HYDROTHERMAL SYNTHESIS OF THE TUNGSTATES Li$_{2}$Fe(WO$_{4}$)$_{2}$ AND Li$_{2}$WO$_{4}$ AND THEIR THERMAL AND X-RAY STUDY

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Abstract

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HYDROTHERMAL SYNTHESIS OF THE TUNGSTATES $Li_2Fe(WO_4)_2$ AND Li_2WO_4 AND THEIR THERMAL AND X-RAY STUDY

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The present work was carried out with the aim of studying the conditions of hydrothermal crystallization of iron tungstates. The use of the hydrothermal method in this case seemed promising in view of the fact that natural minerals of the wolframite group, $(Fe, Mn)WO_4$, occur chiefly in deposits of hydrothermal and pneumatolytic types ([1]).

Minerals of this group and, in particular, ferberite $FeWO_4$ have a monoclinic structure and belong to the holohedral symmetry species L_2PC. By sintering iron and tungsten oxides, the binary systems Fe_2O_3—WO_3, FeO—WO_3 were investigated; in these, along with ferberite, an oxytungstate of composition Fe_2WO_6 ([2,3]) and the normal tungstate of trivalent iron $Fe_2(WO_4)_3$ ([4]) were obtained. Other tungstates containing iron, as well as iron and alkali metals, are not known in the literature.

Experiments on hydrothermal synthesis were carried out in stainless-steel autoclaves. The actual synthesis was performed in "floating" titanium liners with screw-on lids. In the course of the experiments performed it was established (from Debyegrams) that in aqueous solutions of chlorides of trivalent and divalent iron and alkali metals (lithium and sodium), and also in their mixtures, a wolframite phase is formed as the principal product of synthesis. The use of more complex mixed solvents consisting of lithium chloride and alkali-metal tungstates (lithium and sodium) leads to the formation of new crystalline phases –the double tungstate of lithium and divalent iron $Li_2Fe''(WO_4)_2$ and a hydrothermal modification of lithium tungstate Li_2WO_4. A single-phase double tungstate with the greatest yield from the charged batch was obtained at a temperature of 550°, 60% filling, in a solution of LiCl 10% + Na_2WO_4 10% (1 : 1), from a batch $Fe_2O_3 + WO_3(H_2WO_4)$ 1 : 3. In all other cases two compounds crystallize simultaneously, $Li_2Fe(WO_4)_2$ and Li_2WO_4. The formation of compounds with divalent iron from the initial ferric oxide indicates the presence of reducing conditions ([5]). When the concentration of sodium tungstate in the solution was increased to 20% and the synthesis temperature was raised to

575—600°, the yield of hydrothermal Li_2WO_4 increased. In the presence of a temperature gradient, intensive transfer and crystallization of lithium tungstate in the upper zone of the autoclave are observed.

Identification of the new compounds was carried out on the basis of chemical and X-ray analyses.

For both phases, chemical analysis was performed for Fe^{2+} and the total content of iron, tungsten, and the alkali metals Li and Na. For $Li_2Fe(WO_4)_2$ the following was found, in %: Fe^{2+} 10.6; W 64.3; Li 2.3; Na was not detected. Calculated from the formula $Li_2Fe(WO_4)_2$ (in %): Fe^{2+} 9.9; W 64.9; and Li 2.45. In lithium tungstate a content of iron was found that differed for ob-

samples synthesized under different conditions (in %): 0.8; 1.5 and 3.8, W 68.5; 68.0 and 67.3, respectively (calculated W 70.2), Li 3.9 ± 0.5 (calculated 5.3). It is evident that the color of lithium tungstate crystals (orange, yellow to yellow-green) is due to iron impurities. A slight excess of iron in the double tungstate and its content in lithium tungstate, with a simultaneous deficiency of lithium, can apparently be explained by the assumption of partial isomorphous substitution of lithium by iron in the crystal structures of these compounds. According to infrared absorption spectra recorded on a two-beam UR-10 spectrometer, water was not detected in the double tungstate. In the IR spectrum of lithium tungstate, in the region where the deformation vibrations of H_2O appear, near 1630 cm^{-1}, a peak of very low intensity is observed. In this connection, additional investigations were carried out on a derivatograph. The loss on ignition was determined to be equal to 1%, which, recalculated to the chemical formula, corresponds to a water content of ~0.15 molecule. Removal of water from the substance does not occur simultaneously, but continuously from 100° to the temperature of the polymorphic transformation of the hydrothermal modification of lithium tungstate (about 520°).

Fig. 1. Single crystals of $Li_2Fe(WO_4)_2$. 8×

Double tungstate $Li_2Fe(WO_4)_2$ is formed as prismatic crystals of dark-brown color, up to 3 mm in size along the elongation (Fig. 1). The crystals are weakly magnetic. On the basis of optical-goniometric measurements it was found that their growth forms satisfy the holohedral class of the monoclinic system. The monoclinic angle $\beta = 113°$. The symmetry axis L_2 passes along the elongation of the crystals. The results of the measurements are presented in Table 1.

Table 1

Growth forms of $Li_2Fe(WO_4)_2$ crystals

Face symbol	Angle with coordinate axes, deg. +x	Angle with coordinate axes, deg. +y	Angle with coordinate axes, deg. +z	Simple growth form
100	23	90	90	Pinacoid

Fig. 2. Heating curves of $Li_2Fe(WO_4)_2$ crystals

Figure 1: Fig. 2. Heating curves of $Li_2Fe(WO_4)_2$ crystals

Face symbol	Angle with coordinate axes, deg. +x	Angle with coordinate axes, deg. +y	Angle with coordinate axes, deg. +z	Simple growth form
201	54	90	59	»
001	90	90	23	»
$\bar{2}01$	153	90	40	»
$\bar{4}01$	177	90	64	»
110	65	27	90	Rhombic prism
122	80	45	57	Rhombic prism
$\bar{1}11$	111	40	50	Same

The most highly developed simple growth forms are the pinacoids {001} and {$\bar{2}01$}; next in order of importance of development are the pinacoid {100} and the rhombic prisms {110} and {$\bar{1}11$}. The ratio of the unit-cell parameters obtained from the optical-goniometric data is
a : b : c = 2.04 : 1 : 1.17.

The thermal stability of the synthesized crystals was investigated by differential thermal analysis (DTA). Heating curves in air were recorded on an HTP-62 instrument. The average heating rate was 10°/min. Figure 2 presents the heating curves for $Li_2Fe(WO_4)_2$.

On the differential curve, three thermal effects are clearly recorded:

1) An exothermic effect, beginning at a relatively low temperature of about 300° and ending at 584°. This effect is neces-

by heating. It is accompanied by a partial change in the powder X-ray pattern.

2) The reversible endothermic effect at 730° corresponds to a phase transition in the solid state. A high-temperature X-ray study carried out on a URS-50I with a KRV-1200 attachment showed that this effect is associated with a polymorphic transformation into the wolframite structure.

3) The endothermic effect at 944° corresponds to melting of the double tungstate.

Fig. 2. Heating curves of crystals of $Li_2Fe(WO_4)_2$

It was suggested that the tungstate $Li_2Fe(WO_4)_2$ may be regarded as $Li_2WO_4 \cdot FeWO_4$, and an attempt was made to synthesize it also by thermal sintering of mechanical mixtures of the chemical reagents Li_2WO_4 and $FeWO_4$ in an equimolar ratio. Sintering was carried out at 500° for 10 h, then at 600° for 5 h, and at 700° for 12 h, with thorough grinding after annealing at each temperature. The single-phase character of the sinter was monitored by X-ray diffraction. The Debye pattern of the synthesized product is analogous to the Debye pattern recorded from the crystals after heating them to 600°. The DTA curves of the sinter differ from the DTA curves of the hydrothermal crystals by the absence of the first exothermic effect. These results definitively confirm the correctness of the chemical composition of the synthesized crystals.

Lithium tungstate crystallizes in the cubic system. The Debye pattern is indexed in a primitive cubic cell with parameter $a = 8.27 \pm 0.02$ Å and coincides with that given in (6). The density measured by the pycnometric method is 5.43 g/cm^3 and corresponds to a content of 7 formula units in the unit cell. The possible water content is one H_2O molecule per unit cell. X-ray structural investigations of these crystals showed that they possess the noncentrosymmetric Fedorov group $P\bar{4}3m$ (7).

For Li_2WO_4, two crystalline modifications are known: a low-temperature hexagonal one with the phenakite structure Be_2SiO_4, and a high-temperature cubic one with the spinel structure Al_2MgO_4 (8). Under hydrothermal conditions lithium tungstate crystallizes in a new cubic modification. Previously, by this method, crystals were obtained in the systems $CdWO_4(ZnWO_4, MgWO_4)$–LiCl–H_2O (9). The thermal and X-ray studies that we carried out on the synthesized crystals made it possible to establish that the hydrothermal cubic modification is unstable upon heating in air. According to the DTA curves (Fig. 3), it undergoes an irreversible polymorphic transformation. The Debye pattern from the crystals recorded after their heating coincides with the Debye pattern for hexa-

of the hexagonal modification of Li_2WO_4 [10]. According to the high-temperature powder X-ray patterns taken, upon heating the hydrothermal modification transforms directly into the hexagonal one, with unit-cell parameters at 550°: $a = 14.44$ and $c = 9.69$ Å (as against $a = 14.36$ and $c = 9.60$ Å at room temperature). Although the intense process of rearrangement of the crystal lattice occurs at a temperature of $\sim 525°$ and ends by 545°, this process begins at a considerably lower temperature—about 450°. In the powder diffraction pattern recorded at 450°, lines corresponding to the hexagonal phase are already observed.

Fig. 3

Fig. 4

Fig. 3. Heating curves of hydrothermal crystals of lithium tungstate
Fig. 4. Temperature dependence of the unit-cell parameter of hydrothermal crystals of lithium tungstate

The reversible endothermic effect at 620° on the DTA curves is associated with the transition of the hexagonal modification into the high-temperature one, and at 720° with the melting of lithium tungstate.

From the high-temperature powder X-ray patterns for the cubic hydrothermal modification of lithium tungstate, the unit-cell parameter was determined at temperatures of 20, 200, 300, and 450°. Within the measurement error there is a linear dependence of the increase in the cell parameter on temperature (Fig. 4). The coefficient of linear thermal expansion of lithium tungstate, calculated from these data, is equal to $24.7 \cdot 10^{-6}$ deg^{-1}.

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