

Compound Formation in Alkali Tungstate Systems

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Received September 16, 1968

To study compound formation in the systems $\text{Li}_2\text{O}\cdot\text{WO}_3\text{-WO}_3$, $\text{Na}_2\text{O}\cdot\text{WO}_3\text{-WO}_3$ and $\text{K}_2\text{O}\cdot\text{WO}_3\text{-WO}_3$, x-ray powder diffraction analysis was applied to solid state reaction products of alkali carbonate- WO_3 mixtures and also to the products obtained by reheating of solidified melts. The following compositions were confirmed to form compounds: $\text{Li}_2\text{O}\cdot\text{WO}_3$, $\text{Li}_2\text{O}\cdot 2\text{WO}_3$ and $\text{Li}_2\text{O}\cdot 4\text{WO}_3$ in the lithium system, $\text{Na}_2\text{O}\cdot\text{WO}_3$, $\text{Na}_2\text{O}\cdot 2\text{WO}_3$, $\text{Na}_2\text{O}\cdot 4\text{WO}_3$ and $\text{Na}_2\text{O}\cdot 6\text{WO}_3$ in the sodium system, and $\text{K}_2\text{O}\cdot\text{WO}_3$, $\text{K}_2\text{O}\cdot 2\text{WO}_3$, $\text{K}_2\text{O}\cdot 3\text{WO}_3$, $\text{K}_2\text{O}\cdot 4\text{WO}_3$, and $\text{K}_2\text{O}\cdot 6\text{WO}_3$ in the potassium system.

I. INTRODUCTION

Alkali tungstates are used as starting materials for alkali tungsten bronzes¹⁾²⁾³⁾⁴⁾ and other compounds such as silicotungstates⁴⁾ and fluorotungstates⁵⁾. To understand the reactions involved in these and other preparations, phase diagrams and compound formation in alkali tungstate systems are very important, and have been studied by many people with the use of thermal analysis and x-ray diffraction analysis.

The most reliable phase diagram was given by Gelsing *et al.*⁶⁾ for the potassium tungstate system. They showed the presence of the stable compounds K_2WO_4 , $\text{K}_2\text{W}_2\text{O}_7$, $\text{K}_2\text{W}_3\text{O}_{10}$ and $\text{K}_2\text{W}_4\text{O}_{13}$, although they did not examine more acidic compositions. For the lithium and sodium tungstate systems, however, there are great discrepancies in the results of different authors as to the presence or absence of certain compounds, especially for the acidic compositions. The discrepancies arise from the use of inappropriate samples for x-ray diffraction or other analysis. Many authors prepared the samples by cooling melts of pertinent compositions⁴⁾⁵⁾⁷⁾⁸⁾. This method may not give stable compounds which are in equilibrium in solid state. The disadvantage of using solidified melts was avoided by Gelsing *et al.*⁶⁾ by using solid state reaction products for x-ray diffraction analysis. The mixture of starting materials was heated at a temperature below the solidus until the x-ray pattern of the reaction product did not change on further heating.

This method has been adopted in the present study. Another method of sample preparation has been added, however, to make the results more concrete; we reheated the solidified melts to the temperature at which the solid state reaction had taken place, and compared their x-ray diffraction patterns with those of sintered specimens of the same composition.

With the above methods of sample preparation, the compound formation in lithium-, sodium-, and potassium-tungstate systems was investigated systematically in a wide composition range covering the compositions from monotungstate to WO_3 .

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II. EXPERIMENTAL

Starting Materials

Reagent grade alkali carbonates (Fisher Co.) and tungsten trioxide (Alfa Inorganics) were used for all compositions. The carbonates were dried at 300°C before use. X-ray diffraction patterns of WO_3 agreed with published data⁹.

Preparation of Samples

Samples of each composition were prepared by (1) solid state reaction of a mixture of alkali carbonate and WO_3 ; (2) melting followed by solidification on cooling; and (3) reheating of solidified melt. For convenience, the first process will be called sintering, and its product sintered sample throughout this paper. Similarly, the words melting and solidified melt (or sample) will be used for the second process and its product; and reheating and reheated sample for the last process and its product. In the present work these three processes were realized in sequence; namely, sintering was done first, then a portion of sintered sample was melted and solidified. A portion of solidified melt was then reheated.

Fused quartz crucibles were used as containers. No appreciable reaction was observed between the sample and quartz wall during the sintering and reheating processes. In the melting process, however, a slight reaction seems to take place as revealed by a thin white layer produced between the sample and container wall for some of the compositions. Therefore, the surface of melt that contacted the container wall was discarded. Since the layers that did form were quite thin, and overall results of the x-ray diffraction study were consistent, the use of fused quartz crucibles for melting seems to be justified. For sintering, an intimate mixture of alkali carbonate and WO_3 was heated at various temperatures below the solidus, until the x-ray diffraction pattern became stable.

A portion of sintered sample was melted at temperatures ranging from 800°C to 1000°C for 10 minutes. At the melting temperature, clear melts were obtained for most of the compositions. However, 1000°C was not high enough to give a clear melt for the compositions $\text{Na}_2\text{O} \cdot 6\text{WO}_3$, $\text{Na}_2\text{O} \cdot 10\text{WO}_3$, $\text{K}_2\text{O} \cdot 6\text{WO}_3$ and $\text{K}_2\text{O} \cdot 10\text{WO}_3$. After 10 minutes, the melt was cooled down in the furnace, the cooling rate being about 10°/min. at 1000°C, 8°/min. at 900°C, 5°/min. at 800°C, 3.5°/min. at 700°C and 2.8°/min. at 600°C.

A portion of the solidified melt was held at the sintering temperature, until the x-ray diffraction pattern did not change any more.

X-ray Diffraction

X-ray diffraction patterns were recorded by a Norelco diffractometer with the use of copper $K\alpha$ radiation filtered through nickel under the condition: scanning rate 1°/min. and time constant 4. Calibration of diffraction angle was made with NaCl .

III. RESULTS

Lithium Tungstate System

X-ray diffraction patterns were taken for sintered, solidified and reheated samples of seven compositions: $\text{Li}_2\text{O} \cdot \text{WO}_3$, $\text{Li}_2\text{O} \cdot 1.5\text{WO}_3$, $\text{Li}_2\text{O} \cdot 2\text{WO}_3$, $\text{Li}_2\text{O} \cdot 3\text{WO}_3$, $\text{Li}_2\text{O} \cdot 4\text{WO}_3$, $\text{Li}_2\text{O} \cdot 6\text{WO}_3$ and $\text{Li}_2\text{O} \cdot 10\text{WO}_3$ ¹⁰. Sintered and reheated specimens of

identical compositions produced identical end-point x-ray diffraction pattern.

X-ray diffraction patterns of all the samples that reached equilibrium (sintered or reheated) were composed of one or two out of four sets of diffraction lines. These sets of diffraction lines could be ascribed to the compounds Li_2WO_4 , $\text{Li}_2\text{W}_2\text{O}_7$, $\text{Li}_2\text{W}_4\text{O}_{13}$ and WO_3 , respectively. Equilibrium samples of the compositions $\text{Li}_2\text{O} \cdot \text{WO}_3$, $\text{Li}_2\text{O} \cdot 2\text{WO}_3$ and $\text{Li}_2\text{O} \cdot 4\text{WO}_3$ showed, respectively, only one set of lines which could not be constructed out of the other two sets of lines and the lines of WO_3 . Thus, three equilibrium compounds Li_2WO_4 , $\text{Li}_2\text{W}_2\text{O}_7$ and $\text{Li}_2\text{W}_4\text{O}_{13}$ were confirmed to exist in the composition range $\text{Li}_2\text{O} \cdot \text{WO}_3$ - $\text{Li}_2\text{O} \cdot 10\text{WO}_3$.

X-ray diffraction lines of $\text{Li}_2\text{W}_2\text{O}_7$ and $\text{Li}_2\text{W}_4\text{O}_{13}$ are shown in Table 1. Diffraction data of Li_2WO_4 agreed very well with published data⁽¹⁾. Table 2 shows the compounds found in sintered, solidified, and reheated samples of seven compositions examined in the present study.

Table 1. Data on x-ray Diffraction Patterns of the Compounds $\text{Li}_2\text{W}_2\text{O}_7$ and $\text{Li}_2\text{W}_4\text{O}_{13}$.

$\text{Li}_2\text{W}_2\text{O}_7$				$\text{Li}_2\text{W}_4\text{O}_{13}$			
d	I	d	I	d	I	d	I
6.75	4	2.17	9	6.58	5	2.50	7
6.58	56	2.09	6	6.08	9	2.44	11
6.10	100	2.02	2	5.86	4	2.42	16
4.85	2	2.005	8	5.68	1	2.35	1
4.55	1	1.944	2	5.54	1	2.32	4
4.21	2	1.783	1	5.36	3	2.27	2
3.96	5	1.744	6	4.83	4	2.23	1
3.92	27	1.717	2	4.64	5	2.16	2
3.80	48	1.698	1	4.50	3	2.15	3
3.56	1	1.682	2	4.29	18	2.08	3
3.49	3	1.668	6	3.93	8	1.988	2
3.43	4	1.648	5	3.80	3	1.947	12
3.34	5	1.631	1	3.74	2	1.924	2
3.07	4	1.614	3	3.65	5	1.901	3
2.99	10	1.592	3	3.57	100	1.839	5
2.90	1	1.562	2	3.42	6	1.814	10
2.81	3	1.545	2	3.36	3	1.789	5
2.75	6	1.516	3	3.27	1	1.744	1
2.72	1	1.477	2	3.16	32	1.686	1
2.71	13	1.422	3	3.12	22	1.635	8
2.69	13	1.399	6	3.06	2	1.631	9
2.49	1			2.98	3	1.607	5
2.45	16			2.92	3	1.604	6
2.39	2			2.84	3	1.584	7
2.35	2			2.75	3	1.565	2
2.33	3			2.70	3	1.513	1
2.31	3			2.68	3	1.469	4
2.22	1			2.61	1	1.433	2

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Table 2. Crystalline Compounds Present in the Samples of the System $\text{Li}_2\text{O} \cdot \text{WO}_3$ - WO_3 .

Composition	Sample	Heating		Crystalline compounds	Remarks
		Temp. ($^{\circ}\text{C}$)	Time		
$\text{Li}_2\text{O} \cdot \text{WO}_3$	sintered	650	15 hr.	Li_2WO_4	
	solidified	800	10 min.	Li_2WO_4	
	reheated	650	15 hr.	Li_2WO_4	
$\text{Li}_2\text{O} \cdot 1.5\text{WO}_3$	sintered	650	15 hr.	$\text{Li}_2\text{W}_2\text{O}_7 + \text{Li}_2\text{WO}_4$	
	solidified	800	10 min.	$\text{Li}_2\text{W}_2\text{O}_7$	non-equil.
	reheated	650	15 hr.	$\text{Li}_2\text{W}_2\text{O}_7 + \text{Li}_2\text{WO}_4$	
$\text{Li}_2\text{O} \cdot 2\text{WO}_3$	sintered	670	15 hr.	$\text{Li}_2\text{W}_2\text{O}_7$	
	sintered	710	15 hr.	$\text{Li}_2\text{W}_2\text{O}_7$	
	solidified	800	10 min.	$\text{Li}_2\text{W}_2\text{O}_7$	
	reheated	710	15 hr.	$\text{Li}_2\text{W}_2\text{O}_7$	
$\text{Li}_2\text{O} \cdot 3\text{WO}_3$	sintered	690	15 hr.	$\text{Li}_2\text{W}_2\text{O}_7 + \text{Li}_2\text{W}_4\text{O}_{13}$	
	sintered	730	15 hr.	$\text{Li}_2\text{W}_2\text{O}_7 + \text{Li}_2\text{W}_4\text{O}_{13}$	
	solidified	900	10 min.	$\text{Li}_2\text{W}_2\text{O}_7 + \text{WO}_3$	non-equil.
	reheated	730	100 hr.	$\text{Li}_2\text{W}_2\text{O}_7 + \text{Li}_2\text{W}_4\text{O}_{13}$	
$\text{Li}_2\text{O} \cdot 4\text{WO}_3$	sintered	670	17 hr.	$\text{Li}_2\text{W}_2\text{O}_7 + \text{Li}_2\text{W}_4\text{O}_{13} + \text{WO}_3$	non-equil.
	sintered	730	24 hr.	$\text{Li}_2\text{W}_4\text{O}_{13}$	
	solidified	1000	10 min.	$\text{WO}_3 + \text{Li}_2\text{W}_2\text{O}_7$	non-equil.
	reheated	730	3 hr.	$\text{Li}_2\text{W}_4\text{O}_{13}$	non-equil.
	reheated	730	100 hr.	$\text{Li}_2\text{W}_4\text{O}_{13}$	
$\text{Li}_2\text{O} \cdot 6\text{WO}_3$	sintered	730	24 hr.	$\text{Li}_2\text{W}_4\text{O}_{13} + \text{WO}_3$	
	solidified	1000	10 min.	$\text{WO}_3 + \text{Li}_2\text{W}_2\text{O}_7$	non-equil.
	reheated	730	3 hr.	$\text{WO}_3 + \text{Li}_2\text{W}_4\text{O}_{13} + (\text{Li}_2\text{W}_2\text{O}_7)$	non-equil.
	reheated	730	100 hr.	$\text{Li}_2\text{W}_4\text{O}_{13} + \text{WO}_3$	
$\text{Li}_2\text{O} \cdot 10\text{WO}_3$	sintered	730	24 hr.	$\text{WO}_3 + \text{Li}_2\text{W}_4\text{O}_{13}$	
	solidified	1000	10 min.	$\text{WO}_3 + \text{Li}_2\text{W}_2\text{O}_7$	non-equil.
	reheated	730	100 hr.	$\text{WO}_3 + \text{Li}_2\text{W}_4\text{O}_{13}$	

Sodium Tungstate System

Six compositions $\text{Na}_2\text{O} \cdot \text{WO}_3$, $\text{Na}_2\text{O} \cdot 2\text{WO}_3$, $\text{Na}_2\text{O} \cdot 3\text{WO}_3$, $\text{Na}_2\text{O} \cdot 4\text{WO}_3$, $\text{Na}_2\text{O} \cdot 6\text{WO}_3$ and $\text{Na}_2\text{O} \cdot 10\text{WO}_3$ were examined. As in the lithium system, end point x-ray powder patterns of reheated samples agreed with those of sintered samples.

X-ray diffraction patterns of all equilibrium samples were composed of one or two out of five sets of diffraction lines which could be ascribed to the compounds Na_2WO_4 , $\text{Na}_2\text{W}_2\text{O}_7$, $\text{Na}_2\text{W}_4\text{O}_{13}$, $\text{Na}_2\text{W}_6\text{O}_{19}$ and WO_3 , respectively. Equilibrium samples of the compositions $\text{Na}_2\text{O} \cdot \text{WO}_3$, $\text{Na}_2\text{O} \cdot 2\text{WO}_3$, $\text{Na}_2\text{O} \cdot 4\text{WO}_3$ and $\text{Na}_2\text{O} \cdot 6\text{WO}_3$ showed, respectively, only one set of lines that could not be constructed out of the other three sets of lines and lines of WO_3 . Thus the existence of four equilibrium compounds Na_2WO_4 , $\text{Na}_2\text{W}_2\text{O}_7$, $\text{Na}_2\text{W}_4\text{O}_{13}$ and $\text{Na}_2\text{W}_6\text{O}_{19}$ was confirmed.

X-ray diffraction data of $\text{Na}_2\text{W}_2\text{O}_7$ and $\text{Na}_2\text{W}_6\text{O}_{19}$ are tabulated in Table 3. The x-ray diffraction patterns of Na_2WO_4 and $\text{Na}_2\text{W}_4\text{O}_{13}$ agreed very well with published data⁽¹²⁾⁽¹³⁾⁽¹⁴⁾. Table 4 gives a summary of the results obtained by x-ray diffraction for six compositions examined.

Table 3. Data on x-ray Diffraction Patterns of the Compounds $\text{Na}_2\text{W}_2\text{O}_7$ and $\text{Na}_2\text{W}_6\text{O}_{19}$.

$\text{Na}_2\text{W}_2\text{O}_7$				$\text{Na}_2\text{W}_6\text{O}_{19}$			
d	I	d	I	d	I	d	I
7.36	47	1.983	61	8.16	1	2.35	2
5.95	38	1.921	11	6.31	2	2.30	2
5.51	100	1.840	6	6.13	10	2.29	2
4.72	43	1.812	9	6.07	6	2.24	2
4.62	51	1.804	9	5.79	1	2.11	2
3.78	46	1.759	29	5.54	1	2.09	2
3.68	25	1.739	3	5.12	4	2.04	14
3.23	22	1.715	6	4.58	36	1.970	2
3.16	38	1.690	10	4.18	2	1.905	2
3.14	56	1.677	15	4.06	3	1.861	1
3.08	28	1.649	3	3.84	5	1.836	8
3.02	16	1.640	8	3.81	5	1.820	9
2.98	17	1.627	6	3.77	1	1.757	1
2.91	43	1.614	11	3.67	100	1.721	1
2.76	30	1.577	2	3.58	2	1.686	2
2.64	25	1.571	9	3.48	1	1.665	3
2.61	8	1.566	9	3.25	2	1.652	3
2.58	8	1.522	5	3.17	37	1.640	4
2.54	17	1.543	24	3.15	39	1.621	3
2.53	9	1.511	8	3.05	6	1.581	5
2.45	55	1.488	10	2.92	2	1.553	1
2.31	31	1.480	11	2.75	2	1.499	1
2.24	7	1.472	5	2.69	1	1.492	2
2.23	3	1.459	5	2.56	2	1.455	1
2.19	2	1.450	8	2.53	2		
2.16	13	1.445	6	2.51	4		
2.13	6	1.433	8	2.49	6		
2.09	4	1.430	8	2.46	3		
2.08	6	1.424	7	2.44	6		

Potassium Tungstate System

Six compositions $\text{K}_2\text{O} \cdot \text{WO}_3$, $\text{K}_2\text{O} \cdot 2\text{WO}_3$, $\text{K}_2\text{O} \cdot 3\text{WO}_3$, $\text{K}_2\text{O} \cdot 4\text{WO}_3$, $\text{K}_2\text{O} \cdot 6\text{WO}_3$ and $\text{K}_2\text{O} \cdot 10\text{WO}_3$ were examined. Also in this system, x-ray powder patterns of all the reheated samples agreed with those of corresponding sintered samples when the samples were heated long enough to reach equilibrium. X-ray diffraction patterns of all equilibrium samples (sintered or reheated) were composed of one set of diffraction lines, except for the composition $\text{K}_2\text{O} \cdot 10\text{WO}_3$, and each set could be ascribed to the compound K_2WO_4 , $\text{K}_2\text{W}_2\text{O}_7$, $\text{K}_2\text{W}_3\text{O}_{10}$, $\text{K}_2\text{W}_4\text{O}_{13}$ or $\text{K}_2\text{W}_6\text{O}_{19}$. A sintered or reheated sample of $\text{K}_2\text{O} \cdot 10\text{WO}_3$ showed the x-ray pattern, which is a mixture of the patterns ascribed to $\text{K}_2\text{W}_6\text{O}_{19}$ and WO_3 .

The x-ray diffraction data of $\text{K}_2\text{W}_6\text{O}_{19}$ is given in Table 5. X-ray data of other compounds agreed very well with those given by Gelsing *et al.*⁶⁾¹⁵⁾ Table 6 is a

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Table 4. Crystalline Compounds Present in the Samples of the System $\text{Na}_2\text{O} \cdot \text{WO}_3$ - WO_3 .

Composition	Sample	Heating		[Crystalline Compounds]	Remarks
		Temp.(°C)	time		
$\text{Na}_2\text{O} \cdot \text{WO}_3$	sintered	660	15 hr.	Na_2WO_4	
	solidified	800	10 min.	Na_2WO_4	
	reheated	660	15 hr.	Na_2WO_4	
$\text{Na}_2\text{O} \cdot 2\text{WO}_3$	sintered	660	15 hr.	$\text{Na}_2\text{W}_2\text{O}_7$	
	solidified	800	10 min.	$\text{Na}_2\text{W}_2\text{O}_7$	
	reheated	660	15 hr.	$\text{Na}_2\text{W}_2\text{O}_7$	
$\text{Na}_2\text{O} \cdot 3\text{WO}_3$	sintered	610	1 hr.	$\text{Na}_2\text{W}_4\text{O}_{13} + \text{WO}_3 + \text{Na}_2\text{W}_2\text{O}_7$	non-equil.
	sintered	660	40 hr.	$\text{Na}_2\text{W}_2\text{O}_7 + \text{Na}_2\text{W}_4\text{O}_{13}$	
	solidified	850	10 min.	$\text{Na}_2\text{W}_4\text{O}_{13} + \text{Na}_2\text{W}_2\text{O}_7$	non-equil.
	reheated	660	40 hr.	$\text{Na}_2\text{W}_2\text{O}_7 + \text{Na}_2\text{W}_4\text{O}_{13}$	
$\text{Na}_2\text{O} \cdot 4\text{WO}_3$	sintered	710	70 hr.	$\text{Na}_2\text{W}_4\text{O}_{13}$	
	solidified	1000	10 min.	$\text{Na}_2\text{W}_4\text{O}_{13} + \text{WO}_3$	non-equil.
	reheated	710	16 hr.	$\text{Na}_2\text{W}_4\text{O}_{13}$	
	reheated	710	100 hr.	$\text{Na}_2\text{W}_4\text{O}_{13}$	
$\text{Na}_2\text{O} \cdot 6\text{WO}_3$	sintered	610	1 hr.	$\text{WO}_3 + \text{Na}_2\text{W}_4\text{O}_{13} + \text{Na}_2\text{W}_6\text{O}_{19}$	non-equil.
	sintered	710	90 hr.	$\text{Na}_2\text{W}_6\text{O}_{19}$	
	solidified	1000	10 min.	$\text{Na}_2\text{W}_4\text{O}_{13} + \text{WO}_3 + (\text{Na}_2\text{W}_6\text{O}_{19})$	non-equil.
	reheated	710	16 hr.	$\text{Na}_2\text{W}_6\text{O}_{19} + \text{Na}_2\text{W}_4\text{O}_{13} + \text{WO}_3$	non-equil.
	reheated	710	100 hr.	$\text{Na}_2\text{W}_6\text{O}_{19}$	
$\text{Na}_2\text{O} \cdot 10\text{WO}_3$	sintered	610	2 hr.	$\text{WO}_3 + \text{Na}_2\text{W}_4\text{O}_{13} + \text{Na}_2\text{W}_6\text{O}_{19}$	non-equil.
	sintered	710	90 hr.	$\text{WO}_3 + \text{Na}_2\text{W}_6\text{O}_{19}$	
	solidified	1000	10 min.	$\text{WO}_3 + \text{Na}_2\text{W}_6\text{O}_{19}$	non-equil.
	reheated	710	100 hr.	$\text{WO}_3 + \text{Na}_2\text{W}_6\text{O}_{19}$	

Table 5. X-ray Diffraction Data of the Compound $\text{K}_2\text{W}_6\text{O}_{19}$.

d	I	d	I
6.37	64	2.03	5
5.55	1	1.969	1
5.06	1	1.943	1
4.22	1	1.912	6
3.81	39	1.848	4
3.80	16	1.826	18
3.50	1	1.760	1
3.35	4	1.690	3
3.27	20	1.649	11
3.16	100	1.646	11
2.98	4	1.635	11
2.64	10	1.591	4
2.44	30	1.582	8
2.40	2	1.463	7
2.12	5		

Table 6. Crystalline Compounds Present in the Samples of the System $\text{K}_2\text{O} \cdot \text{WO}_3$ - WO_3 .

Composition	Sample	Heating		Crystalline Compounds	Remarks
		Temp. ($^{\circ}\text{C}$)	Time		
$\text{K}_2\text{O} \cdot \text{WO}_3$	sintered	600	24 hr.	K_2WO_4	
	solidified	1000	10 min.	K_2WO_4	
	reheated	600	24 hr.	K_2WO_4	
$\text{K}_2\text{O} \cdot 2\text{WO}_3$	sintered	600	24 hr.	$\text{K}_2\text{W}_2\text{O}_7$	
	solidified	800	10 min.	$\text{X}^* + \text{K}_2\text{WO}_4$	non-equil.
	reheated	600	3 hr.	$\text{K}_2\text{W}_2\text{O}_7 + \text{K}_2\text{W}_3\text{O}_{10}$	non-equil.
	reheated	600	24 hr.	$\text{K}_2\text{W}_2\text{O}_7$	
$\text{K}_2\text{O} \cdot 3\text{WO}_3$	sintered	550	16 hr.	$\text{K}_2\text{W}_3\text{O}_{10} + \text{K}_2\text{W}_6\text{O}_{19} + \text{K}_2\text{WO}_4$	non-equil.
	sintered	600	24 hr.	$\text{K}_2\text{W}_3\text{O}_{10}$	
	solidified	1000	10 min.	$\text{K}_2\text{W}_3\text{O}_{10} + \text{K}_2\text{W}_6\text{O}_{19}$	non-equil.
	reheated	600	24 hr.	$\text{K}_2\text{W}_3\text{O}_{10}$	
$\text{K}_2\text{O} \cdot 4\text{WO}_3$	sintered	600	16 hr.	$\text{K}_2\text{W}_3\text{O}_{10} + \text{K}_2\text{W}_6\text{O}_{19}$	non-equil.
	sintered	710	10 hr.	$\text{K}_2\text{W}_4\text{O}_{13}$	
	solidified	1000	10 min.	$\text{K}_2\text{W}_6\text{O}_{19} + \text{K}_2\text{W}_3\text{O}_{10}$	non-equil.
	reheated	710	10 hr.	$\text{K}_2\text{W}_6\text{O}_{19} + \text{K}_2\text{W}_3\text{O}_{10}$	non-equil.
	reheated	710	100 hr.	$\text{K}_2\text{W}_4\text{O}_{13}$	
$\text{K}_2\text{O} \cdot 6\text{WO}_3$	sintered	600	2 hr.	$\text{K}_2\text{W}_6\text{O}_{19} + \text{WO}_3 + \text{K}_2\text{W}_3\text{O}_{10}$	non-equil.
	sintered	710	100 hr.	$\text{K}_2\text{W}_6\text{O}_{19}$	
	solidified	1000	10 min.	$\text{K}_2\text{W}_6\text{O}_{19}$	
	reheated	710	100 hr.	$\text{K}_2\text{W}_6\text{O}_{19}$	
$\text{K}_2\text{O} \cdot 10\text{WO}_3$	sintered	710	100 hr.	$\text{K}_2\text{W}_6\text{O}_{19} + \text{WO}_3$	
	solidified	1000	10 min.	$\text{K}_2\text{W}_6\text{O}_{19} + \text{WO}_3$	
	reheated	710	100 hr.	$\text{K}_2\text{W}_6\text{O}_{19} + \text{WO}_3$	

* X is one of the metastable compounds found by Gelsing *et al.*⁶⁾

summary of the results of x-ray analysis on the samples prepared in the three different ways.

IV. DISCUSSION

Lithium Tungstate System.

The present experiments demonstrated the existence of the stable compounds Li_2WO_4 , $\text{Li}_2\text{W}_2\text{O}_7$ and $\text{Li}_2\text{W}_4\text{O}_{13}$, in agreement with the work of Hoermann¹⁶⁾. More recently, Spier⁴⁾ and Spitsyn *et al.*⁷⁾ could not find the compound $\text{Li}_2\text{W}_4\text{O}_{13}$, apparently because their samples were prepared from solidified melts. Solidified melts of $\text{Li}_2\text{O} \cdot 4\text{WO}_3$ prepared for the present study produced x-ray pattern similar to that of Spier, while equilibrium (sintered or reheated) samples showed a characteristic pattern which cannot be constructed from lines of $\text{Li}_2\text{W}_2\text{O}_7$ and WO_3 . Further, x-ray patterns of the equilibrium samples of $\text{Li}_2\text{O} \cdot 3\text{WO}_3$ and $\text{Li}_2\text{O} \cdot 6\text{WO}_3$ consisted of the lines characteristic of the equilibrium samples of $\text{Li}_2\text{O} \cdot 4\text{WO}_3$ composition plus the lines of $\text{Li}_2\text{W}_2\text{O}_7$ or WO_3 , respectively. These results clearly indicate the existence of the compound $\text{Li}_2\text{W}_4\text{O}_{13}$.

Finally, it may be concluded from the present experiments that $\text{Li}_2\text{W}_4\text{O}_{13}$ is the most acidic compound in the Li_2O - WO_3 system. The equilibrium samples of

more acidic compositions $\text{Li}_2\text{O} \cdot 6\text{WO}_3$ and $\text{Li}_2\text{O} \cdot 10 \text{WO}_3$ consisted of $\text{Li}_2\text{W}_4\text{O}_{13}$ and WO_3 .

Sodium Tungstate System

The stable compounds are Na_2WO_4 , $\text{Na}_2\text{W}_2\text{O}_7$, $\text{Na}_2\text{W}_4\text{O}_{13}$ and $\text{Na}_2\text{W}_6\text{O}_{19}$. The existence of the three compounds other than $\text{Na}_2\text{W}_6\text{O}_{19}$ was demonstrated by Hoermann¹⁷⁾, Caillet¹⁵⁾, and Gelsing *et al.*⁹⁾, while Spier⁴⁾ did not find $\text{Na}_2\text{W}_4\text{O}_{13}$, apparently because he used solidified melts for x-ray examination. Caillet prepared the sample by solid state reaction, and our x-ray data on $\text{Na}_2\text{W}_4\text{O}_{13}$ agreed quite well with his data.

The most acidic sodium tungstate compound found in these experiments is $\text{Na}_2\text{W}_6\text{O}_{19}$. Caillet proposed a WO_3 -rich $\text{Na}_2\text{W}_4\text{O}_{13}$ solid solution as the most acidic sodium tungstate phase, probably because his sintering temperature was high enough to have caused a partial melting of his samples. In fact, our solidified melt (non-equilibrium) of $\text{Na}_2\text{O} \cdot 6\text{WO}_3$ consisted mainly of $\text{Na}_2\text{W}_4\text{O}_{13}$ and WO_3 with a small amount of $\text{Na}_2\text{W}_6\text{O}_{19}$.

Potassium Tungstate System

The present experiments demonstrated the compound $\text{K}_2\text{W}_6\text{O}_{19}$ and also confirmed the existence of K_2WO_4 , $\text{K}_2\text{W}_2\text{O}_7$, $\text{K}_2\text{W}_3\text{O}_{10}$ and $\text{K}_2\text{W}_4\text{O}_{13}$, in agreement with Gelsing *et al.*⁶⁾ The existence of $\text{K}_2\text{W}_6\text{O}_{19}$ disagrees with Caillet's conclusion¹⁴⁾. He asserted that the x-ray diffraction lines of the compound $\text{K}_2\text{W}_4\text{O}_{13}$ persists up to the composition of $\text{K}_2\text{O} \cdot 8\text{WO}_3$. This seems to be a misunderstanding caused by his experimental method. He prepared the samples by sintering at 750°C , which may have been too high to avoid partial melting of the samples. As seen in Table 6, the solidified melts (non-equilibrium) of $\text{K}_2\text{O} \cdot 4\text{WO}_3$, $\text{K}_2\text{O} \cdot 6\text{WO}_3$ and $\text{K}_2\text{O} \cdot 10\text{WO}_3$ show x-ray diffraction lines of compound $\text{K}_2\text{W}_6\text{O}_{19}$ as ascribed by us, instead of the lines of our $\text{K}_2\text{W}_4\text{O}_{13}$. Further, diffraction lines of " $\text{K}_2\text{W}_4\text{O}_{13}$ " given by Caillet agree well with the x-ray data of our " $\text{K}_2\text{W}_6\text{O}_{19}$ ", but not with the data of our " $\text{K}_2\text{W}_4\text{O}_{13}$ ". It can be said that Caillet mistook $\text{K}_2\text{W}_6\text{O}_{19}$ for $\text{K}_2\text{W}_4\text{O}_{13}$. Gelsing *et al.*¹⁹⁾ suggested the existence of a compound more acidic than $\text{K}_2\text{W}_4\text{O}_{13}$. This compound is shown here to be $\text{K}_2\text{W}_6\text{O}_{19}$.

This work was done at Rensselaer Polytechnic Institute, Troy, New York during the author's leave of absence from Kyoto University. The author expresses his sincere thanks to Dr. J.D. Mackenzie and Dr. C.B. Willingham, Jr. for their helpful discussions. Financial support by PPG Industries is greatly appreciated.

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