

New modification of $3\text{ZnO}\cdot\text{Nb}_2\text{O}_5$

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Phase relations in the binary system $\text{ZnO}\text{-Nb}_2\text{O}_5$ were studied by Pollard [1] and by Dayal [2, 3]. The existence of the compounds $3\text{ZnO}\cdot\text{Nb}_2\text{O}_5$, α - and β - $\text{ZnO}\cdot\text{Nb}_2\text{O}_5$, and $2\text{ZnO}\cdot 17\text{Nb}_2\text{O}_5$ was established. The compounds $3\text{ZnO}\cdot\text{Nb}_2\text{O}_5$ and β - $\text{ZnO}\cdot\text{Nb}_2\text{O}_5$ were found to melt congruently at 1312 and 1405 °C, respectively, whereas $2\text{ZnO}\cdot 17\text{Nb}_2\text{O}_5$ melted incongruently to yield liquid plus $\text{H}\cdot\text{Nb}_2\text{O}_5$ at 1415 °C. The $\alpha \rightleftharpoons \beta$ phase transformation in $\text{ZnO}\cdot\text{Nb}_2\text{O}_5$ was observed at 1350 °C. The formation of the compounds by solid-state reaction has been reported by various workers [1-8]. Another compound $7\text{ZnO}\cdot\text{Nb}_2\text{O}_5$ having a spinel structure was prepared by Harrison and Delgrosso [4]; pellets containing ZnO and Nb_2O_5 in a molar ratio 7 : 1, when heated slowly from 1400 to 2200 °F (760-1200 °C) in a relatively still air atmosphere, gave the spinel $7\text{ZnO}\cdot\text{Nb}_2\text{O}_5$, whereas rapid heating to 2200 °C (1200 °C) did not lead to spinel formation. In our study on the formation of $3\text{ZnO}\cdot\text{Nb}_2\text{O}_5$ from an amorphous material prepared by the hydrolysis of zinc and niobium double alkoxides, a new modification of $3\text{ZnO}\cdot\text{Nb}_2\text{O}_5$, being metastable, was formed at low temperatures. This letter deals with the formation and transformation of alkoxy-derived $3\text{ZnO}\cdot\text{Nb}_2\text{O}_5$.

Niobium isopropoxide, $\text{Nb}(\text{OC}_3\text{H}_7)_5$ (99.999% pure, Kōjundo Kagaku Kenkyūjo, Saitama, Japan), was used. Anhydrous zinc chloride, ZnCl_2 (99.99% pure), was dissolved in ethanol. As-received sodium was cleaned by removing the superficial crust; a known weight was dissolved in 2-propanol. The mixed solution (in the molar ratio $\text{Zn}^{2+}:\text{Nb}^{5+} = 3:2$) was added, with stirring, to the stoichiometric quantity of sodium isopropoxide containing 2-propanol. Under reflux, precipitates of zinc niobium alkoxide and sodium chloride were obtained. Zinc niobium alkoxide with sodium chloride was hydrolysed by adding aqueous ammonia (28 wt %) at room temperature. The temperature was slowly increased to 70 °C while the resultant suspension was stirred; sodium chloride was dissolved in water at this stage. The hydrolysis product was separated from the suspension by filtration, washed in hot water until chloride ions were no longer detectable, and dried at 120 °C under reduced pressure. The powder thus obtained is termed the "starting powder". X-ray diffraction (XRD) analysis using $\text{CuK}\alpha$ radiation) showed that the starting powder was amorphous. The average particle size of the starting powder, determined by electron microscopy, was about 70 nm.

Thermogravimetry (TG) and differential thermal analysis (DTA) were conducted in air at a rate of

10 °C min⁻¹; α -alumina was used as the reference for the DTA. TG examination showed a weight decrease of 19.6% to 420 °C, attributed to the release of ammonia, organic residues from the parent alcohol, absorbed water and hydrated water [9]. The DTA curve above 420 °C reveals two exothermic peaks at 620-660 °C and 700-750 °C (Fig. 1). As will be described, the first sharp exothermic peak was found to result from the crystallization of the new modification of $3\text{ZnO}\cdot\text{Nb}_2\text{O}_5$ and the second exothermic peak to the new modification transforming to the known phase. No peak was detected in cooling.

Specimens heated at a rate of 10 °C min⁻¹ were examined by high-temperature XRD using Ni-filtered $\text{CuK}\alpha$ radiation. The starting powder, being amorphous, did not exhibit any significant change in structure up to the temperature of the first exothermic peak. The specimen heated at 660 °C after the first exothermic peak gave an XRD pattern resulting from a hitherto undescribed modification of $3\text{ZnO}\cdot\text{Nb}_2\text{O}_5$. The known $3\text{ZnO}\cdot\text{Nb}_2\text{O}_5$ phase was observed in the specimen heated at temperatures above the second exothermic peak. No zinc niobium oxides other than $3\text{ZnO}\cdot\text{Nb}_2\text{O}_5$ and no other species were recognized throughout the heating process. During cooling, the known phase did not transform to the new modification. Clearly, the new modification must be metastable. Table I shows

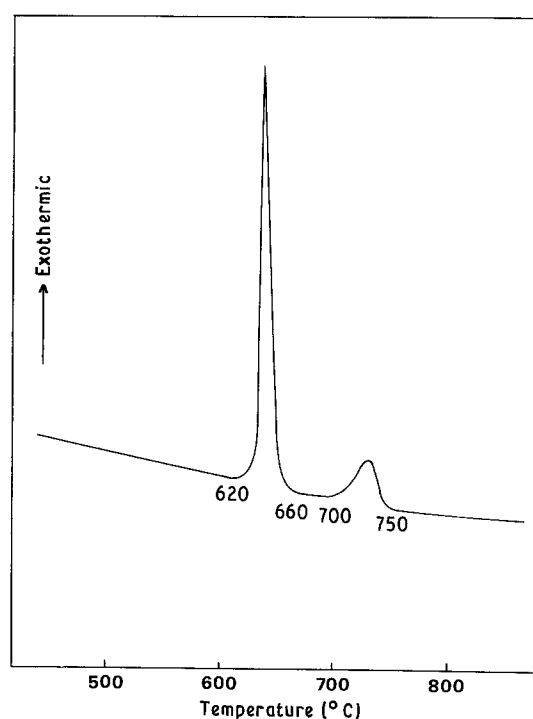


Figure 1 DTA curve for the starting powder.

TABLE I XRD data for the new modification of 3ZnO·Nb₂O₅

d_{obs} (nm)	d_{calc} (nm)	hkl	I/I_0
0.575	0.576	111	25
0.435	0.438	011	5
0.419	0.420	$\bar{2}01$	20
0.393	0.393	$\bar{1}02$	25
0.376	0.378	201	45
0.358	0.358	102	10
0.326	0.326	$\bar{2}11$	10
0.322	0.322	012	15
0.303	0.303	300	35
0.2961	0.2962	$\bar{3}01$	100
0.2946	0.2947	112	95
0.2878	0.2878	202	50
0.2742	0.2742	003	60
0.2735	0.2735	301	80
0.2615	0.2614	310	60
0.2540	0.2540	103	25
0.2469	0.2469	021	35
0.2407	0.2407	$\bar{1}13$	25
0.2360	0.2360	$\bar{1}21$	10
0.2320	0.2320	$\bar{3}12$	10
0.2280	0.2280	113	10
0.2229	0.2229	$\bar{2}03$	15
0.2203	0.2203	$\bar{2}21$	20
0.2190	0.2190	022	5
0.2107	0.2107	$\bar{3}12$	15
0.2100	0.2100	402	10
0.2098	0.2098	122	10
0.2047	0.2047	$\bar{2}13$	5
0.2026	0.2026	$\bar{2}22$	5
0.2001	0.2001	$\bar{3}13$	5
0.1924	0.1924	$\bar{2}22$	10
0.1915	0.1915	$\bar{1}14$	15
0.1892	0.1892	402	10
0.1838	0.1838	$\bar{2}14$	15

Monoclinic: $a = 0.9153$ nm, $b = 0.5176$ nm, $c = 0.8288$ nm and $\beta = 97.06^\circ$.

the X-ray data for the new modification at room temperature. Interplanar spacings were measured with the aid of an internal standard of low-temperature quartz, and unit-cell values were determined by a least-squares refinement. The diffraction lines were indexed as a monoclinic unit cell with $a = 0.9153$ nm, $b = 0.5176$ nm, $c = 0.8288$ nm and $\beta = 97.06^\circ$. The X-ray data for the known phase at room temperature are presented in Table II and compared with those previously reported. According to the data of Harrison and Delgrosso [4], 3ZnO·Nb₂O₅ is classified to be a tetragonal system with $a = 1.223$ nm and $c = 0.637$ nm. On the other hand, Brusset *et al.* [8] described the crystal structure as having an orthorhombic symmetry with $a = 0.5195$ nm, $b = 1.9005$ nm and $c = 0.5897$ nm. The present data were in agreement with those of Brusset *et al.* [8], although the strongest line was different in two patterns. The lattice parameters were estimated as an orthorhombic unit cell with $a = 0.5189$ nm, $b = 1.8987$ nm and $c = 0.5895$ nm.

References

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TABLE II XRD data for 3ZnO·Nb₂O₅

3ZnO·Nb ₂ O ₅ ^a				3ZnO·Nb ₂ O ₅ ^b [4]		3ZnO·Nb ₂ O ₅ ^c [8]	
d_{obs} (nm)	d_{calc} (nm)	hkl	I/I_0	d (nm)	I/I_0	d (nm)	I/I_0
0.563	0.563	011	5	0.5639	3	0.563	6
0.473	0.475	040	5			0.475	7
0.433	0.431	031	10	0.4319	10	0.431	29
0.383	0.382	111	10	0.3862	9	0.382	9
0.332	0.332	132	25	0.3302	24	0.332	18
0.320	0.319	051	40	0.3180	40	0.319	100
0.316	0.316	060	15			0.317	18
0.2948	0.2948	002	15			0.2948	27
0.2719	0.2719	151	100	0.2732	80	0.2721	84
0.2595	0.2595	200	45	0.2623	50	0.2594	14
0.2563	0.2563	102	55	0.2561	60	0.2564	30
0.2464	0.2464	071	5			0.2466	12
0.2373	0.2373	080	5			0.2376	18
0.2277	0.2277	240	5	0.2281	6	0.2279	3
0.2255	0.2255	142	10	0.2268	15	0.2257	7
0.2226	0.2226	171	10			0.2228	8
0.2013	0.2013	251	10	0.2009	25	0.2015	9
0.1955	0.1955	013	10	0.1939	12	0.19552	4
0.1899	0.1899	$\bar{2}61, 0\bar{1}00$	5	0.1902	5	0.19005	18
0.1877	0.1877	033	5	0.1880	3	0.18773	3
0.1855	0.1855	191	5			0.18567	6
				0.1749	100		

^a Orthorhombic: $a = 0.1589$ nm, $b = 1.8987$ nm and $c = 0.5895$ nm.

^b Tetragonal: $a = 1.223$ nm and $c = 0.637$ nm.

^c Orthorhombic: $a = 0.5195$ nm, $b = 1.9005$ nm and $c = 0.5897$.

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