# SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

# Scheelite-Related Triple Molybdates $KCaLn(MoO_4)_3$ in $K_2MoO_4$ -CaMoO<sub>4</sub>-Ln<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> (Ln = Nd, Sm, Eu, Gd) Systems: Synthesis and Characterization

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Abstract—Subsolidus phase ratios in  $K_2MoO_4$ —CaMoO<sub>4</sub>—Ln<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> systems where Ln = Nd, Sm, Eu, and Gd, have been studied by vibrational spectroscopy, X-ray powder diffraction, and differential thermal analysis. Triple molybdates KCaLn(MoO<sub>4</sub>)<sub>3</sub> (Ln = Nd, Sm, Eu, and Gd) have been synthesized; they have a scheelite-derivative structure, monoclinic crystal system (space group *P*21/*n*). Their unit cell parameters have been determined, and IR and Raman spectra characterized.

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Scheelite molybdates and tungstates containing alkaline-earth and rare-earth elements have low thermal expansivities and high chemical and thermal stabilities. Owing to their tunable physicochemical and optical characteristics, they find great application in optical devices, as laser materials, phosphors for light-emitting diodes, catalysts, and solid electrolytes [1–12].

The large extents of crystallization fields of scheelite-related individual compounds and solid solutions are due to the possibility of isovalent and heterovalent substitutions of their alkaline-earth cations by cations of various characters and sizes at framework and extra-framework sites. Extensive cationic isomorphism results in charge misbalance in the scheelite structure due to the geometric features of arrangement of nearest-neighbor polyhedra. It is the appearing local and cooperative distortions that make it possible to tune the properties of phases. These structural specifics of scheelite-related molybdates are responsible for their potential for use as functional electronic materials, chemical sensors, and ionexchange materials, thereby stipulating extensive theoretical and experimental studies of this group of inorganic compounds [3–12].

Of the triple molybdates containing alkaline-earth and rare-earth elements, the series of barium and strontium compounds  $M(Ba)SrLn(MoO_4)_3$  (M = K, Rb, or Cs; Ln = Nd, Sm, Eu, and Gd) are known [3, 4]. Whether other combinations of metal cations are possible has not been analyzed.

The focuses of this study are on subsolidus phase equilibria in  $K_2MoO_4$ -CaMoO<sub>4</sub>-Ln<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> systems where Ln = Nd, Sm, Eu, and Gd; synthesis of

triple molybdates; and their characterization by X-ray diffraction, differential thermal analysis, and vibrational spectroscopy.

#### EXPERIMENTAL

The initial components used to study phase formation in K<sub>2</sub>MoO<sub>4</sub>-CaMoO<sub>4</sub>-Ln<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> systems were K<sub>2</sub>MoO<sub>4</sub>, CaMoO<sub>4</sub>, and Ln<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> samples presynthesized by solid-phase reactions from K<sub>2</sub>CO<sub>3</sub>,  $CaCO_3$ ,  $R_2O_3$  and  $MoO_3$  at temperatures in the range 400–650°C with multiple intermittent grindings every 20-30 h. The calcination time at each temperature was 100-120 h. After being calcined, samples were slowly cooled with the furnace. Unequilibrated samples were annealed additionally; equilibrium was regarded to be attained when the phase composition of the sample remained unchanged upon two consecutive anneals. Synthesis products were identified by X-ray powder diffraction in an FR-552 monochromator chamber (Cu $K_{\alpha}$  radiation; Ge internal standard). The X-ray diffraction patterns were calculated in the Rentgen program.

Vibrational spectra of polycrystalline KCaLn(MoO<sub>4</sub>)<sub>3</sub> samples were recorded on a Bruker FT-IR spectrometer and a Specord M-80 spectrometer with 1.06-nm laser excitation in the near-IR range (back-scattering geometry, resolution: 3-5 cm<sup>-1</sup>). Test samples were Nujol mulls on a polyethylene substrate or KBr pellets. Molybdenum isotope-substituted samples were prepared using <sup>92</sup>MoO<sub>3</sub> and <sup>100</sup>MoO<sub>3</sub> that contained at least 95% of the major isotope.



Fig. 1. 750°C isothermal section of the  $K_2MoO_4$ -CaMoO<sub>4</sub>-Nd<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> system.

Differential thermal analysis experiments were performed on an MOM OD-103 derivatograph (temperature elevation rate: 10 K/min; sample size: 0.3–0.4 g).

#### **RESULTS AND DISCUSSION**

Interactions in  $K_2MoO_4$ – $CaMoO_4$ – $Ln_2(MoO_4)_3$ systems were studied by the crossing sections method in the range 450–800°C. The studies of the  $K_2MoO_4$ –  $CaMoO_4$ – $Ln_2(MoO_4)_3$  systems comprised two stages. First, phase compositions were studied at the intersection points of the sections that radiated from the normal and double molybdates formed in the boundary binaries. The second stage involved the study of the sections that turned to be quasi-binary up to 750°C in order to triangulate the systems (Fig. 1). In view of the similarity of phase ratios in the studied systems, we will not describe each of them; Fig. 1 shows phase ratios in the  $K_2MoO_4$ – $CaMoO_4$ – $Nd_2(MoO_4)_3$  system by the way of example.

The boundary binary  $K_2MoO_4-Ln_2(MoO_4)_3$  was found to form 1 : 1 and 5 : 1 molybdates, which crystallize in different structural types [1]. Reacting  $K_2MoO_4$  with CaMoO\_4 yielded  $K_2Ca(MoO_4)_2$ , which has the palmierite structure. CaLn<sub>2</sub>(MoO<sub>4</sub>)<sub>4</sub> molybdates having large homogeneity extents and a monoclinically distorted scheelite-related structure (space group *C*2/*c*) [3], were synthesized in CaMoO<sub>4</sub>-Ln<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> systems.

Interactions along CaMoO<sub>4</sub>–KLn(MoO<sub>4</sub>)<sub>2</sub> sections were studied in most detail (in 1–2 mol %); for Ln = Nd, Sm, Eu, and Gd, KCaLn(MoO<sub>4</sub>)<sub>3</sub> triple molybdates were formed at 650–750°C. Reaction mixtures were calcined for 140–160 h with intermittent homogenization for equilibration.

The quasi-binary sections in K<sub>2</sub>MoO<sub>4</sub>-CaMoO<sub>4</sub>- $Ln_2(MoO_4)_3$ systems  $KLn(MoO_4)_2$ are:  $KCaLn(MoO_4)_3$ ,  $K_2Ca(MoO_4)_2-KCaLn(MoO_4)_3$ ,  $K_2Ca(MoO_4)_2 - K_5LnR(MoO_4)_4$  $K_2Ca(MoO_4)_2 KLn(MoO_4)_2$ ,  $CaMoO_4 - KCaLn(MoO_4)_3$ ,  $CaLn_2(MoO_4)_4 - KCaLn(MoO_4)_3$ , and CaLn<sub>2</sub>(MoO<sub>4</sub>)<sub>4</sub>-KLn(MoO<sub>4</sub>)<sub>2</sub>. X-ray powder diffraction showed that a KCaLn(MoO<sub>4</sub>)<sub>3</sub> triple molybdate dissolves 2-3 mol % CaMoO<sub>4</sub>; the solubility of a triple molybdate in CaMoO<sub>4</sub> is 10-12 mol %. In CaLn<sub>2</sub>(MoO<sub>4</sub>)<sub>4</sub>, no more than 1.5–2 mol % of a triple molybdate is dissolved. The solubility of  $KLn(MoO_4)_2$ in KCaLn(MoO<sub>4</sub>)<sub>3</sub> is 4–5 mol %; KLn(MoO<sub>4</sub>)<sub>2</sub> dissolves no more than  $2-3 \mod \% \operatorname{KCaLn}(\operatorname{MoO}_4)_3$ . Palmierite continuous solid solutions between the inicomponents are identified along tial the  $K_2Ca(MoO_4)_2 - K_5Ln(MoO_4)_4$ sections. The  $K_2Ca(MoO_4)_2 - KLn(MoO_4)_2$  sections are simple eutectics with component solubility of up to 2 mol %.

Rare-earth molybdates KCaLn(MoO<sub>4</sub>)<sub>3</sub> have a monoclinically distorted scheelite structure, space group  $P2_1/n$ , Z = 9. The compounds are isostructural to each other and to the double molybdate  $\alpha$ -KSm(MoO<sub>4</sub>)<sub>2</sub> and KBaLn(MoO<sub>4</sub>)<sub>3</sub> triple molybdates where Ln = La-Lu or Y [2, 3]. The KCaLn(MoO<sub>4</sub>)<sub>3</sub> structure may be regarded as the product of heterovalent substitution of the alkalineearth element in the scheelite structure by the scheme  $2Ca = K^+ + Ln^{3+}$ . Table 1 lists the crystallographic and thermal characteristics of KCaLn(MoO<sub>4</sub>)<sub>3</sub>, which melt incongruently at temperatures in the range 1020– 985°C without experiencing polymorphic transitions

Table 1. Crystallographic and thermal characteristics of KCaLn(MoO<sub>4</sub>)<sub>3</sub>

Compound		Unit cell p	17/- Å3	Melting		
	<i>a</i> , Å	b, Å	c, Å	β, deg	V/2, A	point, °C
KCaNd(MoO <sub>4</sub> ) <sub>3</sub>	12.178(2)	11.689(3)	16.798(2)	95.66(3)	264.1	1020
KCaSm(MoO <sub>4</sub> ) <sub>3</sub>	12.174(1)	11.467(2)	16.783(2)	95.72(1)	259.2	1005
KCaEu(MoO <sub>4</sub> ) <sub>3</sub>	12.166(3)	11.253(1)	16.761(3)	95.48(2)	254.1	998
KCaGd(MoO <sub>4</sub> ) <sub>3</sub>	12.161(2)	11.132(3)	16.751(4)	94.91(4)	252.2	985

# SCHEELITE-RELATED TRIPLE MOLYBDATES

Ι	<i>d</i> , Å	$d_{\rm obs}^2 \times 10^{-4}$	h	k	l	$d_{\rm calc}^2 \times 10^{-4}$
20	3.32501	144.04	0	0	2	144.02
10	5.06147	390.30	0	1	3	389.03
5	4.91822	413.45	10	0	3	418.10
10	4.83731	427.41	0	2	2	427.94
5	3.88094	664.5	2	2	-2	666.0
2	4.44155	844.3	2	1	-4	844.0
100	3.28750	925.5	3	1	-3	924.0
100	3.21702	966.0	0	3	3	975.1
5	3.05533	1071.6	3	0	-4	1073.5
80	3.4805	1076.9	3	1	3	1078.1
5	3.02868	1090.0	4	0	-1	1089.1
			4	0	0	1088.5
40	2.77749	1297.0	4	0	2	1297.0
50	2.66123	1412.1	2	3	-4	1413.0
2	2.61687	1460.8	1	1	-6	1460.1
3	2.59354					
5	2.57586	1507.1	1	4	-3	1507.5
			4	0	3	1508.0
10	2.53235	1560.1	1	4	3	1559.4
1	2.51098	1586.0	4	1	—4	1587.1
						1585.2
1	2.46090	1651.0	3	3	3	1651.5
			3	2	-5	1652.0
5	2.41070	1720.0	3	3	-4	1729.4
2	2.40031	1736.0	1	0	—7	1736.0
10	2.38644	1757.1	5	0	-2	1757.1
10	2.38109	1764.1	5	1	-1	1764.5
15	2.37393	1774.0	5	1	0	1772.5
3	2.32763	1845.0	5	1	0	184.6
5	2.21680	2035.1	3	4	-2	2035.1
5	2.18068	2105.1	3	1	6	2106.2
5	2.13440	2196.2	2	1	7	2196.3
10	2.12430	2217.1	2	4	-5	2217.1
90	2.05343	2373.1	0	3	7	2572.6
60	2.00434	2489.2	6	0	-2	2487.2
3	1.96637	2586.2	2	4	-6	2587.0
3	1.93903	2660.1	3	0	-8	2659.6
60	1.89350	2789.1	4	3	5	2788.8
1	1.82593	2999.4	1	0	9	3000.2
50	1.80190	3080.0	1	5	-6	3080.0
50	1.79083	3118.0	2	6	-8	3121.0
10	1.78263	3146.9	0	6	4	3146.6
1	1.75564	3244.4	5	4	—4	3243.6
1	1.73008	3340.9	4	2	7	3341.0
2	1.72017	3379.5	7	1	-1	3380.1
70	1.69595	3477.0	6	1	-6	3476.8
60	1.66765	3594.0	7	2	-1	3594.0
1	1.65458	3652.8	2	6	-5	3651.6
50	1.64212	3709.1	1	7	-2	3709.2

**Table 2.** Indexing of the X-ray diffraction pattern for  $KCaGd(MoO_4)_3$ 

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Table 3.	Vibration free	uencies (cr	1 <sup>-1</sup> ) in	Raman	and IR s	pectra of	f KCaLn	$(MoO_4)$	and C	CaMoO <sub>4</sub>
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KCaNd(MoO <sub>4</sub> ) <sub>3</sub>			KCaSm(MoO <sub>4</sub> ) <sub>3</sub>		KCaGd(MoO <sub>4</sub> ) <sub>3</sub>		CaMoO <sub>4</sub>			
ran	nan	Ι	IR							Assignment
<sup>92</sup> Mo	<sup>100</sup> Mo	<sup>92</sup> Mo	<sup>100</sup> Mo	raman	aman IR	raman	IR	raman	IR	
947 928 886 869	945 928 886 869	927	927	932 919 896 868	918	934 915 895	936	879		ν <sub>1</sub>
841 823 806 783 758 706	836 817 796 768 748 705	846 704	840 698	837 816 804 774 749 736	843 801 760 682	842 813 803 771 748 737 705	855 738 686	848 794.5	813	ν <sub>3</sub>
384		427 375	426 375	385 366	456 418 386 354	383 365	474 430 372	403.5 392	431	ν <sub>2</sub>
331 322	384 331 320	329	325	322	327 300	321	320 309	323.5	329	$v_4$ $v_2$ $v_4$
	320	284 262	284 262	286 229	286	285 228	285 224	269	284 237	
205					210			205	200	R
177	202	187	187	170	189	170	168	191.5		Т
155	177 155	157 138 132 125	157 138 - 125	144 128	146 140 127	145 139 129 126	149 137 131	144.5	153	R R R
102				105		103		112		Т
	101				78	77				Т

(Fig. 2). Table 2 shows the results of indexing the KCaGd(MoO<sub>4</sub>)<sub>3</sub> X-ray diffraction pattern. The measured IR and Raman vibrational frequencies in KCaLn(MoO<sub>4</sub>)<sub>3</sub> spectra are shown in Table 3 and in Fig. 3. Here are also shown the vibrational frequencies for CaMoO<sub>4</sub> and their assignment to the internal vibrations in MoO<sub>4</sub> groups and the crystal-lattice

vibrations (the librations (R) in  $MoO_4$  group and the translational vibrations (T) in various subslattices of the crystal).

The data shown indicate the similarity of  $CaMoO_4$ and  $KCaLn(MoO_4)_3$  vibrational spectra, thereby making possible satisfactory interpretation. The differences are explainable by the changes in interatomic



Fig. 2. Derivative thermal curves for  $KCaGd(MoO_4)_3$ .



Fig. 3. IR spectra of (1)  $KCaNd(MoO_4)_3$ , (2)  $KCaEu(MoO_4)_3$ , and (3)  $KCaGd(MoO_4)_3$ .

distances and, as a consequence, in Mo–O bond energies upon isomorphic heterovalent substitutions at cationic sites. The bounds of  $MoO_4$  stretching frequencies extend noticeably both to higher frequencies and lower frequencies, and the number of frequencies measured in this range is three times that in the CaMoO<sub>4</sub> spectrum. The increased number of bands arises from the lowered symmetry of MoO<sub>4</sub> and from the complete removal of degeneration from the triply degenerate vibrations and the manifestation of resonance interactions of vibrations in translationally non-equivalent  $MoO_4$  groups [13].

The measured spectra have an increased number of librations of MoO<sub>4</sub> groups, which are IR-active. Their frequencies are insensitive to molybdenum isotope substitution, are almost unchanged along the series of the compounds studied, and are close to the respective frequencies in CaMoO<sub>4</sub>. The observed number of translational vibrations corresponds to the number expected from theory. The relevant frequencies in some case experience the isotopic effect and undergo systematic modification upon cationic substitutions. The data we gained can serve as evidence that all cations are equally involved in the translational vibrations of KCaLn( $MoO_4$ )<sub>3</sub>. The observed lowering of crystal symmetry upon heterovalent cationic substitutions in the scheelite structure is due to distortions of molybdenum-oxygen tetrahedra.

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