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On the Mo–Ca–O system

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Abstract

Phase equilibria in the Mo–Ca–O system were investigated at 1373 K by means of X-ray diffractometry. The entire phase diagram of the system is presented. Four new phases were found: orthorhombic $CaMo_6O_9$, monoclinic $Ca_5Mo_{18}O_{29}$, tetragonal $Ca_8Mo_7O_{20}$ and orthorhombic $Ca_5Mo_3O_{12}$, apart from the monoclinic $CaMoO_3$ and tetragonal $CaMoO_4$ compounds well known from the literature. All new phases are not superconducting down to 4 K.

1. Introduction

This work is the continuation of our earlier study, published in a previous paper [1] and completing the phase relation data in the ternary part of the Mo–Ca–S–O system. The last complete system will be described in a separate paper.

Two binary phases, *i.e.* MoO_2 [2, 3] and CaO [4], take part in the phase equilibria of the Mo–Ca–O system.

Additional references can be found in refs. 1 and 5.

2. Experimental details

Molybdenum (purity, 99.95%), calcium (purity, 99.92%), MoO_2 (prepared from molybdenum and high purity MoO_3) and $CaMoO_4$ (prepared by sintering according to refs. 6 and 7) were used for the syntheses.

Ternary samples of mass about 2 g pressed were heated in evacuated quartz ampoules at 1273 K. The samples were then ground and subjected to final homogenization at 1373 K. The reaction in the Mo–CaO–Ca region of the system was carried out in an arc-sealed molybdenum capsule under reduced pressure of argon.

All samples were analysed by X-ray powder diffractometry with Cu $K\alpha_1$ radiation. The collected powder data were elaborated using an X-ray powder computer program [8]; however, in the case of compound A ($Ca_5Mo_{18}O_{29}$) the indexing was based on the single-crystal data [9].

The densities of the new phases were determined in CCl_4 at 298 K using a new device [10] for direct and fast filling of a Johnson–Adams pycnometer

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[11]. Contrary to the liquid condensation from vapour phase method [12], our device makes the use of immersion liquids possible irrespective of their boiling point.

The lack of superconductivity (down to 4 K) of the new compounds was confirmed by inductance measurement.

3. Results and discussion

Phase relations in the Mo–Ca–O system at 1373 K were established by investigating a large number of ternary samples (Fig. 1). The disjunctive Mo–CaO line emphasizes the appearance of the two main distinct parts of the diagram: namely the Mo–CaO–Ca and Mo–CaO–O triangles. The first, analogous to the Mo–CaS–Ca region of the Mo–Ca–S system [1], is characterized by deficiency in any ternary phase, if one does not take into account the Ca(Mo, O) liquid solution (the Ca(Mo) solution was predicted theoretically in ref. 13). In the second triangle, Mo–CaO–O, KAMILU compounds exist in a relatively narrow range of chemical compositions. The sum of the phase settings of the compounds completely qualifies the character of the phase relations in this part of the system. The dichotomy of the diagram and nondisteleological [14] phase distribution observed reflects the effect of the Gibbs function minimum during the creation of a phase in the system. The structural data of the Mo–Ca–O compounds were collected in Table 1. We assigned a point character of the ternary compounds (except for $CaMoO_4$) because of the invariability of their X-ray peaks in three-phase regions.

Valence electron concentrations [24] computed for the KAMILU compounds are in the range 5.00–5.75 electrons $atom^{-1}$. Because of this last

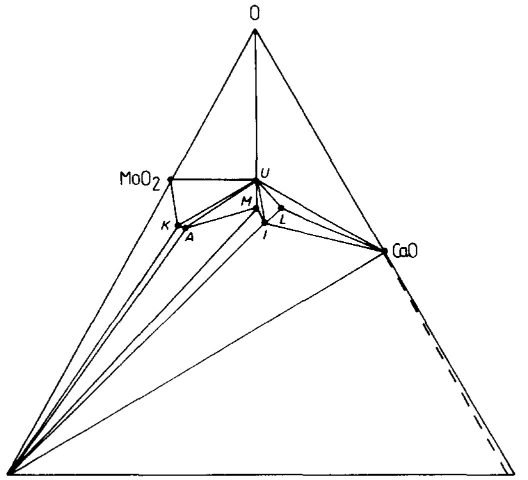

Fig. 1. An isothermal section at 1373 K of the Mo–Ca–O system.

TABLE 1

Structural data of the KAMILU compounds

	Compound	Lattice parameters					M	Z	D_x (Mg m^{-3})	D_m (Mg m^{-3})	References
		a (Å)	b (Å)	c (Å)	β (deg)	U (Å^3)					
K	$CaMo_6O_9$	9.984	10.963	13.817	–	1512.22	759.71	8	6.676	6.67	This work
A	$Ca_5Mo_{18}O_{29}$	22.836	2.847	9.865	94.17	639.67	2391.30	1	6.209	6.19	This work
M	$CaMoO_3$	7.80	7.77	7.80	91.38	472.59	184.02	8	5.17	5.20	[15–17]
I	$Ca_8Mo_7O_{20}$	8.562	–	11.881	–	870.97	1312.21	2	5.005	5.00	This work
L	$Ca_6Mo_3O_{12}$	5.529	5.750	7.947	–	252.67	680.21	1	4.471	4.35	This work
U	$CaMoO_4$	5.224	–	11.430	–	311.93	200.02	4	4.260	4.38–4.53	[18–23]

feature which applies to all the compounds in the system, newly discovered compounds were found to be not superconducting down to liquid-helium temperature.

The other data for the new compounds are given below.

3.1. *The orthorhombic compound K* ($CaMo_6O_9$)

Complete syntheses of the compound $CaO \cdot 4MoO_2 \cdot 2Mo$ were performed at slightly higher temperatures because of the reaction activation energy demanded. The black samples were then finally heated for 2 days at 1373 K.

The X-ray diagram for the primitive unit cell, free of any texture effects, is presented in Table 2. The strongest peak was continuously observed at $2\theta = 13.550°$. In the case of this compound the indexing results need confirmation by single-crystal data.

The triclinic $LiSb_6S_9$ is another compound belonging to very few phases with a 1:6:9 composition [25].

3.2. *The monoclinic compound A* ($Ca_5Mo_{18}O_{29}$)

The synthesis of a black powder of the compound $5CaO \cdot 12MoO_2 \cdot 6Mo$ was usually carried out for a period of 2 days.

The X-ray diffraction data indexed are gathered in Table 3. We were able to refine the primitive monoclinic unit-cell parameters using a complete set of the indices. They are slightly different from the single-crystal data shown in the Table 1. The strongest peak with the (400) indices is a characteristic feature of compound A. However, owing to the preferred orientation phenomenon, we have been able incidentally to observe a distinct signal for the (112) peak as well.

The crystallization process was carried out in a suitably evacuated quartz ampoule containing 4 g of a powder sample of $Ca_{15}Mo_{45}O_{40}$ chemical composition and 50 mg of NH_4Cl. The NH_4Cl, in the presence of oxides of the powder sample, was decomposed into gaseous products at 1373 K. In these conditions, black strip-like flexible crystals suitable for X-ray investigation were grown on the surface of the powder sample in a period of 25 days.

3.3. *The tetragonal compound I* ($Ca_8Mo_7O_{20}$)

Black powder of the compound $8CaO \cdot 6MoO_2 \cdot Mo$ was prepared using a small excess of calcium oxide in an effective time of 24 h at a temperature 20 K above our standard temperature of 1373 K. Compound I thus obtained is stable below that temperature.

A distinct X-ray powder diffraction peaks were unequivocally indexed (Table 4). It seems that the body-centred cell parameters (where $\sqrt{2}a \approx c$, $c = 3a_p$ and a_p is the cell parameter of the real perovskite) of the compound I are involved in the cubic perovskite-type superstructure. X-ray data for $La_{8-x}Sr_xCu_8O_{20}$ [26, 27], $BaLa_4Cu_5O_{13.4}$ [28, 29] and other compounds [30–33] are in good agreement with the last supposition; this is confirmed as one can derive from $Ca_8Mo_7O_{20}$ a deficient real perovskite formula of $CaMo_{0.875}O_{2.5}$. The ternary compound $La_8Fe_7S_{20}$ is, however, a representative of a different type of structure (space group, $Pmc2_1$) [34, 35].

TABLE 2

X-ray powder data for compound K ($CaMo_6O_9$)

d_{exp}	d_{calc}	I/I_0	$h\ k\ l$
6.5294	6.5115	100.0	1 1 1
5.4992	5.4813	13.0	0 2 0
4.3211	4.3148	2.9	2 1 1
3.7924	3.7965	7.2	2 1 2
3.3301	3.3262	4.1	3 0 0
3.1043	3.1020	13.7	3 1 1
2.9536	2.9481	9.7	2 3 0
2.8767	2.8834	37.2	2 3 1
2.8433	2.8436	7.8	3 2 0
2.7663	2.7678	5.6	0 0 5
2.6722	2.6671	28.3	1 0 5
2.4969	2.4947	27.1	4 0 0
2.4807	2.4841	8.5	2 3 3
2.4548	2.4551	7.3	4 0 1
2.4362	2.4325	5.7	4 1 0
2.4038	2.4021	14.7	2 4 0
2.3936	2.3958	19.0	4 1 1
2.3680	2.3667	13.2	2 4 1
2.2678	2.2706	14.9	4 2 0
2.1938	2.1925	17.4	0 5 0
2.1572	2.1574	4.1	4 2 2
2.0539	2.0564	14.4	2 1 6
1.9773	1.9753	4.9	5 0 1
1.9422	1.9440	6.1	5 1 1
1.9228	1.9227	38.5	3 4 3
1.9051	1.9096	18.1	1 1 7
1.8496	1.8519	12.2	0 5 4
1.8213	1.8208	12.6	1 5 4
1.7973	1.7972	4.4	1 6 0
1.7808	1.7826	15.3	4 4 2
1.7035	1.7026	3.1	2 6 1
1.6773	1.6794	17.7	3 1 7
1.6651	1.6631	7.6	6 0 0
1.6473	1.6469	3.1	4 5 0
1.5893	1.5908	2.2	3 6 1
1.5639	1.5645	3.8	6 0 3
1.4660	1.4676	13.4	5 5 1
1.4592	1.4605	9.4	2 7 2
1.4429	1.4434	7.6	5 5 2
1.4263	1.4255	9.0	7 0 0
1.4191	1.4180	6.8	7 0 1

3.4. The orthorhombic compound L ($Ca_5Mo_3O_{12}$)

The substrates CaO, $CaMoO_4$ and molybdenum with an excess of CaO undergo fast reaction at 1373 K, yielding a black powder of the compound $5CaO \cdot 2MoO_2 \cdot MoO_3$ in 1 h.

TABLE 3

X-ray powder data for compound A ($Ca_5Mo_{18}O_{29}$)

d_{exp}	d_{calc}	I/I_0	$h\ k\ l$
9.2575	9.2774	20.8	−1 0 1
8.7943	8.7923	14.8	1 0 1
5.6994	5.6920	100.0	4 0 0
4.9038	4.9152	16.3	0 0 2
4.6403	4.6387	5.2	−2 0 2
4.2490	4.2531	4.3	−5 0 1
4.0224	4.0203	5.6	5 0 1
3.7938	3.7946	16.8	−6 0 0
3.2092	3.2102	4.5	1 0 3
3.1525	3.1581	4.8	−7 0 1
3.0910	3.0925	7.0	−3 0 3
2.9325	2.9308	7.7	3 0 3
2.8469	2.8460	29.6	−8 0 0
2.7569	2.7579	7.7	−5 0 3
2.6618	2.6638	5.4	−3 1 0
2.5709	2.5714	6.4	5 0 3
2.4830	2.4834	8.2	−4 1 1
2.4590	2.4576	12.0	0 0 4
2.4395	2.4383	22.3	1 1 2
2.4135	2.4127	21.2	5 1 0
2.3694	2.3678	8.4	−3 1 2
2.3200	2.3193	9.6	−4 0 4
2.2767	2.2768	5.2	−10 0 0
2.2404	2.2394	7.5	−6 1 1
2.2296	2.2278	6.2	7 0 3
2.1971	2.1981	9.3	4 0 4
2.1325	2.1331	9.7	5 1 2
2.1306	2.1298	9.8	−2 1 3
1.9919	1.9916	2.7	−8 1 1
1.9774	1.9785	4.3	4 1 3
1.9499	1.9513	7.4	8 1 1
1.9321	1.9318	11.2	−8 0 4
1.9287	1.9291	6.1	7 1 2
1.9096	1.9094	3.8	−6 1 3
1.8983	1.8973	17.4	−12 0 0
1.8617	1.8620	5.4	−1 1 4
1.8451	1.8452	8.4	1 1 4
1.8302	1.8300	6.7	−3 1 4
1.8152	1.8156	2.4	−12 0 2
1.7332	1.7327	6.3	9 1 2
1.6386	1.6388	8.2	−2 0 6
1.6140	1.6140	7.1	−11 1 2
1.4601	1.4601	3.5	9 1 4

It was found that the clear powder diagram of compound L (Table 5) is very similar to that of a pale-yellow Ca_3MoO_6 phase ($a = 5.806$ Å, $b = 5.533$ Å and $c = 7.988$ Å), which is stable in the range 1543–1643 K [36]; thus

TABLE 4

X-ray powder data for compound I ($Ca_8Mo_7O_{20}$)

d_{exp}	d_{calc}	I/I_0	$h\ k\ l$
6.9639	6.9462	38.4	1 0 1
6.0625	6.0542	53.6	1 1 0
5.9487	5.9405	21.4	0 0 2
4.2456	4.2402	10.8	1 1 2
3.4736	3.4731	8.6	2 0 2
3.0298	3.0271	3.6	2 2 0
2.7760	2.7750	35.1	3 0 1
2.7532	2.7528	100.0	2 1 3
2.7076	2.7075	29.3	3 1 0
2.4633	2.4637	5.7	3 1 2
2.4412	2.4404	3.6	2 0 4
2.3287	2.3286	19.5	3 2 1
2.2898	2.2896	2.6	1 0 5
2.1408	2.1405	2.3	4 0 0
2.0370	2.0366	15.4	3 2 3
2.0178	2.0181	29.3	3 3 0
2.0005	2.0010	14.8	3 1 4
1.9800	1.9802	23.1	0 0 6
1.9139	1.9145	26.7	4 2 0
1.8817	1.8820	8.6	1 1 6
1.8392	1.8391	12.3	4 1 3
1.8234	1.8222	16.9	4 2 2
1.7360	1.7366	3.7	4 0 4
1.6948	1.6949	12.9	4 3 1
1.6792	1.6791	8.8	5 1 0
1.6650	1.6649	2.6	1 0 7
1.6086	1.6092	9.9	4 2 4
1.5978	1.5983	11.7	3 1 6
1.5713	1.5718	12.9	4 3 3
1.5629	1.5636	4.1	4 1 5
1.5135	1.5136	1.9	4 4 0
1.4849	1.4851	2.9	0 0 8
1.4594	1.4588	4.6	3 0 7
1.4260	1.4270	3.0	6 0 0
1.4126	1.4134	12.2	3 3 6
1.3976	1.3978	9.4	6 1 1
1.3758	1.3764	10.8	4 2 6
1.3537	1.3538	6.4	6 2 0
1.3268	1.3263	3.6	6 1 3
1.3193	1.3199	3.5	6 2 2
1.2804	1.2807	4.3	5 1 6
1.2666	1.2669	6.6	5 4 3
1.2473	1.2480	6.5	2 1 9
1.2315	1.2318	2.9	6 2 4
1.2105	1.2108	8.1	5 5 0
1.2048	1.2055	6.8	4 3 7

TABLE 5

X-ray powder data for compound L ($Ca_5Mo_3O_{12}$)

d_{exp}	d_{calc}	I/I_0	$h\ k\ l$
4.6670	4.6586	11.3	0 1 1
4.5455	4.5387	8.9	1 0 1
3.9891	3.9855	35.8	1 1 0
3.5657	3.5626	4.7	1 1 1
2.8780	2.8751	25.9	0 2 0
2.8155	2.8140	100.0	1 1 2
2.7668	2.7645	29.3	2 0 0
2.4922	2.4915	2.6	2 1 0
2.4286	2.4288	4.3	1 2 1
2.3892	2.3890	6.6	1 0 3
2.3788	2.3774	6.3	2 1 1
2.3293	2.3293	2.1	0 2 2
2.2068	2.2062	4.4	1 1 3
2.1469	2.1466	2.8	1 2 2
1.9923	1.9927	34.7	2 2 0
1.9493	1.9482	3.0	0 2 3
1.9330	1.9329	3.4	2 2 1
1.8387	1.8375	2.9	1 2 3
1.8117	1.8110	8.0	1 3 0
1.7804	1.7813	13.7	2 2 2
1.7657	1.7657	5.9	1 3 1
1.6474	1.6479	15.5	1 3 2
1.6346	1.6345	14.9	0 2 4
1.6130	1.6134	14.3	2 0 4
1.6047	1.6055	28.7	3 1 2
1.4380	1.4375	3.1	0 4 0
1.4067	1.4070	14.5	2 2 4
1.3909	1.3910	2.2	0 2 5
1.3518	1.3518	3.7	0 4 2
1.3386	1.3384	4.6	1 3 4
1.2752	1.2754	2.5	2 4 0
1.2592	1.2593	8.0	2 4 1
1.2568	1.2569	8.5	1 1 6
1.2306	1.2307	1.5	4 2 1
1.2139	1.2144	2.8	2 4 2
1.1875	1.1875	3.0	3 3 3
1.1339	1.1335	3.1	3 4 0
1.1028	1.1031	1.9	2 2 6

both compounds are very probably isostructural. One ought to assume that also in this case compound L has a structure related to that of perovskite [37–45]. Writing the formula $Ca(Ca_{1/4}, Mo_{3/4})O_3$ we indicate the octahedrally coordinated cations by parentheses. Moreover, the lattice constants can be again expressed by the cubic lattice parameter a_p of the normal perovskite by the relationship: $4c^{1/2}=a+b$, where $c=2a_p$.

Compound L undergoes complete hydrolysis degradation at room temperature overnight. In the dry remnants, the compounds $CaMoO_4$ and $Ca(OH)_2$ were identified.

Jantzen *et al.* [46] studied 'the phase chemistry and radionuclide partitioning in the anhydrous cement phases during clinkering'. They showed that in the cement–Purex waste the Ca_3MoO_6 phase was observed at 1273 and 1373 K. However, in the light of our data, their observations concerned, in fact, the L phase $Ca_5Mo_3O_{12}$.

In earlier work, an eutectic character of the MoO_3–$CaMoO_4$ system was revealed [47, 48] and in the MoO_3–CaO system the high temperature phase Ca_3MoO_6 was found [36, 49]. The low temperature compound $CaMo_2O_6$ was discussed in ref. 50. $CaMo_3O_{10} \cdot nH_2O$ (where $n = 1$, 3, 6) compounds were also prepared [51].

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