Low Temperature Synthesis of $Ba_3Ta_2ZnO_9$ (BZT) and $Ba_3Nb_2ZnO_9$ (BZN) by Wet Chemical Route

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Abstract:

Powders of high microwave dielectric material Barium Zinc Tantalate (BZT) and Barium Zinc Niobate (BZN) have been prepared by wet chemical procedure at moderately low temperature ~500^0C. Co-precipitate and mechanical mixtures of hydroxide of Ba(II), Ta(V)/Nb(V) & Zn(II) in 3:2:1 mole proportion on thermal decomposition, showed formation of the desired perovskite phase at 500^0C. The product of co-precipitate and mechanical mixture of hydroxides heated upto740^0C produced single phase BZT. Thermal decomposition of mixture was studied in static air atmosphere by TG & DTA. XRD studies on a sample heated to 500, 740, 780 & 900^0C confirmed the formation of single phase BZT formation at 740^0C and that of BZN at780^0C.

Key words: *BZT, BZN, DTA, TG, XRD, dielectric ceramics, Wet chemical route.*

I. Introduction:

Mixed metal oxide ceramics with Perovskite (ABO_3) structure are of great importance for various electronic applications. Among this family BZT and BZN are very significant members because of their high dielectric constant, low loss factor at resonant frequency and near zero temperature coefficients at resonant frequency. BZT has found applications as small electronic component for use in hand held communication device like cellular phone. Miniaturization of electronic devices and adding more functionalities have given rise to a need for small size microwave resonators with good frequency selectivity and high temperature stability. Since the discovery of excellent microwave dielectric properties exhibited by $Ba(Zn_{1/3}Nb_{2/3})O_3$ and $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics with perovskite structure. Many researchers [1-12] have prepared the material and there are several patents on preparation of BZT [13].

Most of these procedures utilize oxides of Ba, Ta/Nb, Mg/Zn in 3:2:1 mole proportion. Although the material is used by many workers; the reports in print are very few and especially reports on wet chemical route for synthesis are rare except for work done by Maclaren et al. [9], they have used barium acetate, zinc acetate, tantalum oxalate and Ganguly et al. [8] have used $Mg(NO_3)_2.6H_2O$ for the formation of Magnesium Niobate (MN) and Magnesium Tantalate (MT). More popular route for preparation of BZT is solid state route, where stoichiometric amounts of corresponding oxides viz. 3BaO, ZnO, Ta_2O_5/Nb_2O_5 are mixed, milled together manually or using ball-mill and heated at temperature of about 1300^0C [11-14] for few hours.

The main problem associated with high temperature (above 1300^0C) sintering is volatility of ZnO. This leads to non-homogeneity in ZnO concentration is observed on the surface and in the bulk. High temperature sintering results in formation of undesirable binary oxide barium tantalate. Naturally the ZnO deficient phase does not have desired dielectric constant and hence device application fails. To eliminate the problem, sintering temperature must be kept below 1300^0C. This is possible when powders are synthesized by wet chemical route [8]. Such chemically synthesized powders possess fine particle size distribution and low aspect ratio particle morphology, as well as better homogeneity in micro-structure and chemical constitution [1,2]. The resultant powder possesses better sintering ability. Hence wet chemical synthesis is a promising route.

In wet chemical method precursors are added to give either mechanical mixtures or co-precipitate of metal salts in desired mole proportion. Precipitate filtration, drying and calcinations of dried precursor was carried out. The dried precursors were then heated at constant pre decided rate. We have successfully synthesized Barium Zinc Niobate (BZN), Barium-zinc-tantalate (BZT), Zinc tantalate, Magnesium tantalate, Zinc Niobate by wet chemical route [1,2]. This paper reports results on synthesis of single phase BZT and BZN using wet chemical route at temperature as low as 740^0C.

II. Experimentation:

Co-precipitated hydroxides of Ba, Zn, Ta/Nb were prepared in 1:2:3 mole proportion and subjected to heating from ambient to 1000^0C for studying the decomposition. Thermo-gravimetric Analysis (TG) was employed to study the decomposition. After plotting the weight loss curves as a function of temperature few temperatures were selected and the precursors were heated to those temperatures. The XRD analyses of the above heated samples were carried out to monitor various products formed at the pre-decided temperatures. The experimentation is divided into three parts:

1) TG and DTA measurements were carried out using equipments fabricated in house, the decomposition were studied in static air atmosphere using heating rate of 10^0C /min, from ambient to 1000^0C, TG plots are shown in figures 1 to 4 and DTA are shown in Fig 5 and 6.

2) Mixtures were heated up to 500, 740, 900^0C and soaked for 1hr at the final temperature. The products thus obtained were analyzed by Bruker AXS D8 Advance X ray diffractometer in 2θ range 20- 80^0.

3) Surface morphology was recorded on JEOL JSM 6360A Scanning Electron Microscope.

List of samples studied is given below:

Table-1 Samples under study.

Sr No.	Precursor sample	**Sample abbreviation**	Raw material
1.	Binary mixture of Tantalum & zinc in 2:1 mole proportion as co-precipitate.	ZT (cp)	Ta_2O_5 & $Zn (NO_3)_2$
2.	Binary mechanical	ZT (mm)	$Ta(OH)_5$ & $Zn(OH)_2$

	mixture of Tantalum and zinc In 2:1		
3.	Barium, Tantalum and zinc 3:2:1	BZT (cp)	Ba(OH)$_2$ & ZT hydroxide (cp)
4.	Barium, Tantalum & zinc in 3:2:1	BZT (mm)	Ba(OH)$_2$,Ta(OH)$_5$ & Zn(OH)$_2$
5.	Niobium & zinc, 2:1	ZN(cp)	Nb$_2$O$_5$ & Zn (NO$_3$)$_2$
6.	Niobium & zinc 2:1	ZN (mm)	Nb(OH)$_5$ & Zn(OH)$_2$
7.	Barium, Niobium & zinc, 3:1:2	BZN (cp)	Ba(OH)$_2$ & ZN hydroxide (cp)
8.	Barium, Niobium & zinc, 3:1:2	BZN (mm)	Ba(OH)$_2$,Nb(OH)$_5$ & Zn(OH)$_2$

Preparation of hydroxide mixtures:

a) Co-precipitation method (cp):

The procedure was chosen from earlier reports by Ravi et al [1, 2] for preparation of Mg$_4$Ta$_2$O$_9$, MgNb$_2$O$_6$ etc. The major step is dissolution of Ta$_2$O$_5$ and Nb$_2$O$_5$. It was carries in fuming chamber using Teflon beaker on a water bath. The beaker was fitted with long air condenser. 20 hours digestion time was required for Ta$_2$O$_5$ and 8 hours for Nb$_2$O$_5$. After the dissolution required amount of Zinc nitrate was added as solution and precipitation was carried out using ammonium hydroxide solution till the pH reached 9. Voluminous white precipitate was obtained. Filtration, washing and drying was carried out. For preparation of ternary co-precipitate Barium hydroxide was added

to the binary co-precipitate prepared by method given above.

b) Mechanical mixtures (mm):

In case of Mechanical mixtures individual hydroxides were prepared from raw materials as given in the flowchart No.1 and ammonium hydroxide was used as precipitating agent. The resultant precipitates were washed with distilled water till the pH of filtrate was 7, and the precipitate was subjected to drying at 110^{0}C for 5hr. The dried samples were mixed in required proportion (3:2:1 Ba: Ta: Zn) in agate mortar for 2 hrs and stored in vacuum desiccators.

III. Results and Discussion:

It is observed that precipitate washing, filtration and drying temperature play significant role in deciding the homogeneity, and phase formation temperature of BZT and BZN.

TG interpretation
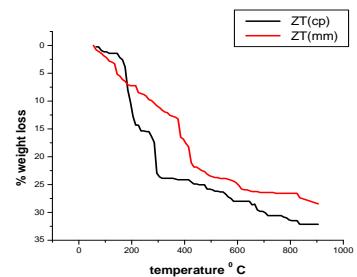
Fig.1 Decomposition pattern of co-precipitate ZT (cp) and ZT mm –hydroxide

As can be seen from above figure decomposition of cp starts and completes at lower temperature. The actual weight loss steps and reactions are given below.
For cp ZnTa$_2$(OH)$_{12}$.2NH$_4$OH$\rightarrow$ ZnTa$_2$O$_6$
For mm Zn (OH)$_2$ +2 Ta
(OH).2NH$_4$OH$\rightarrow$ZnTa$_2$O$_6$
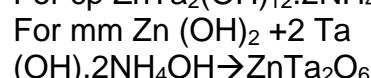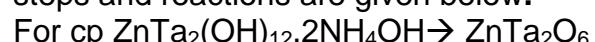
	Temperature °C	% weight loss	Decomposition product	Residual compound
BZT cp	55-260	12.98	-11.8 H2O	Partly dried presursor.
	260-400	20.19	-14.11 H_2O, 2 NH_4OH	$ZnTa_2(OH)_{12}$ + 2BaO+ 1 $Ba(OH)_2$
	400-800	9.61	-7 H_2O 1from Ba, 6from Ta + Zn cp	3Ba2TaZnO9 (cp) hydroxide
BZT mm	80-180	4.77	-3H_2O (2from Zn and 1from Ta/Ba)	Amorphous precursor
	190-290	5.53	-3.5 H_2O	ZnO
	300-730	3.15	-2 H_2O	$Ba_3Ta_2ZnO_9$

Sr. No	Temperature °C	% wt loss	Decomposition product	Residual compound
ZT cp	115-245	16.77	- 2 NH_4OH -2 H_2O	partial Ammonia expulsion & decomposition
	255-455	25.81	-4H_2O	$ZnTa_2O_6$
ZT mm	55-260	10.37	2 NH_4OH	NH_4OH Free ZT
m	260-	10.	4.15	ZnO +

	400	69	H_2O	Ta-intermediate
	400-800	5.36	2.08 H_2O	$ZnTa_2O_6$
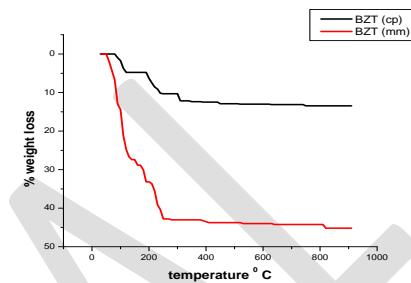
Fig.2 Decomposition pattern of co-precipitate BZT (cp) and BZT mm –hydroxide For cp $ZnTa_2$ $(OH)_{12}.2NH_4OH$ +3$Ba(OH)_2$→$Ba_3ZnTa_2O_9$
For mm
$Ba(OH)_2.8H_2O+Zn(OH)_2+2Ta(OH)_5$→$Ba_3ZnTa_2O_9$
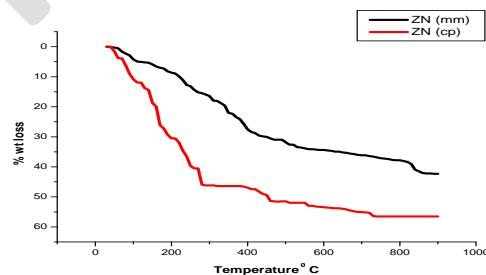
Fig.3 Decomposition of co-precipitate ZN(cp) and ZN (mm) hydroxide $ZnNb(OH)_7$ → $ZnNb_2O_6$
Decomposition reactions for mm $Zn(OH)_2$+ $Nb(OH)_5.7H_2O.(1H_2O,1 NH_4OH)$→ $ZnNb_2O_6$

Decomposition reactions for cp

	Temperature	% W loss	Decomposition product	Residual compound
BZN cp	100-200	14.21	-10.82 H_2O	Dehydrated BZN (cp)
	273-530	14.76	-11.23 H_2O	Anhydrous BZN (cp)
	560-660	12	-9.1 H_2O	BZN (cp) oxide
BZN mm	100-290	7.24	- 5.5 H_2O	Dehydrated BZN mm
	350-400	26.94	-21.6 H_2O	BZN mm anhydrous
	575-695	7.65	-5.8 H_2O	BZN mm oxide

adsorbed water, absorbed water, ammonia water of crystallization and water released due to decomposition of hydroxide respectively. The DTA plots obtained for various samples are shown in Fig 5 and 6 below. The decomposition pattern of ZT mm & cp are almost identical. ZT mm decomposition occurs in 55 to 350 and 350 to 600^0C in two steps and in ZT cp occurs in four steps. Desorption, dehydration & decomposition are all endothermic reactions. In all the four DTA samples a sharp endothermic peak is observed at around 390^0C which is assigned to decomposition of ZT hydroxide.

Fig.4 Decomposition pattern of co-precipitate BZN (cp) and BZN mm –hydroxide
For cp
$Ba(OH)_2.8 H_2O + ZnNb(OH)_7 \rightarrow Ba_3ZnNb_2O_9$
For mm
$Ba(OH)_2.8 H_2O + Zn(OH)_2 + 2Nb(OH)_5 \rightarrow Ba_3ZnNb_2O_9$
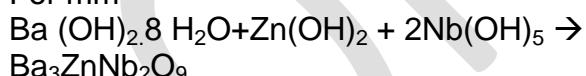
c) DTA interpretation:

DTA measurements were carried out on DTA instrument fabricated in house. The decompositions sequence was studied in static air atmosphere using heating rate of 10^0C /min, from ambient to 900^0C. The exothermic and endothermic peaks observed in DTA plots were assigned to the loss of

	Temperature ^0C	% W loss	Decomposition product	Residual compound
ZN cp	155-225	16.75	-5 H_2O	Dehydrated ZN
	225-305	6.04	-1.8 H_2O	Anhydrous ZN
	435-685	9.36	- 2.85 H_2O	ZN oxide
ZN mm	55-155	10.38	-1 NH_4OH -1 H_2O	Desorption of 1ammonia & water
	155-295	21.54	- 3.5 H_2O	Dehydration
	357-435	8.72	2.66 H_2O	Completion of dehydration & decomposition of Zn
At higher tem	500-875	6.02	2 H_2O	Formation of binary oxide of Zn-Nb

perature around 660-670 ^{0}C co-precipitate shows a small exothermic peak & mm shows small endothermic peak which is little conflicting but at temperature up to750^{0}C shows same reversal reaction enthalpies. It shows different stabilities of binary oxides formed which lead us to select co-precipitated product over mechanical mixture as starting material for ternary oxides. In DTA of BZT a broad endothermic peak observed due to large amount of water of crystallization at 100 for co-precipitate and at 140^{0}C for mechanical mixture.

For BZN mm closely separated endothermic peaks due to release of large amount of associated water. In cp single endothermic peak due to close association of molecules is observed.
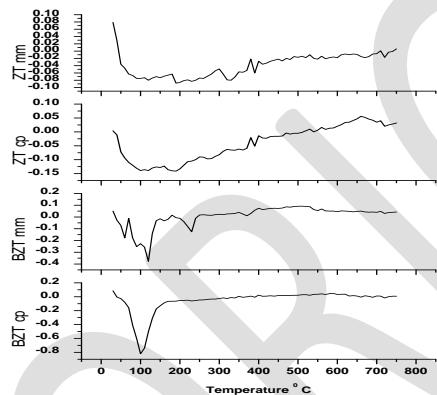
Fig 5 DTA plots of ZT, BZT (cp, mm)
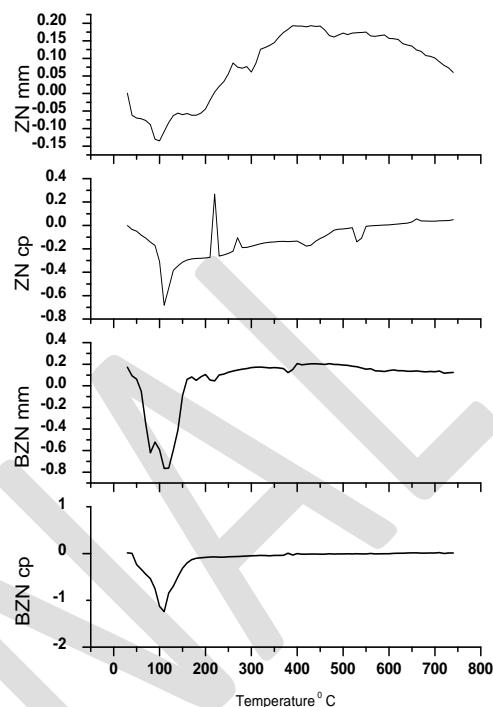
Fig. 6 DTA plots of ZN, BZN (cp, mm)

d) XRD studies:

Conformation of the phases formed at various stages of decomposition was done by XRD. XRD patterns recorded for mechanical mixture of BZT – hydroxides heated up to 500, 740^{0}C and on another sample heated up to 980^{0}C for 2 hrs are shown in Fig 7-9. It can be easily seen that the sample heated to 500^{0}C shows very poor crystallinity whereas the sample heated at 740^{0}C shows single phase BZT, on heating the sample up to 900^{0}C the crystallinity reduces and very low intensity peaks are observed corresponding to BZT phase. The XRD patterns were recorded for ternary hydroxide Ba Zn Nb heated up to and heated at 740^{0}C for one hour. Fig 4 c shows the XRD patterns for mm, cp and solid state mixture of Ba, Zn and Nb oxides in 3:2:1 mole proportion. Comparison of the patterns

reveal that BZN cp mixture heated at 740^0C for one hr gives single phase BZN compound as reported by C. T. Lee [14] where as the solid state mixture shows binary oxides ZN in addition to BZN . This indicates that for solid state oxide mixture 740^0C temperatures is not sufficient for the formation of single phase ternary BZN oxide.
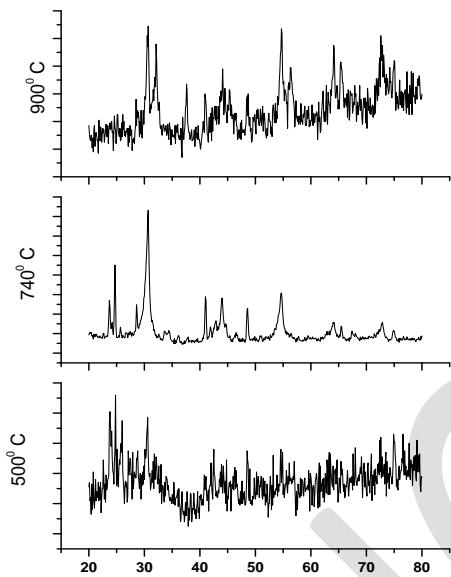

Fig. 7 XRD of BZT heated to various temperatures
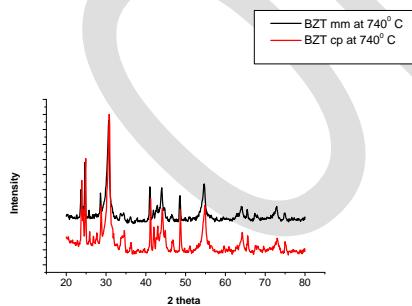

Fig. 8 XRD for BZT cp & mm heated to 740^0C

2θ
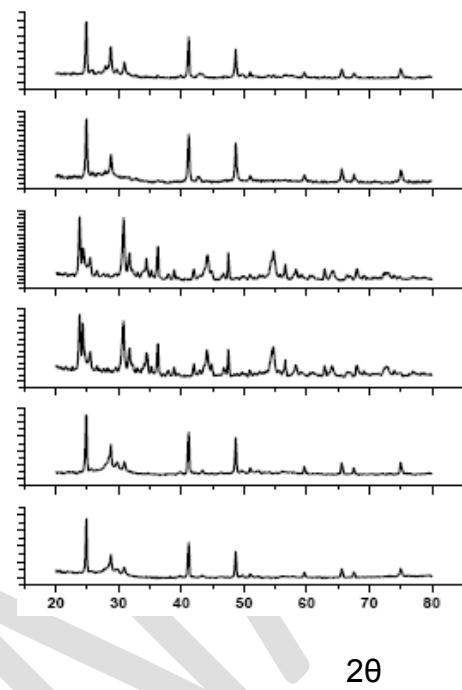
Fig. 9 XRD of BZN cp, mm , ss heated to 740^0C

e) SEM Studies:

Fig 10 a, b show SEM images of sintered BZT powder and The SEM image shows regions of about 1 micron size rods with uniform size and shape.
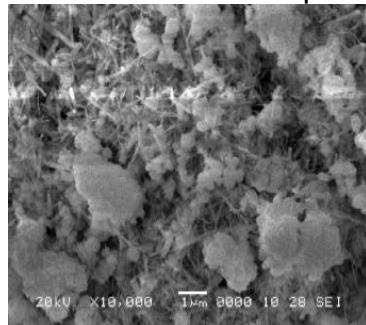

Fig.10 a SEM image of BZT
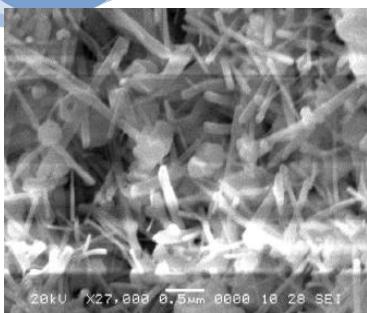
Fig.10 b SEM image of BZT
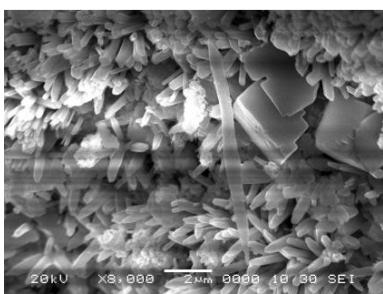

Fig. 10 (c) SEM image of BZN mm
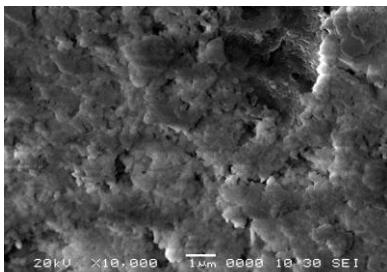
Fig. 10 (d) SEM image of BZN cp

IV. Conclusions:

Wet chemical route is better suited for preparation of binary and ternary oxides of Zinc Tantalate and Barium Zinc Tantalate as compared to Solid state route.
All hydroxides mixture cp as well as mm seem to have high tendency to adsorb ammonia as well as water. This Ammonia and water is deeply embedded in the system and require higher temperature (260^0C for ZN mm) for removal.

Formation of ZT occurs at Temperature as low as 680^0C for cp and single phase ZT oxide is formed at 740^0C for mm.

Formation of single phase BZT occurs at temperature below 740^0C and the crystalline single phase disintegrates at temperatures around 900^0C as can be seen from Fig. 7, the decomposition product of co-precipitate has better crystallinity; as compared to that of mechanical mixture. No high temperature sintering is required for the formation of single phase BZT if hydroxide route is adopted.

Decomposition of ZT is complete at 740 but complete decomposition of ZN/BZN requires temperature more than 840^0C.Sintering time of 1 hr. at 740^0C for BZN & 1 hr at 880^0C for BZT is sufficient. In case of BZN cp and mm (Fig. 10 c and d) it was observed in mm sample there are two type of grains a needle like which is in majority and flat plates in lesser concentration. SEM image of cp sample shows a single grain type which more homogeneous hence it appears to better than mm.

SEM images showed formation of uniform rods with plumbite structure having 1micron size, on further magnification of a crystal lump similar rod like structure is observed within the lump. The high dielectric constant of the material appears to be due to fractality observed in the crystal structure.

V. Acknowledgements:

VI. References:

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