

POLYMORPHISM OF ZIRCONIUM MOLYBDATE  $Zr(MoO_4)_2$

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ABSTRACT

Zirconium molybdate  $Zr(MoO_4)_2$  exhibits a polymorphic transition of the reconstructive type. The new, low-temperature form has been characterized by powder X-ray diffraction and vibrational spectroscopy. All the diffraction peaks are satisfactorily indexed by a monoclinic cell  $a = 9.76_3$   $b = 7.93_1$   $c = 7.45_1$  Å  $\beta = 97.86^\circ$ . The calculated density is 4.78 for  $Z = 4$ , against an experimental value of 4.74. This density is much higher than that of the high-temperature form ( $d = 3.93$ ). This densification of the structure is in agreement with the interpretation of the vibrational spectrum, which points to a sixfold coordination of molybdenum, against a fourfold coordination in the high-temperature form.

Zirconium molybdate  $Zr(MoO_4)_2$  has been synthesized by several authors (ref. 1-6), and there is a general agreement about its structure: it is hexagonal with  $a = 10.1$ ;  $c = 11.7$  Å, and  $Z = 6$ . The full structure has been determined and refined to  $R = 0.082$  on a single crystal of the parent compound  $Hf(MoO_4)_2$  (ref. 6): Mo is located in a distorted tetrahedron, whereas there are two types of Hf cations, characterized by either a sixfold, or a twelvefold, coordination.

We have evidenced a low temperature form of  $Zr(MoO_4)_2$  which can be obtained, either by direct synthesis at  $600^\circ\text{C}$ , or by tempering the hexagonal form at the same temperature. The return to the hexagonal form is readily obtained by heating the new form at  $700^\circ\text{C}$ .

The X-ray powder diagram of the low-temperature polymorph is very complex, but the Visser's indexation program (ref. 7) leads to a monoclinic cell which allows the indexation of all the observed diffraction peaks down to  $d = 1.400$  Å:  $a = 9.76_3$   $b = 7.93_1$   $c = 7.45_1$  Å  $\beta = 97.86^\circ$ . This indexation is of course only tentative, but the agreement between observed and calculated  $d$  values is good (Table 1): moreover, the calculated density is 4.78 for  $Z = 4$ , against an experimental value of 4.74. This density is much higher than that of the hexagonal, high temperature form ( $d_{\text{calc}} = 3.93$ ;  $d_{\text{exp}} = 3.91$ ). This suggests that the polymorphic transition is associated with important structural modifications. This point has been investigated by vibra-

TABLE 1. X-ray powder diagram of low-temperature  $Zr(MoO_4)_2$ 

I	h	k	l	$d_{obs}$	$d_{calc}$
36	1	1	0	6.120	6.133
5	0	1	1	5.395	5.403
7	2	0	0	4.830	4.836
12	0	2	0	3.964	3.966
6	0	0	2	3.692	3.690
22	2	1	1	3.434	3.436
12	1	2	$\bar{1}$	3.358	3.356
5	1	1	2	3.293	3.291
4	1	2	$\bar{1}$	3.218	3.220
27	2	0	2	3.152	3.149
100	2	2	0	3.065	3.066
13	3	1	0	2.985	2.986
9	2	0	2	2.755	2.757
30	0	2	2	2.704	2.702
2	1	3	0	2.550	2.550
2	0	3	1	2.488	2.489
5	1	0	$\bar{3}$	2.467	2.466
3	3	2	$\bar{1}$	2.449	2.449
4	4	0	0	2.413	2.418
5	0	1	3	2.351	2.350
9	4	1	$\bar{1}$	2.294	2.294
8	1	3	2	2.136	2.134
7	4	1	1	2.127	2.129
6	3	3	0	2.0441	2.0442
16	2	1	3	2.0124	2.0127
12	0	4	0	1.9832	1.9827
25	4	2	$\bar{2}$	1.8985	1.8986
12	1	4	1	1.8657	1.8658
8	3	3	$\bar{2}$	1.8580	1.8578
3	0	0	4	1.8457	1.8452
4	5	0	1	1.8127	1.8113
2	2	4	$\bar{1}$	1.8027	1.8024
3	5	1	2	1.7731	1.7725
3	0	4	2	1.7471	1.7466
10	1	1	4	1.7254	1.7262
	3	3	2		1.7259
4	4	2	2	1.7160	1.7182
12	4	3	1	1.6948	1.6956
16	2	4	$\bar{2}$	1.6788	1.6778
sh	4	3	2	1.6737	1.6738
8	5	2	1	1.6475	1.6476
6	2	3	3	1.6356	1.6351
5	2	4	2	1.6099	1.6098
9	4	1	3	1.5843	1.5848
4	4	0	4	1.5755	1.5744
8	6	0	$\bar{2}$	1.5582	1.5573
2	4	3	2	1.5463	1.5463
9	4	4	0	1.5328	1.5331
5	5	2	$\bar{2}$	1.5023	1.5031
	6	2	$\bar{1}$		1.5010
2	2	3	4	1.4918	1.4926
2	1	3	4	1.4710	1.4700
5	2	5	1	1.4654	1.4645
6	1	0	5	1.4304	1.4304

tional (IR and Raman) spectroscopy.

For the high-temperature form, vibrational frequencies are observed in the 1000-740  $\text{cm}^{-1}$  region, and below 400  $\text{cm}^{-1}$ . No band is observed between 700 and 400  $\text{cm}^{-1}$ , and this is consistent with the existence, in this structure, of "isolated"  $\text{MoO}_4$  tetrahedra.

By contrast, the spectrum of the low-temperature form is much more complex, the vibrational frequencies being spread over the whole 1000-40  $\text{cm}^{-1}$  frequency range ; the strongest IR band is observed at 612  $\text{cm}^{-1}$  (Fig. 1).

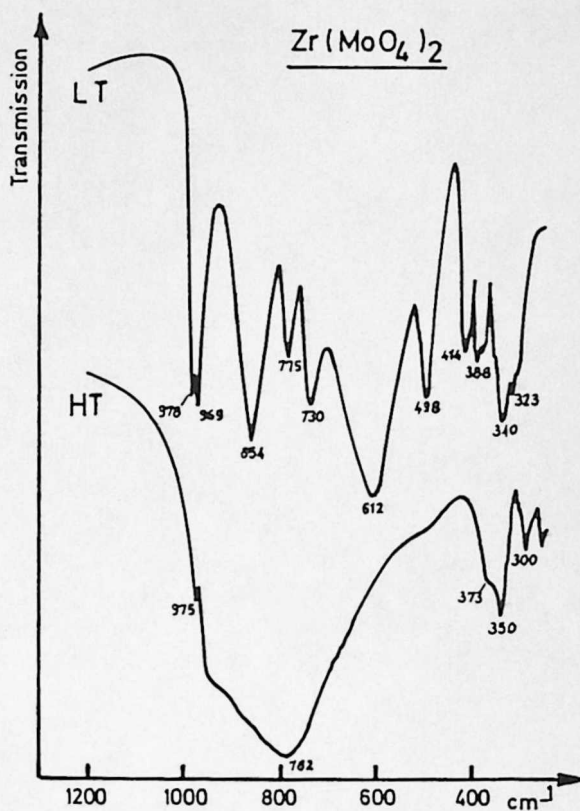


Fig. 1. IR spectra of the low (LT) and high (HT) temperature forms of  $\text{Zr}(\text{MoO}_4)_2$ .

This points to an increase of the coordination of molybdenum, which goes from tetrahedral to octahedral ; this type of structural modification is in agreement with the large increase in density ; however, it is impossible to decide if the structure is built up of  $\text{MoO}_6$  octahedra only, or of an association of  $\text{MoO}_4$  and  $\text{MoO}_6$  groups.

The transition has also been investigated by DTA. The low  $\rightarrow$  high temperature transition appears as an endothermic peak at  $679^\circ\text{C}$  for a heating rate of  $60^\circ\text{C/hr}$ . This temperature should be considered as an upper limit : since the transition is of the reconstructive type, it is not very rapid, and the equilibrium temperature is probably slightly lower. The reverse transition to the low-temperature form could not be observed by DTA. No low-temperature form has been obtained for the isomorphous compound  $\text{Hf}(\text{MoO}_4)_2$ . However, solid solutions  $\text{Zr}_{1-x}\text{Hf}_x(\text{MoO}_4)_2$  can be converted into the low-temperature form, at least for  $x \leq 0.4$ . Their study by DTA shows that the transition temperature decreases with increasing values of  $x$ .

This points to the possible existence of a low-temperature form of  $\text{Hf}(\text{MoO}_4)_2$  ; but at the relatively low transition temperature, the transformation rate would be negligibly small.

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