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THERMAL BEHAVIOUR OF HYDRATED PYROCHLORES $K(NbW)O_6 \cdot H_2O$ AND $K(TaW)O_6 \cdot H_2O$

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ABSTRACT

The pyrochlore-type compounds $KMWO_6 \cdot H_2O$ (M = Nb and Ta) have been synthesized and their dehydration kinetics have been studied by thermogravimetric analysis. The proposed diffusion mechanism follows the structural model previously described in the literature.

INTRODUCTION

The mixed oxides $KMWO_6 \cdot H_2O$ (M = Nb and Ta), have been prepared by Darriet et al. [1] from mixtures of KMO_3 (M = Nb, Ta) and WO_3 at 900 °C under O_2 flow for 12 h. Mavi et al. [2] have also synthesized $KTaWO_6 \cdot H_2O$ by heating Ta_2O_5, WO_3 and K_2CO_3 at 850 °C for 45 h followed by additional thermal treatment. In both cases, the solid phases obtained with pyrochlore-type structure rehydrate in air at ambient temperature leading to the compounds formulated as $KMWO_6 \cdot H_2O$.

In the pyrochlore structure [3] the cations are ordered on the f.c.c. sublattice, occupying the 16c and 16d sites. The anion sublattice is built up from three different oxygen sites, two being occupied (48f and 8a positions) and the third site remaining empty (8b).

From the crystallographic study of the materials cited above, it was concluded that K^+ cations and H_2O molecules are statistically distributed in the 16d positions, with the 8b position unoccupied. The M (Nb or Ta) and W atoms are also disordered in the 16c sites. Therefore, a more correct formulation for these compounds would be $(KH_2O)(MW)O_6$, (M = Nb, Ta).

In this paper a new general method of synthesis of these materials is presented. They are characterized by the X-ray diffraction powder method and their thermal dehydration processes were also studied.

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EXPERIMENTAL DETAILS

The pyrochlores $(KH_2O)(MW)O_6$ were prepared by heating a mixture of KNO_3, WO_3 and M_2O_5 ($M = Nb$, Ta) in stoichiometric proportions in a porcelain crucible at 900 °C for 12 h. In both cases a white microcrystalline powder was obtained. Reactants were supplied by Merck (F.R.G.).

The X-ray diffraction patterns were obtained in a Siemens Kristalloflex powder diffractometer, equipped with a D-500 generator, using Cu Kα radiation and W ($a = 3.16524$ Å [4]) as internal standard, at a scanning rate of 0.1° 2θ min^{-1}.

Thermal analysis was carried out in a Mettler TG50 thermobalance and in a Mettler DSC30 cell attached to a Mettler TA3000 controller. Sample sizes were about 20 mg for TG and about 5 mg for DSC. Thermal runs were performed at a rate of 5 °C min^{-1}.

RESULTS AND DISCUSSION

Crystallographic data for the $(KH_2O)(MW)O_6$ compounds are shown in Table 1. These results are in agreement with those previously cited in the

TABLE 1

X-Ray diffraction data for the $(KH_2O)(MW)O_6$ compounds

$(KH_2O)(NbW)O_6$				$(KH_2O)(TaW)O_6$			
h k l	*d*(exp)	*d*(calc)	I/I_0	*h k l*	*d*(exp)	*d*(calc)	I/I_0
1 1 1	6.074	6.064	69	1 1 1	6.078	6.063	72
3 1 1	3.169	3.167	59	3 1 1	3.163	3.166	64
2 2 2	3.033	3.032	100	2 2 2	3.029	3.031	100
4 0 0	2.627	2.626	30	4 0 0	2.622	2.625	34
3 3 1	2.410	2.409	9	3 3 1	2.407	2.409	14
4 2 2	2.145	2.144	3	3 3 3	2.019	2.021	19
3 3 3	2.022	2.021	16	4 4 0	1.855	1.856	39
4 4 0	1.857	1.857	40	5 3 1	1.774	1.775	21
5 3 1	1.775	1.775	20	5 3 3	1.601	1.601	10
5 3 3	1.601	1.602	10	4 4 4	1.514	1.514	11
6 2 2	1.583	1.583	14	5 5 1	1.469	1.470	12
4 4 4	1.515	1.516	11	5 5 3	1.365	1.366	11
5 5 1	1.471	1.471	12	8 0 0	1.310	1.311	6
5 5 3	1.368	1.367	9	5 5 5	1.210	1.211	5
6 2 2	1.313	1.313	5	6 6 2	1.202	1.203	12

$(KH_2O)(NbW)O_6$:
$a = 10.502(3)$ Å
Space group: *Fd3m*
$Z = 8$
$d_{exp} = 4.89$ g cm^{-3}
$d_x = 4.93$ g cm^{-3}

$(KH_2O)(TaW)O_6$:
$a = 10.500(7)$ Å
Space group: *Fd3m*
$Z = 8$
$d_{exp} = 5.89$ g cm^{-3}
$d_x = 5.94$ g cm^{-3}

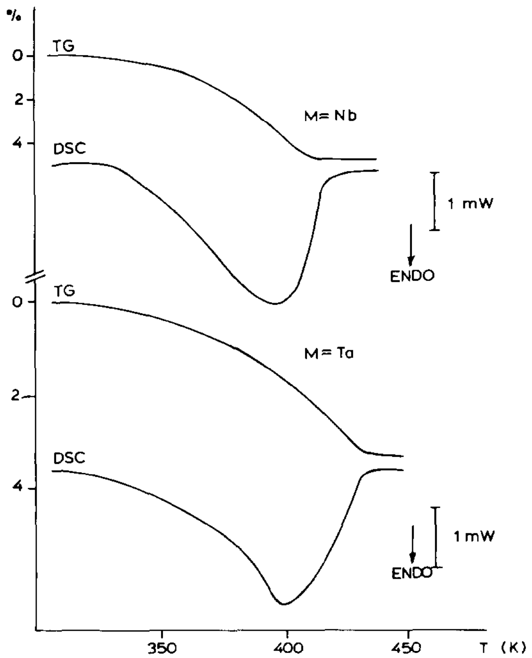

Fig. 1. TG and DSC curves of $(KH_2O)(MW)O_6$ (M = Nb, Ta) compounds.

literature [1,2]. The cell parameters are better refined than previously reported.

The lattice parameters of the anhydrous products were determined similarly ($a = 10.370(1)$ Å for $K(NbW)O_6$; $a = 10.379(1)$ Å for $K(TaW)O_6$). The values were closely related to those reported by Darriet et al. [1].

TABLE 2

Kinetic data corresponding to the dehydration process of $(KH_2O)(NbW)O_6$

T (K)	α	$\alpha' \times 10^2$ (K^{-1})
343	0.1204	0.534
348	0.1497	0.643
353	0.1849	0.767
358	0.2267	0.906
363	0.2759	1.062
368	0.3331	1.231
373	0.3991	1.411
378	0.4742	1.595
383	0.5584	1.773
388	0.6511	1.929
393	0.7502	2.033
398	0.8523	2.031

TABLE 3

Kinetic data corresponding to the dehydration process of $(KH_2O)(TaW)O_6$

T (K)	α	$\alpha' \times 10^2$ (K^{-1})
338	0.1212	0.588
343	0.1531	0.686
348	0.1902	0.811
353	0.2343	0.944
358	0.2848	1.092
363	0.3437	1.254
368	0.4102	1.416
373	0.4855	1.593
378	0.5692	1.751
383	0.6601	1.878
388	0.7561	1.937
393	0.8523	1.923

TABLE 4

Analysis of the data corresponding to the dehydration of $(KH_2O)(NbW)O_6$

Mechanism	r	i	E
D1	−0.9998	0.443	83.56
D2	−0.9999	0.032	82.41
D3	−0.9999	−0.145	84.16
D4	−0.9999	−0.478	84.16
F1	−0.9994	−0.658	38.79
R2	−0.9994	−0.158	38.79
R3	−0.9994	−0.324	38.79

These materials spontaneously rehydrate in air, leading to the corresponding stoichiometric monohydrates. The water molecules occupy some of the 16d positions together with the K^+ cations, and their elimination originates a slight contraction of the crystal structure, which contributes to its stability.

TABLE 5

Analysis of the data corresponding to the dehydration of $(KH_2O)(TaW)O_6$

Mechanism	r	i	E
D1	−0.9998	0.446	76.94
D2	−0.9998	0.037	77.66
D3	−0.9998	−0.143	79.29
D4	−0.9998	−0.473	79.29
F1	−0.9969	−0.757	33.24
R2	−0.9969	−0.257	33.24
R3	−0.9969	−0.425	33.24

Nevertheless, the low temperatures at which the complete dehydration occurs (below 80 °C in isothermal treatments and below 125 °C in the dynamic treatments), suggest that these molecules are weakly bonded. Figure 1 shows the TG and DSC curves obtained in the above cited conditions.

In order to establish the dehydration mechanism, kinetic analysis of the TG curves was performed. Tables 2 to 5 show the results obtained according to the method proposed by Jerez et al. [5]. E, r and i are, respectively, the activation energy, correlation coefficient and intercept of the straight line. As can clearly be seen, the best fit (for the i value closest to zero) corresponds, in both cases, to two-dimensional diffusion kinetics (D2 mechanism in the classification of Sharp et al. [6]).

This diffusion kinetic model is consistent with the structural model stated above, with the water molecules occupying defined lattice positions from which they can diffuse to the outside without substantial changes in structure. In this way, the dehydration process is reversible, as in fact is experimentally observed.

The activation energies for the dehydration of both compounds are very similar ($E = 82.41$ kJ mol^{-1} for $(KH_2O)(NbW)O_6$; $E = 77.66$ kJ mol^{-1} for $(KH_2O)(TaW)O_6$) because of their structural similarity. Dehydration enthalpies, measured by DSC, ($\Delta H = 48.6$ kJ mol^{-1} for $(KH_2O)(NbW)O_6$; $\Delta H = 47.1$ kJ mol^{-1} for $(KH_2O)(TaW)O_6$) are also very similar.

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