Journal of Alloys and Compounds, 190 (1992) L19–L21
JALCOM 456

Letter

A new strontium molybdate: $SrMo_5O_8$

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(Received August 1, 1992)

There is some evidence in the literature [1–4] on the existence of strontium molybdates with molybdenum valency equal to four, five and six, namely, the black–brownish $Sr_2Mo(IV)O_4$, $SrMo(IV)O_3$ of perovskite structure (the product of the $SrMo(V)_2O_6$ dismutation), the tetragonal $SrMo(VI)O_4$, $Sr_3Mo(VI)O_6$ of perovskite structure and the $SrMo(VI)_3O_{10}\cdot nH_2O$ (where $n = 1.75$, 3, 4) prepared in water.

We report here the experimental details on the existence of a new strontium molybdate, $SrMo_5O_8$ (J-phase), with average molybdenum valency equal to 2.8. This compound was prepared from high purity $SrMoO_4$ (synthesized according to the procedure described in ref. 5), MoO_2 [6] and powdered molybdenum. The substrates in an appropriate chemical composition were

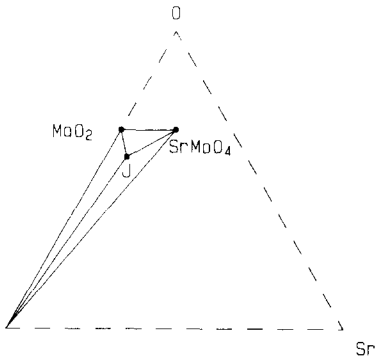

Fig. 1. The localization of the J-$SrMo_5O_8$ in the diagram of Mo-Sr-O system.

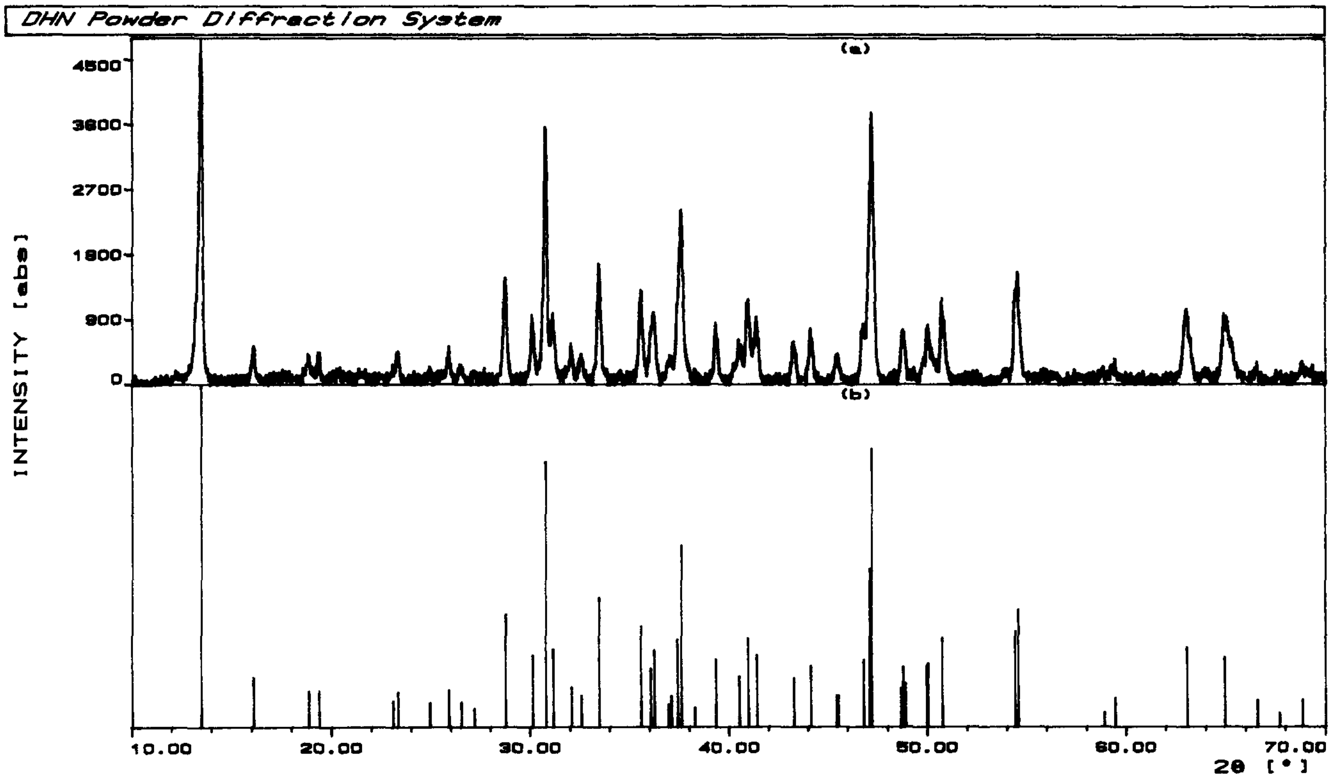

Fig. 2. X-ray powder diffraction diagram of the J-$SrMo_5O_8$; (a) experimental data; (b) stick diagram representing indexed pattern from Table 1.

0925-8388/92/$5.00

TABLE 1. X-ray diffraction pattern of J-$SrMo_5O_8$

h	k	l	$2\Theta_{obs}$	$2\Theta_{calc}$	$\Delta 2\Theta$	d_{obs}	I/I_o
1	1	0	13.48	13.48	0.00	6.5623	100
−1	1	1	16.08	16.09	−0.01	5.5058	15
−2	0	1	18.85	18.86	−0.01	4.7051	11
0	2	0	19.36	19.36	0.00	4.5816	11
0	2	1	23.06	23.05	0.01	3.8542	8
−1	2	1	23.31	23.31	0.00	3.8127	10
0	0	2	24.93	24.92	0.01	3.5691	7
−2	0	2	25.87	25.86	0.01	3.4411	11
1	2	1	26.49	26.48	0.01	3.3617	7
2	2	0	27.16	27.16	0.00	3.2808	6
−3	1	1	28.74	28.75	−0.01	3.1033	33
3	1	0	30.11	30.11	0.00	2.9653	21
1	3	0	30.77	30.76	0.01	2.9038	78
−3	0	2	31.14	31.13	0.01	2.8700	23
−1	3	1	32.05	32.04	0.01	2.7900	12
2	2	1	32.54	32.52	0.02	2.7490	9
−3	2	1	33.45	33.46	−0.01	2.6768	38
1	2	2	35.56	35.55	0.01	2.5225	30
−4	0	1	36.04	36.04	0.00	2.4902	17
2	0	2	36.23	36.23	0.00	2.4777	23
−3	2	2	36.92	36.92	0.00	2.4326	7
−1	1	3	37.07	37.07	0.00	2.4230	9
−4	1	1	37.39	37.40	−0.01	2.4033	26
−2	1	3	37.57	37.57	0.00	2.3921	53
−4	0	2	38.25	38.25	0.00	2.3513	6
0	4	0	39.32	39.31	0.01	2.2896	20
−3	1	3	40.49	40.49	0.00	2.2260	15
−1	2	3	40.95	40.93	0.02	2.2023	26
−2	2	3	41.39	41.39	0.00	2.1797	21
1	1	3	43.26	43.28	−0.02	2.0899	15
−3	2	3	44.12	44.11	0.01	2.0511	18
3	1	2	45.41	45.41	0.00	1.9956	9
4	1	1	45.50	45.47	0.03	1.9918	9
−1	3	3	46.77	46.78	−0.01	1.9406	20
−4	3	1	47.06	47.06	0.00	1.9293	46
−2	3	3	47.19	47.20	−0.01	1.9244	81
−1	0	4	48.65	48.64	0.01	1.8701	12
−4	2	3	48.75	48.78	−0.03	1.8664	18
4	3	0	48.87	48.86	0.01	1.8620	13
1	4	2	49.94	49.91	0.03	1.8248	18
−5	2	1	50.01	50.00	0.01	1.8223	19
1	5	0	50.73	50.73	0.00	1.7981	26
−4	4	1	54.37	54.39	−0.02	1.6859	28
2	4	2	54.53	54.52	0.01	1.6815	35
−6	0	3	58.86	58.87	−0.01	1.5675	4
3	2	3	59.42	59.45	−0.03	1.5541	9
−2	5	3	63.05	63.05	0.00	1.4732	23
6	0	1	64.94	64.94	0.00	1.4349	21
−5	3	4	66.56	66.56	0.00	1.4037	8
−4	2	5	67.68	67.67	0.01	1.3833	4
1	6	2	68.82	68.83	−0.01	1.3630	8

well ground, pressed into pellets and homogenized in evacuated quartz ampoules at 1373 K for one day.

X-ray powder diffraction analysis of the Sr–Mo–O samples belonging to the $SrMoO_4$–MoO_2–Mo triangle has revealed that at 1373 K the J-phase remains in equilibrium with $SrMoO_4$, MoO_2 and Mo (Fig. 1). Under an excess of oxygen the J-phase undergoes an oxidation according to the equation:

$$SrMo_5O_8 + 4O_2 = SrMoO_4 + 4MoO_3.$$

This fact was a main obstacle to the elaboration of a simple method for single crystal growth.

Figure 2 shows the X-ray powder diffraction diagram of the J-phase collected on a Siemens D-5000 diffractometer (Bragg–Brentano geometry, CuKα radiation). The sample was also measured with an internal standard (silicon) in order to improve the accuracy. The absolute error on the position of the peaks was estimated at less than 0.02° (2Θ). This data was used in the indexing procedure (program ITO [7]) followed by a subsequent LSQ refinement of the lattice parameters. The results obtained were as follows:

Crystallographic system: monoclinic;
Bravais lattice: primitive;
$a=9.959(1)$ Å, $b=9.160(1)$ Å, $c=7.564(1)$ Å, $\beta=109.24(1)°$, $V=651.446$ Å^3, $Z=4$, $M=695.32$, $d_x=7.09$ g cm^{-3}, $d_m=7.04(2)$ g cm^{-3}, $F(20)=47.7$ (0.0076, 55).

The experimental density d_m was measured pycnometrically. M is a molecular weight and $F(20)$, a Smith-Snyder figure of merit [8]. the indexed pattern is presented in Table 1.

The lattice parameters of $SrMo_5O_8$ show very large similarity to those of some molybdates of ferrous metals, *i.e.* $FeMoO_4$, $CoMoO_4$ and $NiMoO_4$. Therefore, we suppose that their crystal structures should also be similar. The structure of $SrMo_5O_8$ seems to be a densified modification of $CoMoO_4$ [9] in which an additional eight molybdenum atoms fill the vacant positions in the distorted perovskite lattice of $CoMoO_4$. Unfortunately, till now, we have not found any proper structural model.

The J-phase with valence electron concentration equal to 5.71 [10] is not a superconductor down to the liquid-helium temperature.

Acknowledgments

The authors express their thanks to Dr K. Rogacki for low temperature resistivity measurements.

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