Subsolidus Phase Relations in the Systems $M_2^+O-M^{2+}O-V_2O_5$ (M⁺ = Li, Na, K, Rb, Cs; $M^{2+} = Mg$, Ca)

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Abstract—Subsolidus phase relations in the M₂O(M₂CO₃)–MgO–V₂O₅ and M₂O(M₂CO₃)–CaO–V₂O₅ (M = Li, Na, K, Rb, Cs) systems are studied. Twenty mixed vanadates are obtained, of which Rb₂CaV₂O₇, Cs₂CaV₂O₇, LiMg₄(VO₄)₃, RbCaVO₄, and CsCaVO₄ are identified for the first time. Structural data are summarized for all of the mixed vanadates: the space group and lattice parameters are indicated for 14 compounds (for 6 compounds, such data are obtained for the first time), and *I* and *d* data are presented for 8 compounds. Partial series of Ca₃(VO₄)₂-based solid solutions with the general formula Ca_{3-x}M_{2x}(VO₄)₂ (M = Na, K, Rb, Cs) are identified in the range 0 < *x* ≤ 0.14. Six phase diagrams (M⁺ = Li, Rb, Cs; M²⁺ = Mg, Ca) are investigated and are compared with the phase diagrams of the other ternary systems in question. The key features of the ternary phase diagrams and, hence, the reactivity of the constituent oxides are shown to vary systematically in going from Li₂O to Cs₂O and from MgO to SrO, which is interpreted in terms of the variation in the ionic radius of the alkali and alkaline-earth metals.

INTRODUCTION

By examining the effect of the M⁺ or M²⁺ metal on the phase relations in $M_2^+O-M^{2+}O-V_2O_5$ systems, one can establish relationships between the reactivities of the M²⁺O or M_2^+O oxides in such systems. This work, dealing with the M²⁺ = Mg and Ca systems, continues our earlier study [1], where we examined such relationships for M⁺ = Li, Na, K, Rb, Cs and M²⁺ = Sr.

The Na₂O(K₂O)–MgO(CaO)–V₂O₅ phase diagrams were reported in [2–6]. For the other systems, phasediagram data are missing. Data on mixed vanadates existing in unexplored systems are given in [7]. In particular, the Li₂O–MgO–V₂O₅ system was shown to contain the orthovanadate LiMgVO₄, solid-solution series Li_{2x}Mg_{1.5-x}VO₄ (0.10 < x < 0.15) [8], and Li₃Mg₁₈V₁₁O₄₇ [7, card 46-0189] (Fig. 1, symbols *1–3*). The Rb₂O–CaO–V₂O₅ system contains the ternary metavanadate Rb₂Ca(VO₃)₄ [9]. Structural data, detailed or not, have been reported for only half of the known vanadates in the systems in question.

In addition, new data have recently been reported on some of the systems studied earlier. According to the structural analysis results reported by Martin and Muller-Buschbaum [10], the composition of the mixed metavanadate in the $K_2O-CaO-V_2O_5$ system is $K_3Ca(VO_3)_5$, rather than $K_2Ca(VO_3)_4$ [6, 11]. In addition to the ternary vanadates identified in [6], this system was shown to contain a compound of composition $KCa_{10}V_7O_{28}$ [12], isostructural with $Ca_3(VO_4)_2$ [12].

The objective of this work was to identify the phases existing in the systems $M_2^+ O-M^{2+}O-V_2O_5$ (M⁺ = Li, Na, K, Rb, Cs; M²⁺ = Mg, Ca), to clarify a number of controversial issues, to determine the structural parameters of several ternary vanadates, to systematize the available information about these systems, and to examine variations in reactivity across the M_2^+O and $M^{2+}O$ oxide series.



Fig. 1. Portion of the Li₂O–MgO–V₂O₅ phase diagram at subsolidus temperatures: (*1*) LiMgVO₄, (2) Li_{2x}Mg_{1.5-x}VO₄ (0.1 < x < 0.15), (3) Li₃Mg₁₈V₁₁O₄₇, (4) LiMg₄(VO₄)₃, (5) Mg₃(VO₄)₂.

EXPERIMENTAL

Samples for this investigation were prepared by solid-state synthesis (Naber furnace). Thoroughly ground mixtures of extrapure-grade V_2O_5 , MgO (or CaCO₃), and alkali carbonates were reacted at a temperature 10–15°C below the melting point or the decomposition temperature of the reaction products for 100–130 h with repeated intermediate grindings. In addition, we reacted mixtures of presynthesized magnesium, calcium, and alkali vanadates. We prepared and characterized at least three samples for each assumed join to be studied and at least two samples for each assumed three-phase region. The phase purity of the synthesized ternary vanadates was checked carefully.

The phase composition of the samples was determined by x-ray diffraction (XRD) on a DRON-2 powder diffractometer (Cu K_{α} radiation), using JCPDS– ICDD PDF 2 data [7]. Structural characterization of new vanadates was carried out on a STADI-P (STOE, Germany) automatic x-ray diffractometer (Cu K_{α} radiation, diffracted beam pyrolytic graphite monochromator, α -Al₂O₃ internal standard (NIST SRM 676, USA), Si external standard with a = 5.43075(5) Å). XRD patterns were taken at room temperature in the angular range $2^{\circ} \le 2\theta \le 120^{\circ}$ with a step size of 0.02°. The results were analyzed using STOE SOFTWARE. Structural analogs were sought for using ICDD PDF 2 (2002) data. Indexing schemes were checked with NBS AIDS83.

RESULTS AND DISCUSSION

The $M_2^+O-M^{2+}O-V_2O_5$ phase diagrams studied in this work at subsolidus temperatures are displayed in Figs. 2 and 3. The phase diagrams of six systems ($M^+ =$ Li, Rb, Cs; $M^{2+} = Mg$, Ca) were mapped out for the first time, and those of three systems ($M^+ = Na$, $M^{2+} = Mg$; $M^+ = Na$, $M^{2+} = Ca$; $M^+ = K$, $M^{2+} = Ca$) were refined.

Strictly speaking, none of the systems studied are pseudoternary because they contain vanadium bronzes (VBs) [13], which form at $p_{O_2} = 0.21 \times 10^5$ Pa via partial reduction of vanadium (accompanied by oxygen loss) and belong to the corresponding M₂O–V₂O₄– V₂O₅ systems. It is, however, common practice to include VBs in the M₂O–V₂O₅ systems (Figs. 2, 3). Another conventional simplification is that the compositions of VBs are represented in phase diagrams by points, even though the alkali-metal content of these compounds may vary in a narrow range [13].

In the $M_2O-V_2O_5$ (M = Li, Na, K, Rb, Cs) systems (Figs. 2, 3), we obtained the same phases as in earlier studies [1]. The MgO-V₂O₅ system contains magnesium meta-, pyro-, and orthovanadates [14]. The cal-

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cium vanadates obtained in this work coincide with those reported in [5].

The Rb₂O(Cs₂O)–MgO–V₂O₅ and Li₂O–CaO–V₂O₅ systems contain no mixed vanadates. The phase equilibria in these systems involve only alkali and alkaline-earth vanadates. The other combinations of oxides react to form mixed vanadates. In particular, our results on the pseudobinary system Li₃VO₄–Mg₃(VO₄)₂ in conjunction with earlier data for Li_{2x}Mg_{1.5 - x}VO₄ and Li₃Mg₁₈V₁₁O₄₇ [7] suggest that this system contains, along with LiMgVO₄, a new mixed orthovanadate of composition LiMg₄(VO₄)₃ (Fig. 1, point 4). The samples close in composition to this compound (Fig. 1, symbols 2, 3) consist of LiMg₄(VO₄)₃ and trace amounts of Mg₃(VO₄)₂ or MgO and Mg₃(VO₄)₂. LiMg₄(VO₄)₃ is isostructural with NaMg₄(VO₄)₃ (Table 1).

The M₂O–CaO–V₂O₅ (M = Na, K, Rb, Cs) systems contain Ca₃(VO₄)₂-based substitutional solid solutions with the general formula Ca_{3-x}M_{2x}(VO₄)₂ (0 < x ≤ 0.14). The lattice parameters of the terminal solid solutions (rhombohedral, sp. gr. *R*3*c*) are listed in Table 2. The NaVO₃–Ca(VO₃)₂ system contains two partial solidsolution series in the composition ranges 0–5 mol % Ca(VO₃)₂ and 0–17 mol % NaVO₃ [11, 19, 21].

By firing a 1.5 : 1 : 2.5 mixture of K_2CO_3 , $CaCO_3$, and V_2O_5 at 350°C for 200 h, followed by slow cooling, or at 450°C for 50 h, followed by quenching, we obtained $K_3Ca(VO_3)_5$, in accordance with earlier data [10]. In contrast to what was reported by Glazyrin *et al.* [11], we detected no polymorphic transformations of this compound. Heat treatment of a 1 : 1 : 2 mixture of the same reagents ($K_2Ca(VO_3)_4$ stoichiometry) under the same conditions led to the formation of $K_3Ca(VO_3)_5$ and $Ca(VO_3)_2$.

It was, therefore, reasonable to expect that a ternary metavanadate of the same stoichiometry exists in the Rb system. However, reacting 1:1:2 and 1.5:1:2.5mixtures of Rb_2CO_3 , $CaCO_3$, and V_2O_5 , we obtained phase-pure $Rb_2Ca(VO_3)_4$ in the former case and a mixture of this vanadate with RbVO₃ in the latter case. Thus, the vanadates existing in the joins (systems) NaVO₃-Ca(VO₃)₂, KVO₃-Ca(VO₃)₂, and $RbVO_3$ - $Ca(VO_3)_2$ are $Na_2Ca(VO_3)_4$, $K_3Ca(VO_3)_5$, and $Rb_2Ca(VO_3)_4$, respectively. The fact that the K-containing vanadate differs in stoichiometry from the other two vanadates correlates with the specific behavior of potassium and its compounds, which often do not fit in with general trends exhibited by the other alkali metals and their compounds. In particular, this refers to the systems M_3VO_4 -Ca₃(VO₄)₂ (Fig. 3) and MVO₃- $Sr(VO_3)_2$ [1] with M = Li, Na, K, Rb, and Cs.

Of the compounds listed in Table 1, the mixed vanadates $Rb_2CaV_2O_7$, $Cs_2CaV_2O_7$, $LiMg_4(VO_4)_3$, RbCaVO₄, and CsCaVO₄ and the solid solutions



Fig. 2. Schematic phase diagrams of $M_2O(M_2CO_3)$ – $MgO-V_2O_5$ systems at subsolidus temperatures: M = (a) Li, (b) Na, (c) K, (d) Rb, (e) Cs: (1) LiMgVO_4, (2) MMg_4(VO_4)_3, (3) Na_6Mg_3(VO_4)_4, (4) K_2Mg(VO_3)_4, (5) K_2MgV_2O_7.

 $Ca_{3-x}M_{2x}(VO_4)_2$ (M = K, Rb, Cs), $0 < x \le 0.14$ (Table 2) were synthesized for the first time. Some of these compounds, and also Na₂Ca(VO₃)₂, KCaVO₄, and the Ca₃(VO₄)₂-based solid solution, were characterized by

XRD (Tables 1, 2). The powder XRD data for $LiMg_4(VO_4)_3$, $Cs_2CaV_2O_7$, and Cs_2CaVO_4 are presented in Table 3. We also confirmed the existence of some other mixed vanadates (Figs. 2, 3; Table 1).

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Fig. 3. Schematic phase diagrams of $M_2O(M_2CO_3)$ –CaO– V_2O_5 systems at subsolidus temperatures: M = (a) Li, (b) Na, (c) K, (d) Rb, (e) Cs: (1) $M_2Ca(VO_3)_4$, (2) $K_3Ca(VO_3)_5$, (3) $Na_2Ca_7(V_2O_7)_4$, (4) $Na_3Ca_2V_3O_{11}$, (5) $M_2CaV_2O_7$, (6) $MCaVO_4$, (7) $NaCa_4(VO_4)_3$, (8) $K_4Ca(VO_4)_2$, (9) $Ca_3(VO_4)_2$ -based solid solution, (10) $NaVO_3$ -based solid solution, (11) $Ca(VO_3)_2$ -based solid solution.

In the context of the $M_2^+ O-M^{2+}O-V_2O_5$ (M⁺ = Li, Na, K, Rb, Cs; $M^{2+} = Mg$, Ca, Sr) phase diagrams (Figs. 2 and 3 in this work and Fig. 2 in [1]), several important points warrant mention. In going from Li₂O

to Cs_2O or from MgO to SrO, the key features of these ternary phase diagrams vary systematically. This is associated primarily with the effect of the cation size on the reactivity of the constituent oxides and on the nature

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Compound	Structure	Source	Compound	Structure	Source	
Metavanadates			Orthovanadates			
$K_2Mg(VO_3)_4$	<i>I</i> , <i>d</i> *	[3]	LiMgVO ₄	Orthorhombic, <i>Cmcm</i> , $a = 5.6283$ Å, b = 8.6123 Å, $c = 6.2381$ Å	[7, card. 78-2263]	
Na ₂ Ca(VO ₃) ₄	Tetragonal, <i>P</i> 4/ <i>nbm</i> , $a = 10.43849$ Å, $c = 4.93875$ Å	[7, card. 52-0705]	LiMg ₄ (VO ₄) ₃	Tetragonal, $I\bar{4} 2d$, $a = 6.86707(2)$ Å, c = 18.95455(1) Å	This work	
K ₃ Ca(VO ₃) ₅	Orthorhombic, <i>Cmma</i> , $a = 25.953$ Å, b = 15.688 Å, $c = 7.804$ Å	[10]	$Na_6Mg_3(VO_4)_4$	<i>I</i> , <i>d</i> *	[2]	
Rb ₂ Ca(VO ₃) ₄	<i>I</i> , <i>d</i> *	[9]	NaMg ₄ (VO ₄) ₃	Tetragonal, $I\bar{4}2d$, $a = 6.89$ Å, $c = 19.292$ Å	[17]	
	1	NaCaVO ₄	Low-temperature form: orthorhombic,	[7, card. 75-2310] [18]		
				<i>Cmcm</i> , $a = 5.8726$ Å, b = 9.3028 Å, $c = 7.1526$ Å		
				High-temperature form: hexagonal,		
				$P\bar{3}m1, a = 5.57$ Å, $c = 7.33$ Å	[18]	
$K_2MgV_2O_7$	Tetragonal, $P4_2/mnm$, a = 8.38 Å, $c = 11.376$ Å	[15]	NaCa ₄ (VO ₄) ₃	I, d^*	[19]	
$Na_2Ca_7(V_2O_7)_4$	<i>I</i> , <i>d</i> *	[5]	K ₄ Ca(VO ₄) ₂	<i>I</i> , <i>d</i> *	[6]	
K ₂ CaV ₂ O ₇	<i>I</i> , <i>d</i> *	[6]	KCaVO ₄	Low-temperature form: monoclinic sub- cell**,	This work	
				a' = 5.6821(3) Å, $b' = 9.9953(6)$ Å, $c' = 7.6883(4)$ Å, $\beta = 91.92^{\circ}$		
				High-temperature form: hexagonal,		
				$P6_3/mmc$, $a = 5.718(7)$ Å, $c = 7.528(9)$ Å		
Rb ₂ CaV ₂ O ₇	Monoclinic, $C2/c$, $a = 10.3419(1)$ Å, b = 5.9656(1) Å, $c = 13.8865(2)$ Å, $\beta = 104.953^{\circ}$	This work	RbCaVO ₄	Monoclinic subcell ^{**} , $a' = 5.729(7)$ Å, b' = 10.10(1) Å, $c' = 7.758(9)$ Å, $\beta = 91.92^{\circ}$	This work	
$Cs_2CaV_2O_7$	$\begin{vmatrix} \text{Monoclinic, } C2/c, a = 10.59218(7) \text{ Å}, \\ b = 6.09025(4) \text{ Å}, c = 14.06766(6) \text{ Å}, \\ \beta = 104.629^{\circ} \end{vmatrix}$	This work	CsCaVO ₄	<i>I</i> , <i>d</i> *	This work	
$\begin{array}{c} Na_{3}Ca_{2}V_{3}O_{11} \\ (Na_{3}Ca_{2}(VO_{4})(V_{2}O_{7})) \end{array}$	Monoclinic, $C^{2/c}$, $a = 23.791$ Å, $b = 8.706$ Å, $c = 10.891$ Å, $\beta = 109.74^{\circ}$	[16]				

Table 1. Crystallographic data	for ternary vanadates i	in M ₂ O-MgO(CaO)-V	V ₂ O ₅ systems
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* The structure was not determined; only powder XRD data were presented. ** The true unit cell was not identified; data are presented for a subcell derived from the high-temperature form: $a'_{\rm m} \sim a_h, b'_{\rm m} \sim a_h \sqrt{3}, c'_{\rm m} \sim c_h$.

Table 2. Lattice parameters of $Ca_{3-x}M_{2x}(VO_4)_2$ solid solutions with x = 0.14

М	<i>a</i> , Å	<i>c</i> , Å	Source
-(Ca ₃ (VO ₄) ₂)	10.809	38.028	[7, card 70-0790]
Na	10.815	38.075	[20]
Κ	10.830	37.860	[12]
Rb	10.881	37.924	This work
Cs	10.922	37.912	This work

and structure of the reaction products. It is, therefore, reasonable to analyze the effect of the difference in ionic radius between M^+ and M^{2+} [22].

As an illustration, consider the pseudobinary joins $M_3VO_4\text{--}Mg_3(VO_4)_2$ and $M_3VO_4\text{--}Sr_3(VO_4)_2$ (M = Li,

Na, K, Rb, Cs) in the ternary phase diagrams under discussion. In the former case, there are three types of phase relations: (1) The join contains two mixed vanadates; the orthovanadates are stable over the whole composition range (Fig. 2a, Li system). (2) The join also contains two mixed vanadates, but the Mg-containing orthovanadates are only stable in the composition range 50–100 mol % Mg₃(VO₄)₂ (Fig. 2b, Na system). (3) The vanadates $M_3^+ VO_4$ (M⁺ = K, Rb, Cs) and Mg₃(VO₄)₂ do not coexist and decompose into other compounds (Figs. 2c-2e). In the latter case, M_3VO_4 and Sr₃(VO₄)₂ always coexist, independent of the alkali metal, but only in the Li₃VO₄-Sr₃(VO₄)₂ system do the constituent orthovanadates not interact, while the Na, K, Rb, and Cs systems contain mixed orthovanadates (Fig. 2 in [1]).

Table 3. XRD data for ternary vanadates

hkl	<i>I</i> , %	d, Å	hkl	<i>I</i> , %	d, Å	<i>I</i> , %	<i>d</i> , Å
LiMg ₄ (VO ₄) ₃			Cs ₂ CaV ₂ O ₇			CsCaVO ₄	
101	3	6.4564	002	8	6.8054	7	3.870
004	10	4.7387	111	3	5.1124	13	3.136
103	18	4.6502	2 02	17	4.7045	34	3.112
112	7	4.3219	111	25	4.6884	29	3.081
105	31	3.3186	ī12	1	4.4343	12	3.060
202	8	3.2283	112	2	3.9122	100	2.972
211	54	3.0315	ī13	53	3.6707	10	2.161
204	100	2.7803	004	29	3.4029	9	2.138
213	17	2.7620	204	59	3.2365	8	1.958
116	12	2.6478	113	100	3.2286	13	1.723
220	1	2.4279	311	86	3.0544		
215	2	2.3862	020	75	3.0450		
008	7	2.3696	310	2	2.9795		
206	17	2.3248	021	4	2.9713		
301	1	2.2727	311	11	2.7852		
310	1	2.1715	022	11	2.7795		
224	2	2.1606	114	2	2.6981		
303	5	2.1521	<u>-</u> 221	2	2.6342		
312	2	2.1165	400	13	2.5622		
217	4	2.0310	Ī15	27	2.5542		

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