

*Li<sub>2</sub>Zr(WO<sub>4</sub>)<sub>3</sub>, a wolframite-type compound*By LUKE L. Y. CHANG, B.S., Ph.D.<sup>1</sup>Department of Geological Sciences, Cornell University,  
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[Taken as read 8 June 1967]

*Summary.* The compound Li<sub>2</sub>Zr(WO<sub>4</sub>)<sub>3</sub> has been synthesized. It has the monoclinic wolframite-type structure with cell dimensions  $a$  4.78 Å,  $b$  5.70 Å,  $c$  4.96 Å, and  $\beta$  92° 10'. The univalent and tetravalent cations are randomly arranged in the divalent cation sites in the wolframite-type lattice.

**T**UNGSTATES of the  $R^{2+}WO_4$ -type generally belong to one of two structural groups depending on the sizes of the divalent cation they contain. Cations larger than calcium form the scheelite-type compound, whereas smaller divalent cations give rise to a tungstate of wolframite structure. Zambonini (1920) and Beintema (1935) indicated that the divalent cation in the scheelite-type tungstates could be replaced by a trivalent cation with suitable size to form a defect scheelite. Sillén and Sundvall (1943) prepared a series of tungstates of the  $R^+R^{3+}(WO_4)_2$ -type, which has the scheelite structure with random distribution of univalent and trivalent cations.

In recent studies, two tungstates, Sm<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> and Zr(WO<sub>4</sub>)<sub>2</sub>, were found to be stable along with several phases in the systems Sm<sub>2</sub>O<sub>3</sub>-WO<sub>3</sub> (Chang, Scroger, and Phillips, 1966) and ZrO<sub>2</sub>-WO<sub>3</sub> (Chang, Scroger, and Phillips, 1967) respectively. By introducing sodium into the samarium tungstate, a scheelite-type compound, NaSm(WO<sub>4</sub>)<sub>2</sub>, was produced like those prepared by Sillén and Sundvall (1943). This note describes a wolframite-type compound derived from the cubic Zr(WO<sub>4</sub>)<sub>2</sub>.

Samples of the compositions, Li<sub>2</sub>Zr(WO<sub>4</sub>)<sub>3</sub>, Na<sub>2</sub>Zr(WO<sub>4</sub>)<sub>3</sub>, and K<sub>2</sub>Zr(WO<sub>4</sub>)<sub>3</sub>, were prepared from reagent grade alkali carbonates, zirconium dioxide, and tungsten anhydride. Heat treatments were conducted at 750° C in platinum crucibles in air.

The compound, Li<sub>2</sub>Zr(WO<sub>4</sub>)<sub>3</sub>, has a wolframite-type structure as can be seen from X-ray diffraction data listed in table I together with those of MnWO<sub>4</sub> for comparison. The absence of any superlattice reflections indicates that this compound has both the univalent and the tetravalent

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cations arranged in a random way through the divalent cation sites of a wolframite-type lattice. Cell dimensions calculated from measurements made on 220, 022, 030, and 211 are:  $a$  4.78 Å,  $b$  5.70 Å,  $c$  4.96 Å, and  $\beta$  92° 10'. This compound melts at 890° ± 5° C and exhibits no phase transition.

TABLE I. X-ray Diffraction Data for Li<sub>2</sub>Zr(WO<sub>4</sub>)<sub>3</sub> and MnWO<sub>4</sub>

Li <sub>2</sub> Zr(WO <sub>4</sub> ) <sub>3</sub>			MnWO <sub>4</sub> *		Li <sub>2</sub> Zr(WO <sub>4</sub> ) <sub>3</sub>			MnWO <sub>4</sub> *	
$d$	$R_I$	$hkl$	$d$	$R_I$	$d$	$R_I$	$hkl$	$d$	$R_I$
5.67 Å	9	010	5.76 Å	22	2.20 Å	16	$\bar{1}02$	2.237 Å	16
4.78	100	100	4.84	63	2.17	34	121	2.209	26
3.74	45	011	3.78	59	2.04	11	$\bar{1}12$	2.087	7
3.65	43	110	3.70	56	2.02	7	112	2.057	11
2.99	80	$\bar{1}10$	2.996	100	2.00	2	$\bar{2}11$	2.051	12
2.90	90	111	2.954	95	1.987	16	211	2.021	10
2.85	14	020	2.880	29	1.901	5	030	1.9205	5
2.48	30	{002}	2.497	54	1.871	7	022	1.8871	16
		{021}			1.832	18	220	1.8507	16
2.45	14	120	2.474	9	1.763	27	130	1.7843	26
2.39	34	200	2.416	19					

\* H. E. Swanson, M. C. Monis, R. P. Stinchfield, and E. H. Evan, 1963, Nat. Bur. Stand. Monograph 25, Sec. 2, p. 24.

The X-ray diffraction analyses made on samples of Na<sub>2</sub>Zr(WO<sub>4</sub>)<sub>3</sub> and K<sub>2</sub>Zr(WO<sub>4</sub>)<sub>3</sub> reveal no evidence to suggest any structural relationship of these compounds to either the wolframite or the scheelite type. It is evident that only in the compound Li<sub>2</sub>Zr(WO<sub>4</sub>)<sub>3</sub> have both univalent and tetravalent cations sizes very well within the range required to form one of the two structural types under consideration.

Like almost all compounds containing zirconium, hafnium can replace zirconium and form a similar compound. In this case, the wolframite-type Li<sub>2</sub>Hf(WO<sub>4</sub>)<sub>3</sub> was obtained.

*Acknowledgement.* The author wishes to thank Dr. R. I. Harker for reading the manuscript.

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[Manuscript received 20 February 1967]