A. N. Rebenko. The results obtained are presented in Table 1.

With increasing atomic number of the rare-earth element, all unit-cell parameters in the $KLn(WO_4)_2$ series decrease.

The presence of high-temperature phase transitions in the synthesized crystals and the melting temperatures were determined by differential thermal analysis (DTA).

The DTA curves were recorded on a low-frequency thermographic recorder NTR-62M at an average heating rate of $10°$/min. The temperature was measured with Pt–Pt 10% Rh thermocouples; their hot junctions were placed directly in the substance under study and in the reference material (aluminum oxide) in quartz microcrucibles. Samples of ~ 1 g were used. The accuracy of the temperature measurement does not exceed $\pm 10°$. The results of the DTA measurements are summarized in Table 2.

Thermographic studies in combination with X-ray data showed that:

a) All double potassium–rare-earth tungstates melt congruently in the temperature range 1045–1120°.

b) The tungstates of the light rare-earth elements La, Ce, Pr, and Nd, which have the scheelite structure, do not undergo polymorphic transformations upon heating.

Fig. 1. Differential heating curves of potassium–rare-earth tungstates $KLn(WO_4)_2$, where Ln : 1—Eu, 2—Tu, 3—Yb, 4—Lu

c) On the DTA curves of the tungstates of the heavier rare-earth elements, with the exception of the last element (lutetium), in addition to the effect corresponding to melting, an intense endothermic effect appears, apparently due to a polymorphic transformation (Fig. 1). This effect is reversible, as indicated by its reproducibility on cooling curves, as well as by the identity of Debyegrams taken from the initial substance and from the substance that had undergone melting.

d) The polymorphic transformation in all tungstates takes place at high temperature (above 1000°) near the melting point. The temperature interval between the melting points and the polymorphic transformation decreases with increasing atomic number of the rare-earth element from Gd (70°) to Yb (15°). One may assume the presence in $KLu(WO_4)_2$ of a polymorphic transformation immediately before melting, as a result of which the thermal effects are not resolved on the DTA curves.

Table 2

DTA data for $KLn(WO_4)_2$

Ln	Temperature of polymorphic transformation, °C	Melting temperature, °C	Temperature, °C	Ln	Temperature of polymorphic transformation, °C	Melting temperature, °C	Temperature, °C
La	–	1120	–	Tb	1025	1080	55
Ce	–	1060	–	Dy	1025	1075	50
Pr	–	1080	–	Ho	1025	1070	45
Nd	–	1075	–	Er	1040	1080	40
Sm	1010	1060	50	Tu	1030	1055	25
Eu	1010	1065	55	Yb	1030	1045	15
Gd	1005	1075	70	Lu	–	1090	–

Thus, under ordinary conditions, double potassium–rare-earth tungstates synthesized from solution in the melt exist in

two crystalline structures: tetragonal scheelite for La, Ce, Pr, and Nd, and monoclinic of the $KY(WO_4)_2$ type for the remaining rare-earth elements. These results agree with those given in ([2]) concerning the structural type of $KLa(WO_4)_2$ and $KCe(WO_4)_2$ crystals, but do not confirm the assumption that $KEu(WO_4)_2$ and $KTb(WO_4)_2$ crystals belong to the triclinic system ([1]).

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Note: Figure translations are in progress. See original paper for figures.