

Reaction Study and Phase Formation in Bi₂O₃-ZnO-Nb₂O₅ Ternary System.

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ABSTRACT

The formation of two structurally related phases; cubic pyrochlore and monoclinic zirconolite in Bi₂O₃-ZnO-Nb₂O₅ (BZN) ternary system was investigated. Phase pure Bi₄Zn_{4/3}Nb_{8/3}O₁₄ synthesized via conventional solid state methods at 950°C was refined and fully indexed with space group C2/c; lattice parameters, a = 13.1109(3) Å, b = 7.6764(2) Å, c = 12.1528(2) Å and α = γ = 90° and β = 101.33°, respectively. Reaction study revealed that Bi₅Nb₃O₁₅ and BiNbO₄ phases are two important precursors that react with ZnO at higher temperatures during phase formation. The pyrochlore does not form at the conventionally predicted composition Bi₄Zn_{4/3}Nb_{8/3}O₁₄, which falls in the zirconolite region. Instead, cubic pyrochlore forms at substantially lower Bi concentrations in BZN system. The two interrelated areas, a trapezoidal cubic pyrochlore subsolidus, and a rectangular shaped monoclinic zirconolite subsolidus serve to confirm the data consistency over various phase assemblages and compatibility in the phase diagram.

(Keywords: diagram, pyrochlores, monoclinic zirconolite, subsolidus)

INTRODUCTION

A phase diagram is a pictorial representation of the thermodynamic equilibria among phases present in a system. It is summarized in a graphical form of temperature (occasionally pressure) against composition over certain phases or mixtures of phases that exist under conditions of no macroscopic changes with time. The phase diagram provides an indispensable

source of information to scientists, giving further insights into phase compatibility, processing control, physical, and chemical properties of compositions studied. However, no single phase diagram is ever completely finished as it tends to change over time with improvement of data accuracy. In practice, the experimental phase diagram is a compromise between the constraints imposed by the phase rule and the observed experimental data. In this case, the prejudices of experimentalists, the sophistication of instrumentation, and the type of accumulated experimental data should be taken into consideration. Nonetheless, any real information is always better than none at all [1-2].

In addition to the cubic pyrochlore in Bismuth Zinc Niobates (BZN) ternary system, it has been reported that a second anion-deficient fluorite phase, of probable stoichiometry Bi₄Zn_{4/3}Nb_{8/3}O₁₄ exists [3-7]. However, there is uncertainty in the literature as to its precise crystal symmetry and stoichiometry. It has been described as an orthorhombic phase by Wang *et al.* (1997), but recent studies indicate it has a monoclinic unit cell, space group C2/c, a = 13.1037(9) Å, b = 7.1635(3) Å, c = 12.1584(6) Å, β = 101.318(5), with a zirconolite-like crystal structure [5-6]. Its crystal structure, whilst like pyrochlore, can be described as an anion-deficient fluorite, features a distinct type of cation arrangement on the metal sites and cannot be derived from distorted pyrochlore structure. There is also evidence that the phase may have variable composition, by forming solid solutions in the direction of excess ZnO. The stoichiometry of phase in monoclinic zirconolite is usually given as Bi₄Zn_{4/3}Nb_{8/3}O₁₄, whilst, a deficient Bi_{1.9}(Zn_{1/3}Nb_{2/3})₂O_{6.85} phase has been proposed recently [8].

Given the unexpected complexity of phase formation which is mentioned above, a study of the synthesis, reaction pathway, solid solution mechanisms, structure, and stoichiometry of related phases in the BZN system was carried out. This is particularly important given the interest in commercial applications of BZN materials and the inconsistencies and discrepancies in the literature over the characterization of the BZN phases [9-13]. Work since the 1990's has clarified many of the fundamental aspects of the materials. However there are still some remaining problems; for instance, electrical properties of BZN samples have often been reported on multiphase samples as detailed knowledge of the structure-property relations for the individual phases is unavailable, but is especially important if these phases have variable compositions and the information is essential in order to control and optimize properties. Hence, it is necessary to construct a complete phase diagram of the BZN ternary system including phases of different crystal symmetries.

EXPERIMENTAL PROCEDURE

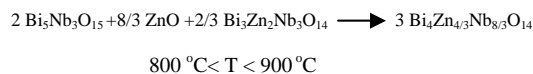
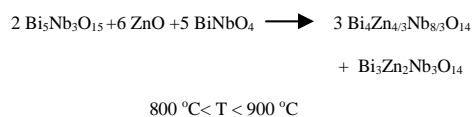
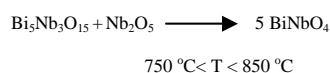
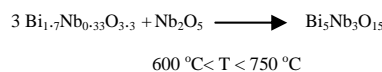
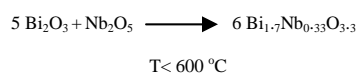
High purity oxides Bi₂O₃ (Alfa Aesar, 99.99%), ZnO (Alfa Aesar, 99.99%), and Nb₂O₅ (Alfa Aesar, 99.9%) were used as starting materials in the sample preparation. All oxide powders were treated at different temperatures: Bi₂O₃ was pre-heated at 300°C and the latter were at 600°C for 3 hours, respectively. Stoichiometric quantities of the oxides were weighted and mixed with acetone in an agate mortar. The resulting powder was transferred into a gold boat and pre-fired at 700°C for 24 hours in a muffle furnace. Subsequently, the mixture was fired at temperatures of 800°C and 950°C for 24 hours with intermediate regrinding. Samples were analyzed by X-ray powder diffraction using an automated Shimadzu diffractometer XRD 6000 in 2θ range of 10-70° at 2°/min. Selected samples were analyzed at a scan rate of 0.1°/min and the data were used for cell parameter refinement using Chekcell software. The analyzed data were used for the construction of phase diagram using Microcal Origin 60.

RESULTS AND DISCUSSION

The components of Bi₂O₃-ZnO-Nb₂O₅ system are two unreactive oxides, ZnO and Nb₂O₅, together

with a volatile and reactive oxide Bi₂O₃. Therefore, it is necessary to find appropriate heat treatment conditions such that the temperature is suitable for the ZnO and Nb₂O₅ to react, but not too high so that volatilization of Bi₂O₃ occurs before it can be combined chemically. The samples were heated in a step-wise cycle, with lower temperature stages being used to ensure initial reaction of the Bi₂O₃. The formation mechanism of Bi₄Zn_{4/3}Nb_{8/3}O₁₄ at different temperatures was investigated and shown in Figure 1.

The XRD patterns indicate that Bi_{1.7}Nb_{0.3}O_{3.3} and Bi₅Nb₃O₁₅ are formed from a reaction between Bi₂O₃ and Nb₂O₅ below 600°C. With increasing reaction temperature, Bi_{1.7}Nb_{0.3}O_{3.3} gradually disappears. Bi₅Nb₃O₁₅ is more stable and reacts with Nb₂O₅ to form BiNbO₄ at temperatures above 750°C. Both Bi₅Nb₃O₁₅ and BiNbO₄ act as important precursors in forming monoclinic zirconolite phase. On the other hand, ZnO is only involved in chemical reaction above 700°C. Finally, the phase pure monoclinic zirconolite phase of nominal composition Bi₄Zn_{4/3}Nb_{8/3}O₁₄ is formed at 950°C. The phase formation mechanism agrees reasonably with that reported by Chen *et al.* (2003) where it is noted that Bi₅Nb₃O₁₅ and BiNbO₄ are the important precursors that reacted with ZnO at temperatures above 800°C in the formation of monoclinic zirconolite phase [14].



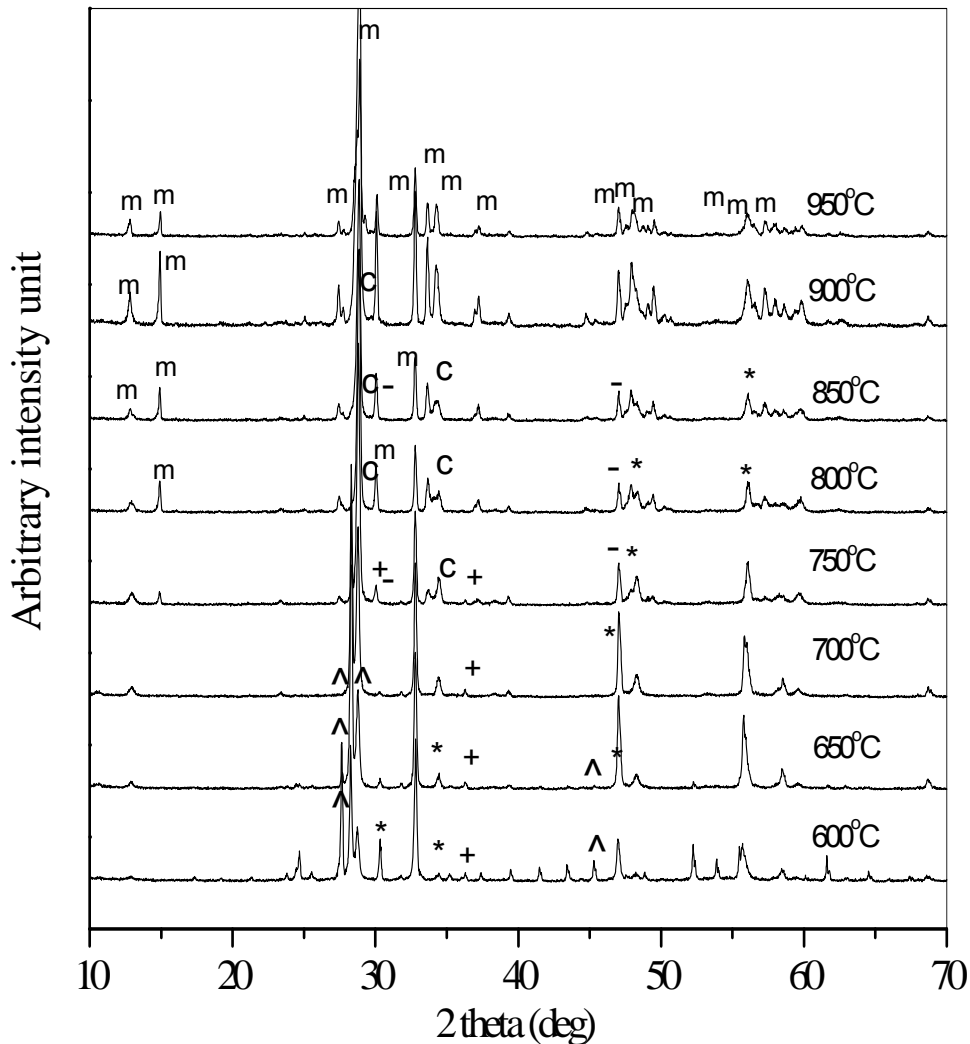


Figure 1: XRD Diffraction Patterns for $\text{Bi}_4\text{Zn}_{4/3}\text{Nb}_{8/3}\text{O}_{14}$ Evolution with Synthesis Temperature $m = \text{Bi}_4\text{Zn}_{4/3}\text{Nb}_{8/3}\text{O}_{14}$, $\wedge = \text{Bi}_{1.7}\text{Nb}_{0.33}\text{O}_{3.3}$, $* = \text{Bi}_5\text{Nb}_3\text{O}_{15}$, $+ = \text{ZnO}$, $- = \text{BiNbO}_4$, $C = \text{Cubic Pyrochlore}$.

In a related study, the formation of orthorhombic pyrochlore was proposed somewhat related to the $6s^2$ lone pair electrons of Bi ions. If A sites of the pyrochlore structure are occupied by Bi ions only, the coupling among $6s^2$ lone pairs may cause distortion of the cell. When a certain number of Zn ions enter the A sites, the coupling among Bi ions is broken, and a cubic pyrochlore phase occurs. When the number of Zn ions in A sites gets smaller, the coupling of $6s^2$ lone pair electrons of Bi has stronger influence at lower temperature. In addition, the coupling effect becomes weaker with

increasing firing temperature. Therefore, orthorhombic pyrochlore transforms to cubic pyrochlore. The higher the ratio of Zn:Bi in A sites, the lower the phase transformation temperature from orthorhombic pyrochlore to cubic pyrochlore. The coupling of $6s^2$ lone pair electrons of Bi ions could also be affected by the character of B site ions [3].

Apart from direct solid state reaction, monoclinic zirconolite phase was synthesized via the intermediate columbite (ZnNb_2O_6) precursor at

950°C. It was reported with the intermediate precursor method one could avoid formation of recalcitrant bismuth niobates and minimize volatility of ZnO [6]. However, experimental results show no significant difference between direct synthesis and intermediate columbite precursor method (Figure 2). No change in XRD patterns (i.e. peak shifting or broadening/narrowing) is observed. The samples are refined and indexed using Chekcell software. The observed and calculated 2 theta values are shown in Table 1.

XRD data of $\text{Bi}_4\text{Zn}_{4/3}\text{Nb}_{8/3}\text{O}_{14}$ can be fully indexed on a monoclinic cell, space group C2/c with $a = 13.1109(3) \text{ \AA}$, $b = 7.6764(2) \text{ \AA}$, $c = 12.1528(2) \text{ \AA}$ and $\alpha = \gamma = 90^\circ$ and $\beta = 101.33^\circ$. This agrees

reasonably with the cell constant of $a = 13.1037(9) \text{ \AA}$, $b = 7.1635(3) \text{ \AA}$, $c = 12.1584(6) \text{ \AA}$, $\beta = 101.318(5)$ reported by Levin *et al.* (2002) using neutron diffraction studies [6]. In this study, the standard heat treatment for the monoclinic zirconolite phase and compositions around is finalized at sintering temperature of 950°C (direct solid state reaction) based on the formation and reaction pathway study, together with repeating heat treatment for various durations at temperatures ranging from 900 – 1050 °C.

The results of phases prepared in the region around stoichiometric monoclinic zirconolite phase and other compositions in overall BZN phase diagram are summarized in Table 2.

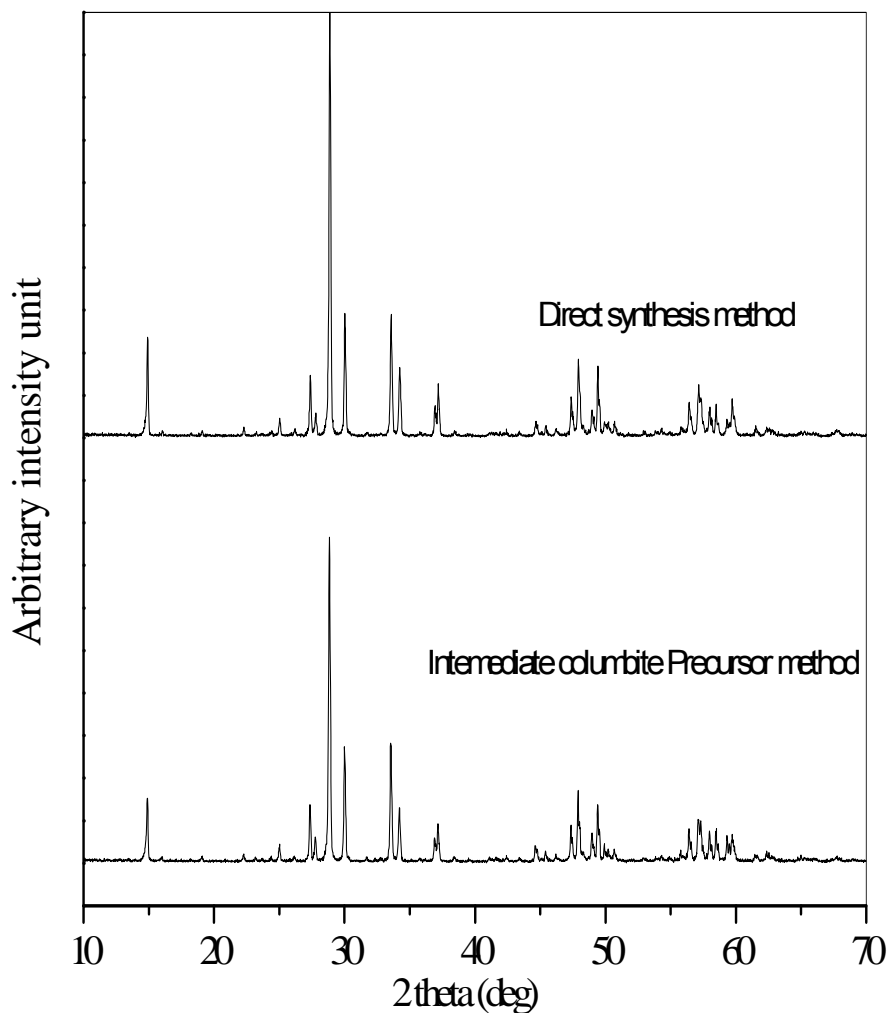


Figure 2: XRD Diffraction Patterns of $\text{Bi}_4\text{Zn}_{4/3}\text{Nb}_{8/3}\text{O}_{14}$ with Different Synthesis Methods.

Table 1: First 25 lines of the Indexed X-ray Diffraction Pattern for Monoclinic Zirconolite $\text{Bi}_4\text{Zn}_{4/3}\text{Nb}_{8/3}\text{O}_{14}$ with $a = 13.1109(3) \text{ \AA}$, $b = 7.6764(2) \text{ \AA}$, $c = 12.1528(2) \text{ \AA}$ and $\alpha = \gamma = 90^\circ$ and $\beta = 101.33^\circ$.

h	k	l	2θ(Observed)	2θ(Calculated)	Δ (2θ)
0	0	2	14.869	14.869	0.000
-1	-1	3	24.990	24.981	0.009
-2	2	1	27.350	27.342	0.008
4	0	0	27.767	27.758	0.009
2	2	1	28.837	28.827	0.010
0	0	4	30.000	29.995	0.005
-2	-2	3	33.545	33.539	0.006
4	0	2	34.198	34.203	-0.005
-4	0	4	36.899	36.891	0.008
-2	-2	5	44.633	44.621	0.012
4	0	4	45.396	45.396	0.000
0	4	0	47.361	47.369	-0.008
-6	2	1	47.904	47.908	-0.004
-3	-3	4	48.965	48.975	-0.010
2	2	5	49.396	49.399	-0.003
0	4	2	49.912	49.925	-0.013
-6	2	3	50.209	50.212	-0.003
6	2	1	50.674	50.673	0.001
-4	4	2	56.415	56.419	-0.004
-6	2	5	57.126	57.139	-0.013
8	0	0	57.34	57.336	0.004
6	2	3	57.975	57.982	-0.007
-2	-2	7	58.472	58.462	0.010
4	0	6	59.306	59.31	-0.004
4	4	2	59.737	59.713	0.024
0	0	8	62.328	62.338	-0.010

Table 2: Results of Phases Present in Compositions Prepared in the Bi₂O₃-ZnO-Nb₂O₅ Ternary System.

No	Cation Ratio			Phases present after 48h at 950°C	No	Cation Ratio			Phases present after 48h at 950°C
	Bi:	Zn:	Nb:			Bi:	Zn:	Nb:	
2	37.50	25.00	37.50	ZnO, P	133	46.80	19.00	34.20	Z, P
4	38.50	25.00	36.50	ZnO, P	135	42.60	21.40	36.00	Z, P
28	38.00	25.00	37.00	ZnO, P	136	43.60	20.80	35.60	Z, P
29	36.00	25.00	39.00	ZnNb ₂ O ₆ , P	137	47.00	20.00	33.00	ZnO, Z, P
6	35.00	25.00	40.00	ZnNb ₂ O ₆ , P	138	46.00	17.00	37.00	Bi ₅ Nb ₃ O ₁₅ , Z, P
7	34.00	25.00	41.00	ZnNb ₂ O ₆ , P	139	48.00	16.00	36.00	Bi ₅ Nb ₃ O ₁₅ , Z, P
8	32.00	27.00	41.00	Zn ₃ Nb ₂ O ₈ , ZnNb ₂ O ₆ , P	140	48.60	20.00	31.40	Z, P
9	32.00	30.00	38.00	Zn ₃ Nb ₂ O ₈ , ZnO, P	141	48.00	20.00	32.00	Z, P
10	32.00	32.00	36.00	Zn ₃ Nb ₂ O ₈ , ZnO, P	142	48.00	21.00	31.00	Z, P
11	32.00	34.00	34.00	Zn ₃ Nb ₂ O ₈ , ZnO, P	144	46.00	23.00	31.00	Z, P
12	32.00	36.00	32.00	ZnO, P	145	47.00	18.00	35.00	Z, P
13	40.00	25.00	35.00	ZnO, Z, P	146	51.00	19.00	30.00	Bi ₃ NbO ₇ , ZnO, Z
14	42.00	25.00	33.00	ZnO, Z, P	147	54.00	15.00	31.00	Bi ₃ NbO ₇ , Z
15	44.00	25.00	31.00	ZnO, Z, P	148	52.00	14.00	34.00	Bi ₅ Nb ₃ O ₁₅ , Z
16	36.00	26.00	38.00	Zn ₃ Nb ₂ O ₈ , ZnO, P	149	46.00	15.00	39.00	BiNbO ₄ , Bi ₅ Nb ₃ O ₁₅ , P
30	35.00	27.00	38.00	Zn ₃ Nb ₂ O ₈ , ZnO, P	150	52.60	17.00	30.40	ZnO, Z, P
17	34.00	28.00	38.00	Zn ₃ Nb ₂ O ₈ , ZnO, P	151	44.00	23.00	33.00	Bi ₃ NbO ₇ , ZnO, Z
18	33.00	29.00	38.00	Zn ₃ Nb ₂ O ₈ , ZnO, P	152	70.00	20.00	10.00	Bi ₃ NbO ₇ , ZnO, Bi _{7.65} Zn _{0.35} O _{11.33}
23	34.87	23.00	42.00	BiNbO ₄ , ZnNb ₂ O ₆ , P	153	47.00	19.00	34.00	Z, P
24	32.50	27.50	40.00	Zn ₃ Nb ₂ O ₈ , ZnNb ₂ O ₆ , P	154	44.00	21.60	34.40	ZnO, Z, P
36	39.10	21.90	39.10	BiNbO ₄ , P	155	44.00	17.00	39.00	BiNbO ₄ , Bi ₅ Nb ₃ O ₁₅ , P
25	39.47	21.05	39.47	BiNbO ₄ , P	156	40.00	10.00	50.00	BiNbO ₄ , ZnNb ₂ O ₆ , P
38	39.89	20.20	39.89	BiNbO ₄ , P	157	20.00	20.00	60.00	BiNbO ₄ , ZnNb ₂ O ₆ , P
39	36.76	26.47	36.76	ZnO, P	158	60.00	7.00	33.00	Bi ₃ NbO ₇ , Bi ₅ Nb ₃ O ₁₅ , Z
40	36.73	23.47	39.80	ZnNb ₂ O ₆ , P	159	50.00	10.00	40.00	BiNbO ₄ , Bi ₅ Nb ₃ O ₁₅ , P
41	35.71	23.47	40.82	ZnNb ₂ O ₆ , P	160	55.00	30.00	15.00	Bi ₃ NbO ₇ , ZnO, Bi _{7.65} Zn _{0.35} O _{11.33}
42	40.31	23.47	36.22	ZnO, Z, P	161	40.00	40.00	20.00	Bi ₃ NbO ₇ , ZnO, Z
43	36.22	23.47	40.31	ZnNb ₂ O ₆ , P	162	5.00	15.00	80.00	Bi ₂ Nb ₁₀ O ₂₈ , ZnNb ₂ O ₆ , Nb ₂ O ₅
44	41.33	23.47	35.20	ZnO, Z, P	163	49.80	15.20	35.00	Bi ₅ Nb ₃ O ₁₅ , Z, P
45	42.35	23.47	34.18	ZnO, Z, P	164	47.40	19.00	33.60	Z, P
46	40.82	23.47	35.71	ZnO, Z, P	173	20.00	10.00	70.00	BiNbO ₄ , Bi ₂ Nb ₁₀ O ₂₈ , ZnNb ₂ O ₆
56	41.50	21.00	37.50	Bi ₅ Nb ₃ O ₁₅ , P					
57	41.00	21.50	37.50	Bi ₅ Nb ₃ O ₁₅ , P	Single phase compositions in monoclinic zirconolite subsolidus area				
61	37.50	21.00	41.50	BiNbO ₄ , ZnNb ₂ O ₆ , P	165	47.60	19.00	33.40	Z
66	36.80	21.60	41.60	BiNbO ₄ , ZnNb ₂ O ₆ , P	167	47.80	19.00	33.20	Z

75	41.00 22.60 36.40	Z, P	129	48.00 19.00 33.00	Z
76	42.00 22.00 36.00	Z, P	169	48.50 19.00 32.50	Z
77	43.00 21.00 36.00	Z, P	128	49.20 19.00 31.80	Z
78	40.40 20.80 38.80	BiNbO ₄ , Bi ₅ Nb ₃ O ₁₅ , P	124	48.60 18.40 33.00	Z
79	35.60 24.00 40.40	ZnNb ₂ O ₆ , P	122	49.60 18.40 32.00	Z
81	35.40 28.60 36.00	ZnO, P	125	48.80 18.00 33.20	Z
83	36.20 20.80 43.00	BiNbO ₄ , ZnNb ₂ O ₆ , P	104	48.60 17.60 33.80	Z
84	50.00 15.00 35.00	Bi ₅ Nb ₃ O ₁₅ , Z, P	117	50.00 17.60 32.40	Z
85	49.00 16.00 35.00	Z, P	170	49.40 17.50 33.10	Z
86	52.00 16.00 32.00	Bi ₃ NbO ₇ , Z	119	49.40 17.27 33.33	Z
87	50.00 18.00 32.00	Bi ₃ NbO ₇ , Z	103	49.20 17.20 33.60	Z
101	50.80 16.67 32.53	Bi ₃ NbO ₇ , Z	100	50.00 17.00 33.00	Z
106	51.60 16.67 31.73	Bi ₃ NbO ₇ , Z	118	49.13 16.67 34.20	Z
107	48.00 18.00 34.00	Z, P	102	49.40 16.67 33.93	Z
108	47.40 18.40 34.20	Z, P	20	50.00 16.67 33.33	Z
109	48.80 16.67 34.53	Z, P	105	50.80 16.20 33.00	Z
110	52.00 15.40 32.60	Bi ₃ NbO ₇ , Z	99	50.00 16.00 34.00	Z
111	45.20 19.80 35.00	Z, P	171	50.40 16.00 33.60	Z
112	46.80 18.80 34.40	Z, P	123	50.00 15.80 34.20	Z
113	46.20 19.20 34.60	Z, P	120	50.87 15.80 33.33	Z
114	48.33 16.67 35.00	Z, P	121	51.20 15.80 33.00	Z
115	47.33 16.67 36.00	Bi ₅ Nb ₃ O ₁₅ , Z, P	166	50.00 15.20 34.80	Z
116	51.40 15.80 32.80	Bi ₃ NbO ₇ , Z	168	50.20 15.20 34.60	Z
127	46.00 17.80 36.20	Bi ₅ Nb ₃ O ₁₅ , Z, P	134	50.60 15.20 34.20	Z
130	44.00 20.60 35.40	Z, P	172	50.90 15.20 33.90	Z
131	44.80 19.00 36.20	Z, P	126	51.00 15.20 33.80	Z
132	46.00 21.00 33.00	ZnO, Z, P	143	51.60 15.20 33.20	Z

Z = monoclinic zirconolite phase P = cubic pyrochlore.

The existence of other ternary oxide phases and the phase diagram compatibility relationships are investigated; a number of additional compositions are prepared within the system using the predetermined reaction condition. The monoclinic zirconolite solid solutions formed a compositional area in the phase diagram rather than a single, stoichiometric phase Bi₄Zn_{4/3}Nb_{8/3}O₁₄.

In this case, the ideal M composition Bi₄Zn_{4/3}Nb_{8/3}O₁₄ is marked as an open circle (Figure 3) with its approximate position correct according to literature. The M phase is located almost at the center of the subsolidus region, which is clearly contradictory to P phase as the ideal P is not included in the cubic subsolidus region [15-16].

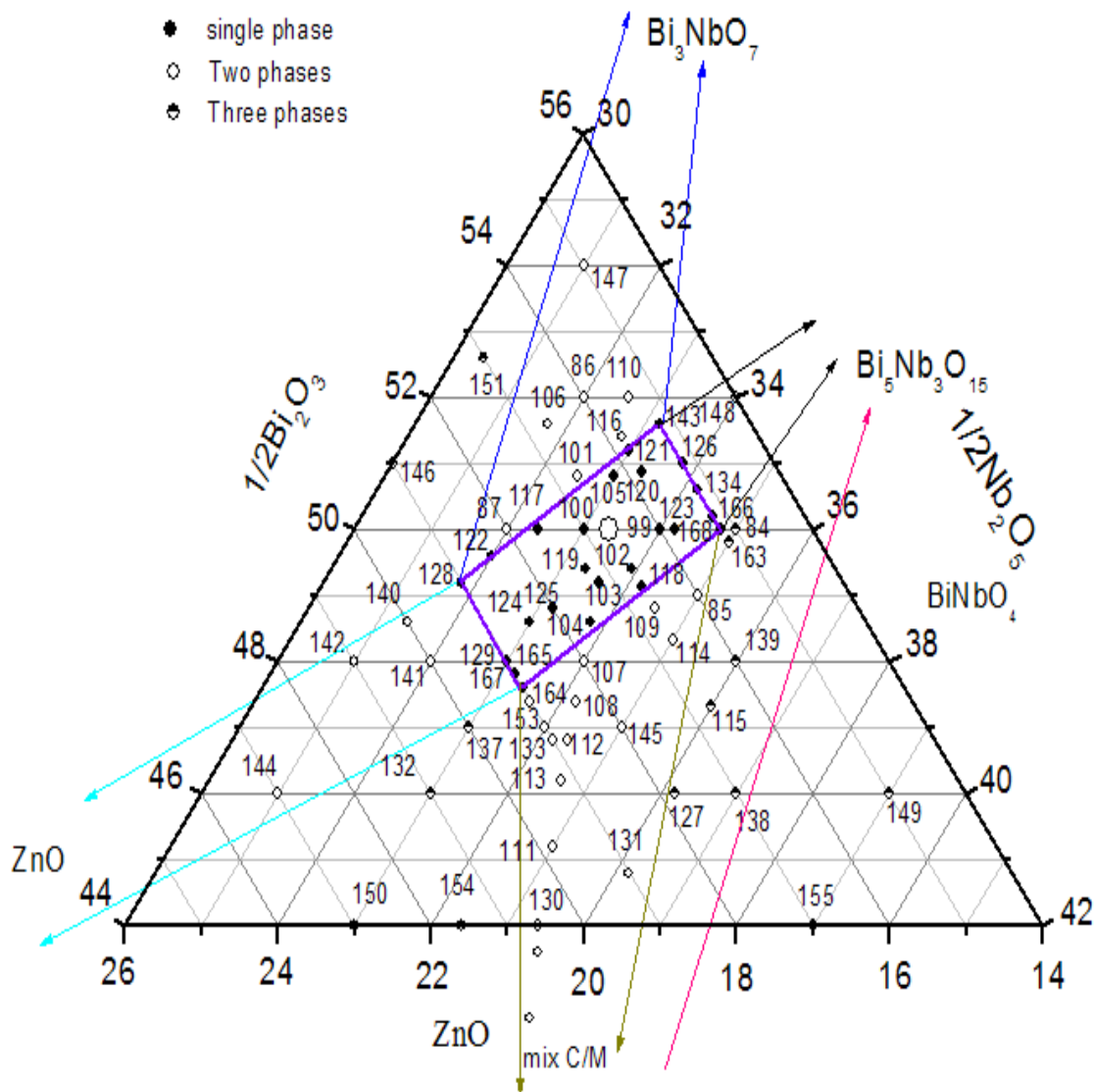


Figure 3: Compositional Range of the Monoclinic Zirconolite Phase at 950°C.

The solid solution area has a rectangular shape with two of the edges parallel and corresponding to ZnO contents of $19 \pm 0.5\%$ and $15.2 \pm 0.5\%$, respectively. The two limiting edges with constant ZnO content act as indicators for proposing the solid solution formation mechanism. Hence the solid solution area can be partially described in terms of a one-to-one replacement of Bi for Nb, together with, presumably, a variation in oxygen content that provides the charge balance for the variation in Bi:Nb ratio, $\text{Bi}^{3+} \rightarrow \text{Nb}^{5+} + \text{O}^{2-}$. In addition, two parallel edges of composition 128-143 and 165-166 suggested a possible mechanism, $\text{Bi}^{3+} + \text{Nb}^{5+} + \text{O}^{2-} \rightarrow 3 \text{Zn}^{2+}$. It may be

possible to represent the solid solution area by different mechanisms similar to those proposed for the cubic pyrochlore solid solution area. However, a detailed study is required before a firm proposal can be made.

According to Wang *et al.* (1997), the relation between $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$ and $\text{Bi}_4\text{Zn}_{4/3}\text{Nb}_{8/3}\text{O}_{14}$ could be elucidated as a binary join using a common chemical formula: $(\text{Bi}_{3x}\text{Zn}_{2-3x})(\text{Zn}_x\text{Nb}_{2-x})\text{O}_7$ ($2/3 \geq x \geq 1/2$) [3]. In a subsequent study, the relationship between the α , nominal cubic pyrochlore $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ and β , monoclinic pyrochlore was represented by a similar formula

$(\text{Bi}_{3x}\text{Zn}_{2-3x})(\text{Zn}_x\text{Nb}_{2-x})\text{O}_7$ ($0.5 \leq x \leq 0.67$) at 1000°C . The crystal structure gradually transformed from β phase to α phase with decreasing x values. There was a α - β coexisting phase area between the two single pyrochlore areas. The single α phase could be formed at $x = 0.5, 0.55$ and 0.56 , respectively. Meanwhile, the β phase started to form at $x = 0.57$ and became completely phase pure at $x = 0.67$. When x value was reduced to 0.45 , a small amount of $\text{Zn}_3\text{Nb}_2\text{O}_8$ phase was discernable [17]. In our study, a narrower limit for α phase i.e. at composition 51 (39.80 mole % Bi: 23.47 mole % Zn: 36.73 mole % Nb) compared to that of reported (42.00 mole % Bi: 22 mole % Zn: 36.00 mole % Nb at $x = 0.56$); at $x = 0.45$ a two phase mixture is obtained.

Combining the cubic, monoclinic subsolidus region, and those of previously reported binary phase equilibria for the perimeter systems: Bi_2O_3 -

Nb_2O_5 [18-20], Bi_2O_3 - ZnO [22-23] and ZnO - Nb_2O_5 [24-25], a complete phase diagram of the Bi_2O_3 - ZnO - Nb_2O_5 ternary system is constructed for compositions prepared at 950°C at atmospheric pressure (Figure 4). From the data obtained, the locations of the various phases and the extent of solid solution formation have been identified. The results here allow for a limited interpretation of the shape and size of the area within which the pyrochlores must exist so that the phase diagram remains coherent. It is now clear that the Bi_2O_3 - ZnO - Nb_2O_5 system contains two ternary phases (Figure 4). These phases, referred to here as P and M, are a cubic phase with the pyrochlore structure and a monoclinic phase with the zirconolite structure. P is a solid solution phase that occupies an area of the Bi_2O_3 - ZnO - Nb_2O_5 phase diagram which does not include the so called ideal stoichiometry $\text{Bi}_3\text{Zn}_2\text{Nb}_3\text{O}_{14}$.

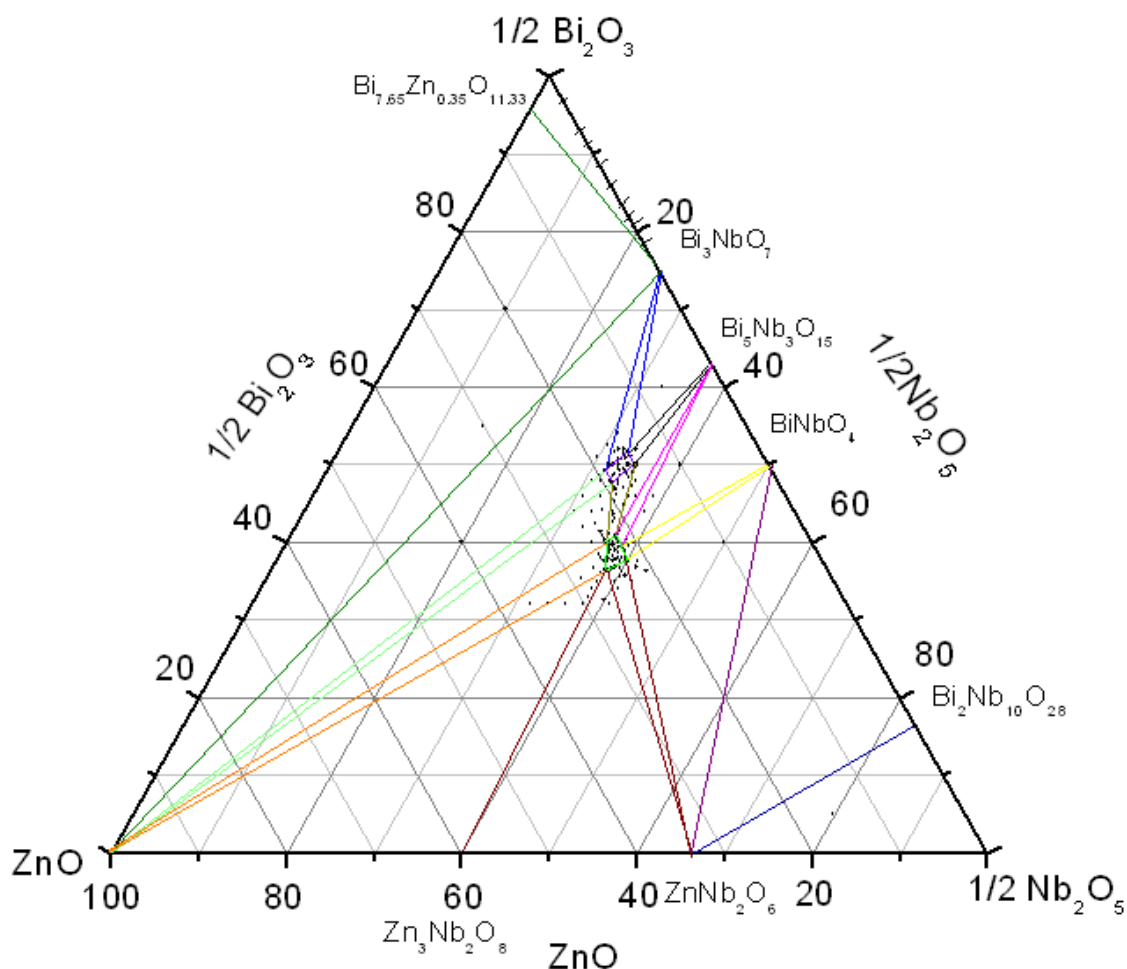


Figure 4: Bi_2O_3 - ZnO - Nb_2O_5 Subsolidus Phase Diagram at 950°C .

The overall phase diagram presented here shows reasonably good agreement with that reported by Vanderah *et al.* in 2005 [15]. Both P and M are non-stoichiometric compounds that form solid solution regions. The pyrochlore does not form at the conventionally predicted composition $\text{Bi}_4\text{Zn}_{4/3}\text{Nb}_{8/3}\text{O}_{14}$, which falls in the zirconolite region. Instead, cubic pyrochlore forms at substantially lower Bi concentrations in BZN system. The single-phase field for the pyrochlore structure falls completely outside compositions predicted for conventional pyrochlores (i.e., those with Bi^{3+} on the A sites and a $\text{Zn}^{2+}/\text{Nb}^{5+}$ mixture on the B sites). It has been suggested that the unconventional placement of small B-type cations such as Zn^{2+} on the large A-cation sites, accompanied by displacive disorder in the $\text{A}_2\text{O}'$ network, is required for stabilization of the pyrochlore structure in the BZN system [3,15].

An important novelty in our results is the detailed study of the monoclinic zirconolite subsolidus region whereby extensive range of solid solutions form by variation of the Bi/Nb ratio to either side of unity. There has been no indication in the literature of such a compositional variation, until recently when a small triangle containing $\text{Bi}_4\text{Zn}_{4/3}\text{Nb}_{8/3}\text{O}_{14}$ in the region of zirconolite in a concurrent work by Vanderah *et al.* (2005). The present study shows that the monoclinic zirconolite subsolidus area form a rectangular shaped region above the cubic pyrochlores. In conclusion, the results presented in Figure 4 and 5, with the various two-phase and three-phase regions surrounding the cubic and monoclinic zirconolite phase region, serve to confirm that a fully consistent set of data has been obtained and that, in particular, the various phase assemblages shown are fully consistent with the results presented in Table 2

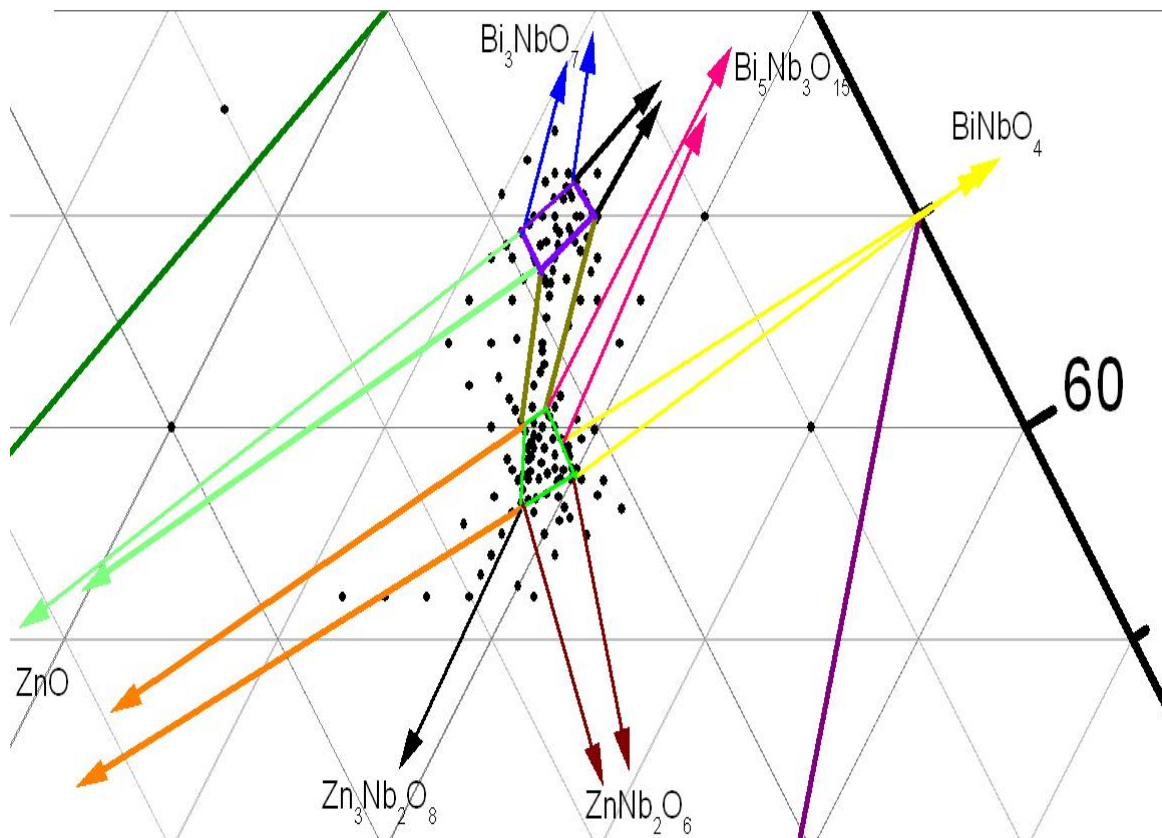


Figure 4: Expanded Region of the $\text{Bi}_2\text{O}_3\text{-ZnO-Nb}_2\text{O}_5$ Subsolidus Phase Diagram Showing the Solid Solution Areas of the Cubic Pyrochlore and Monoclinic Zirconolite Phase at 950°C .

NB: Cubic pyrochlore subsolidus area is denoted by the trapezium shape in Green; Monoclinic zirconolite subsolidus area is denoted by the rectangular shape in blue.

CONCLUSION

The formation of two structurally related phases; cubic and monoclinic zirconolite phase in Bi_2O_3 - ZnO - Nb_2O_5 ternary system was investigated. Both $\text{Bi}_5\text{Nb}_3\text{O}_{15}$ and BiNbO_4 are important precursors and ZnO reacts with these bismuth niobates in the formation of these phases. The final firing temperature of both phases is finalized at 950°C under atmospheric pressure.

The current study has successfully determined several areas of phase compatibility, based on the existence of ternary oxide pyrochlore compositions, $\text{Bi}_3\text{Zn}_2\text{Nb}_3\text{O}_{14}$, and $\text{Bi}_4(\text{Zn}_{1/3}\text{Nb}_{2/3})_4\text{O}_{14}$. Two inter-related areas, a trapezoidal cubic pyrochlore subsolidus region and a rectangular shaped subsolidus region formed by monoclinic zirconolite phase, are present in the phase diagram of Bi_2O_3 - ZnO - Nb_2O_5 ternary system.

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REFERENCES

1. Roth, R.S. and Vanderah, T.A. 2004. "Experimental Determination of Phase Equilibria Diagram in Ceramic Systems". *Solid State Ionics*. 192:3-18
2. West, A.R. 1999. "Phase Diagram". In: *Basic Solid State Chemistry*. John Wiley & Sons, Ltd.: New York, NY. 226-240.
3. Wang, X.L., Wang, H., and Yao, X. 1997. "Structure, Phase Transformation, and Dielectric Properties of Pyrochlores Containing Bismuth". *Journal of American Ceramic Society*. 80:2745-48.
4. Nino, J.C., Reaney, I.M., Lanagan, M.T., and Randall, C.A. 2002. "Transmission Electron Microscopy Investigation of Bi_2O_3 - ZnO - Nb_2O_5 Pyrochlore and Related Phases". *Materials Letters*. 57:414-19
5. Nino, J.C., Lanagan, M.T., and Randall, C.A. 2001b. "Phase Formation and Reactions in the Bi_2O_3 - ZnO - Nb_2O_5 - Ag Pyrochlore System". *Journal of Materials Research*. 16[5]:1460-64.
6. Levin, I., Amos, T.G., Nino, J.C., Vanderah, T.A., Reaney, I.M., Randall, C.A., and Lanagan, M.T. 2002b. "Crystal Structure of the Compound $\text{Bi}_3\text{Zn}_2\text{Nb}_3\text{O}_{14}$ ". *Journal of Materials Research*. 17:1406-11.
7. Valant, M. and Davies, P.K. 2000. "Crystal Chemistry and Dielectric Properties of Chemically Substituted $(\text{Bi}_{1.5}\text{Zn}_{1.0}\text{Nb}_{1.5})\text{O}_7$ and $\text{Bi}_2(\text{Zn}_{2/3}\text{Nb}_{4/3})\text{O}_7$ Pyrochlores". *Journal of American Ceramic Society*. 83[1]:147-53.
8. Choi, G.K., Kim, D.W., Cho, S.Y., and Hong, K.S. 2004. "Influence of V_2O_5 Substitution to $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$ Pyrochlore on Sintering Temperature and Dielectric Properties". *Ceramics International*. 30:1187-90.
9. Cheng, H.F., Chen, Y.C., Liu, H.L., Hwa, L.G., and Lin, I.N., 2004. "Correlation of Microwave Dielectric Properties and Crystallinity for Pulsed Laser Deposited $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$ Thin Films". *Journal of European Ceramic Society*. 24:1791-94.
10. Kamba, S., Porokhonskyy, V., Pashkin, A., Bovtun, V., and Petzelt, J. 2002. "Anomalous Broad Dielectric Relaxation in $\text{Bi}_{1.5}\text{Zn}_{1.0}\text{Nb}_{1.5}\text{O}_7$ Pyrochlore". *Physics Review B*. 66:054106.
11. Randall, C.A., Nino, J.C., Baker, A., Youn, H.-J., Hitomi, A., Thayer, R., Edge, L.E., Sogabe, T., Anderson, D., Shrout, T.R., Trolier-Mckinstry, S., and Lanagan, M.T. 2003. "Bi-Pyrochlore and Zirconolite Dielectrics for Integrated Passive Component Applications". *American Ceramic Society Bulletin*. 9101-08
12. Ren, W., Trolier-Mckinstry, S., Randall, C.A., and Shrout, T.R. 2001. "Bismuth Zinc Niobate Pyrochlore Dielectric Thin Films for Capacitive Application". *Journal of Applied Physics*. 89[1]: 767-74.
13. Thayer, R.L., Randall, C.A., and Trolier-Mckinstry, S. 2003. "Medium Permittivity Bismuth Zinc Niobate Thin Film Capacitors". *Journal of Applied Physics*. 94[3]:1941-47.
14. Chen, S.Y., Lee, S.Y., and Lin, Y.J. 2003. "Phase Transformation, Reaction Kinetics and Microwave Characteristics of Bi_2O_3 - ZnO - Nb_2O_5 Ceramics". *Journal of European Ceramic Society*. 23:873-81.
15. Vanderah, T.A., Levin, I. and Lufaso, M.W. 2005. "An Unexpected Crystal-Chemical Principle for the

Pyrochlore Structure". *European Journal of Inorganic Chemistry*. 2895-2901.

16. Tan, K.B., Lee C.K., Zainal Z., Miles G.C., and West, A.R. 2005. "Stoichiometry and Doping Mechanism of the Cubic Pyrochlore Phase in the System $\text{Bi}_2\text{O}_3\text{-ZnO-Nb}_2\text{O}_5$ ". *Journal of Materials Chemistry*. 15:3501-3506.
17. Wang, H., Yao, X., Zhang, L-Y. and Xia, P. 1999. "Phase Transition of Pyrochlore Structure in $\text{Bi}_2\text{O}_3\text{-ZnO-Nb}_2\text{O}_5$ System". *Ferroelectrics*. 239: 95-101.
18. Ling, C.D. 1998. "Structural Relationships among Bismuth-Rich Phases in the $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5$, $\text{Bi}_2\text{O}_3\text{-Ta}_2\text{O}_5$, $\text{Bi}_2\text{O}_3\text{-MoO}_3$, and $\text{Bi}_2\text{O}_3\text{-WO}_3$ Systems". *Journal of Solid State Chemistry*. 148:380-405.
19. Yaremchenko, A.A., Kharton, V.V., Naumovich, E.N. and Vecher, A.A. 1998. "Oxygen Ionic Transport in Bi_2O_3 -Based Oxides: The Solid Solutions $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5$ ". *Journal of Solid State Electrochemistry*. 2[3]:146-49.
20. Roth, R.S. and Waring, J.L. 1962. "Phase Equilibrium Relations in the Binary System Bismuth Sesquioxide-Niobium Pentoxide". *Journal Res. Natl. Bur. Stand., Sect A*. 66A[6]:451-63.
21. Safronov, G.M., Batag, V.N., Stepanyuk, T.V., and Fedorov, P.M. 1971. "Equilibrium Diagram of the Bismuth Oxide-Zinc Oxide System". *Russian Journal of Inorganic Chemistry (English Translation)*. 16[3]:460-461.
22. Li, J.G. 1994. "Some Observations on Wetting in the $\text{Bi}_2\text{O}_3\text{-ZnO}$ System". *Journal of Materials Science Letters*. 13[6]:400-403.
23. Dayal, R.R. 1972. "The Binary System $\text{ZnO-Nb}_2\text{O}_5$ ". *Journal of Less-Common Metals*. 26:381-90.
24. Yamaguchi, O., Maruyama, N. and Hirota, K. 1991. "New Modification of $3\text{ZnO.Nb}_2\text{O}_5$ ". *Journal of Materials Science Letters*. 10[8]:445-447.

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