$Ba_3ZnTa_{2-x}Nb_x0_9$ and $Ba_3MgTa_{2-x}Nb_x0_9$: synthesis, structural and dielectric studies

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Abstract

Oxides of the families $Ba_3ZnTa_{2-x}Nb_x0_9$ and $Ba_3MgTa_{2-x}Nb_x0_9$ were obtained by the solid state reaction route at 1573 K and were found to crystallize in the disordered (cubic) perovskite structure. In $Ba_3ZnTa_{2-x}Nb_x0_9$ and $Ba_3MgTa_{2-x}Nb_x0_9$ the entire range ($0 \leq x \leq 1$) of solid solutions could be synthesized. The dielectric constant decreases with increase in frequency for all compositions in the range 40 Hz to 100 kHz (e_r varies from 16 to 22). The dielectric loss (D) shows a broad maximum for both $Ba_3ZnTa_{2-x}Nb_x0_9$ and $Ba_3MgTa_{2-x}Nb_x0_9$ The maxima is centered around 2 kHz in the former and near 10 kHz in the latter.

Keywords: A. Oxides; B. Chemical synthesis; C. X-ray diffraction; D. Dielectric properties

1. Introduction

There has been a continuous increase in the requirement of dielectric materials in view of their importance in electronic devices. In recent years, materials for dielectric resonators have received much attention due to their need in the area of microwave communication. They permit miniaturization of microwave devices such as duplex filters, down converters, and voltage controlled oscillators.

The complex oxide $A(B_{1/3}B^1{}_{2/}3)O_3$ constitutes a special family of perovskite oxides. The series of compounds in this family were first prepared by Roy [1] and Galasso et al. [2] in

the 1950s. When B is substituted by Zn or Mg and B^1 by Nb or Ta, these compounds show extremely low dielectric loss (D) at microwave frequencies [3]. BZT ($Ba3ZnTa_2O_9$) and BMT($Ba_3MgTa_2O_9$) are disordered at lower temperature and become ordered at higher temperatures (at about 1673 K for BZT and 1873 K for BMT) [3-6]. Pure barium zinc niobate ($Ba_3ZnNb_2O_9$) was earlier reported as a disordered perovskite [7], but it is now known that with proper annealing (1623 K for 12 h) a fully ordered 1:2 perovskite structure can be obtained [8]. Higher temperature annealing or quenching leads to disordered structures [8,9].

We have synthesized solid solutions between $Ba_3ZnTa20_9$-$Ba3ZnNb_20_9$ and $Ba_3MgTa20_9$-$Ba3MgNb_20_9$. Since $Ta20_5$ is 3 times more expensive than Nb_2O_5, it would be very economical to obtain niobates with good dielectric properties, comparable with the tantalates such as BagZnTa^c, or BagMgTa^c,, which are already being used in devices [3,4]. In this paper we report the synthesis, structural characteristics as well as dielectric data in the 40Hz-100kHz region of the above-mentioned families of oxides sintered at relatively low temperatures (1573 K).

2. Experimental

The starting materials were $BaCO_3$, ZnO, MgO, T a ^ ^ and Nb_2O_5. Stoichiometric quantities were weighed, mixed, ground, and then calcined at 1273 K for 30 h with two intermittent grindings. The calcined powder was ground and then pressed into pellets with 5% polyvinylalcohol (PVA) solution, at 4 ton pressure. The pellets were sintered at 1273 K for 48 h followed by sintering at 1473 K for 24 h and 1573 K for 12 h.

Powder X-ray diffraction (PXRD) was carried out using a JEOL JDX-8P diffractometer with Cu Ka radiation. Lattice parameters were calculated by a least-squares fit to the observed d-values. The grain sizes of the samples were obtained by scanning electron microscopy (SEM) using a Cambridge Stereoscan 360 electron microscope. The density of ceramics was measured by Archimedes method. The dielectric constant and dielectric loss were measured on well sintered pellets (1573 K) of 10 mm diameter (silver electroded) using a Keithley 3330 LCZ meter in the frequency range 40Hz-100kHz.

3. Results and discussion

The PXRD of $Ba_3ZnTa_{2-x}Nb_xO_9$ (where $0 \leq x \leq 1$) could be indexed in a cubic cell for all the compositions sintered at 1273 K. The cubic structure persists even after sintering at 1573 K. Fig. 1 shows a typical PXRD pattern, of BagZnTaNbOg sintered at 1573 K. The lattice parameter *a* calculated from the indexed powder pattern was —4.1 A. No impurity peaks were present in the powder diffraction patterns. The various compositions (x ranging from 0.1 to 1) and their respective lattice constants are listed in Table 1. BagZnTa^c, (x = 0 composition) sintered at 1473 K has a cubic structure with $a \sim 4.1$ A [10], while it is hexagonally ordered when sintered at temperatures above 1673 K [3,6],

The density of the $Ba_3ZnTa_{2-x}Nb_x0_9$ samples sintered at 1573 K was above 93% of the

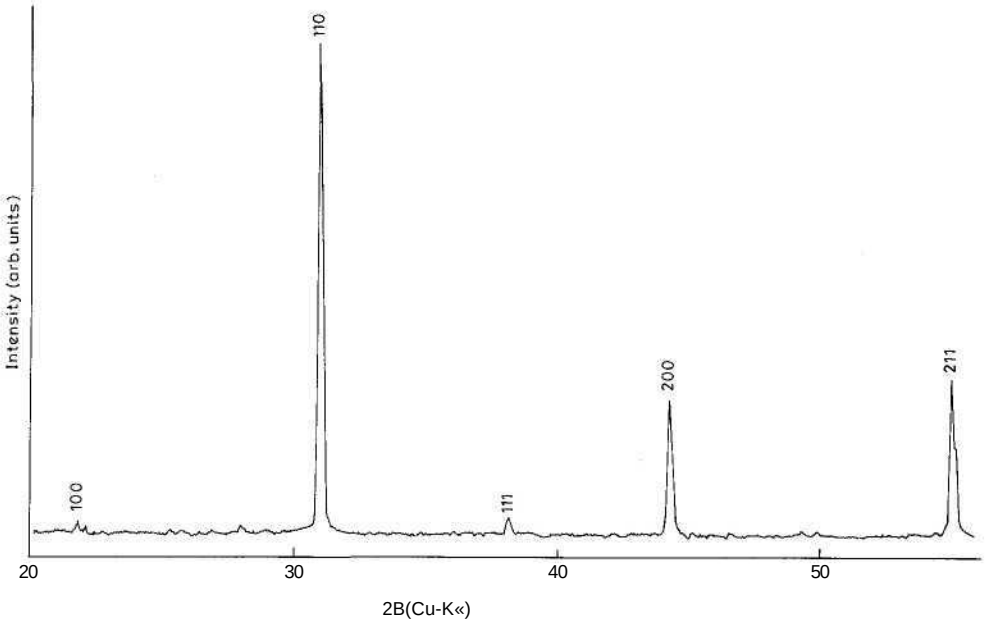

Fig. 1. Powder X-ray diffraction pattern of $Ba_3ZnTaNbO_9$ sintered at 1573 K.

theoretical value for all compositions. Scanning electron micrographs for samples annealed at 1573 K for 12 h show a grain size diameter in the range 2-3 [xm, while samples heated to only 1273 K had grains of less than 0.5 [xm (Fig. 2).

For the materials synthesized at 1273 K, $Ba_3MgTa2_{-x}Nb_x0_9$ ($0 \leq x \leq 1$) shows the presence of a cubic phase. A small amount (5%) of $Ba_5Ta_40_{15}$ impurity phase was observed in these samples. An increase in sintering temperature from 1273 to 1573 K did not lead to any phase transformation, and all the lines could be indexed to the cubic cell. The various compositions and lattice parameters are listed in Table 2. The lattice parameter *a* was in the range 4.09-4.1 A. The relative density for all the samples sintered at 1573 K was about 92% of the theoretical value. The particle size was found by SEM to be in the range 1-3 [xm for samples sintered at 1573 K for 12 h (the sample after 1273 K heat treatment had a grain size of less than 0.5 (xm). The SEM photographs of $BagMgTa!_5Nb_{0\,5}O_9$ sintered at 1273 and 1573 K (Fig. 2) are very similar to those of the Zn analogue.

Table 1
Details of the compositions and structural parameters of the phases in the $Ba3ZnTa_{2-x}Nb_xO_9$ ($0.1 \leq x \leq 1$) system sintered at 1573 K

Composition	"cubic (A)
$Ba_3ZnTaj_{\ 9}Nb_{0\ }jO_9$	4.080(1)
$Ba_3ZnTaj_{\ 75}Nb_{0\,25}O_9$	4.086(1)
$Ba_3ZnTa!_5Nb_{05}O_9$	4.086(1)
$Ba_3ZnTa!_{\ 25}Nb_{0\,75}O_9$	4.091(1)
$Ba_3ZnTaNbO_9$	4.085(1)

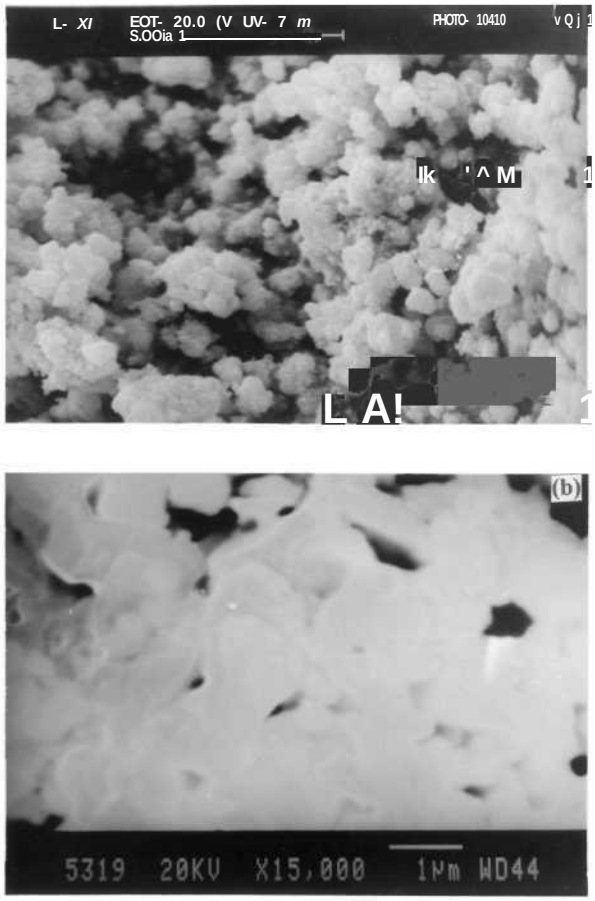

Fig. 2. Scanning electron micrographs of $Ba_3ZnTaj_5Nb_{05}O_9$ sintered at (a) 1273 K and (b) 1573 K.

The dielectric properties of $Ba_3ZnTa_{2-x}Nb_xO_9$ solid solutions were investigated in the 40Hz-100kHz frequency range. The dielectric constant for all the compositions of $Ba_3ZnTa2_{-x}Nb_x0_9$ (x = 0.1 to 1) at room temperature decreases with increase in frequency over the range of frequencies covered in the present studies (Fig. 3). At 100 kHz, it varies between 16 and 18.6. The dielectric constant of $Ba_3ZnTa_90_Q$ sintered at 1473 K is —12 at

Table 2
Details of the composition and structural parameters in the $Ba3MgTa_{2-x}Nb_xO_9$ ($0.1 \leq x \leq 1$) system sintered at 1573 K

Composition	"c_{ubic} (Å)
$Ba_3MgTa_{19}Nb_{01}O_9$	4.093(1)
$Ba_3MgTa!_{.75}Nb_{0.25}O_9$	4.086(1)
$Ba_3MgTa_{15}Nb_{05}O_9$	4.086(1)
$Ba_3MgTa_{125}Nb_{075}O_9$	4.086(3)
$Ba_3MgTaNbO_9$	4.096(1)

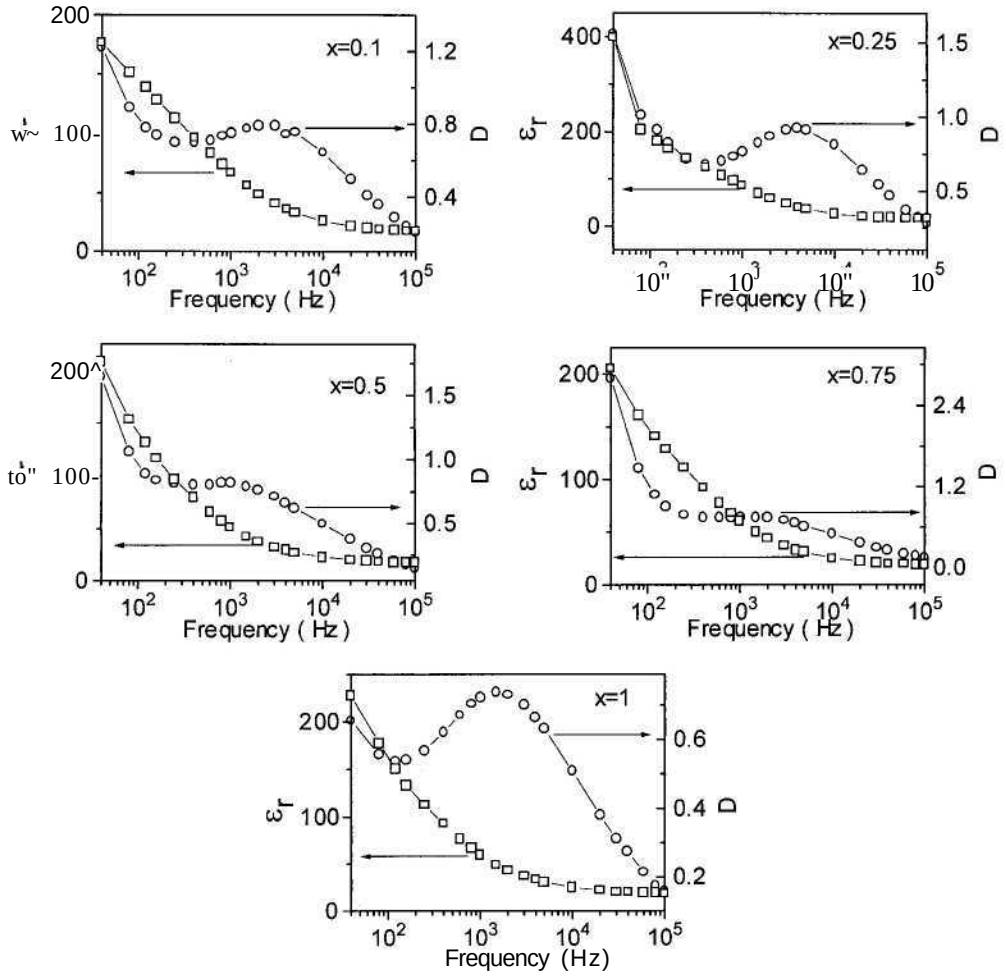

Fig. 3. Plot of the variation of the dielectric constant (e_r) and dielectric loss (D) with frequency for the five compositions studied in the $Ba_3ZnTa_{2-x}Nb_xO_9$ system.

100 kHz [10]. The dielectric loss tangent (D = tanS) of BagZnTa^Nt^Og (x = 0.1 to 1) decreases initially up to about 1 kHz and exhibits a broad peak centered at about 3 kHz for x = 0.1. Subsequently, it decreases with increase in frequency up to 100 kHz. The dielectric constant of this system (at 1 kHz) decreases from 67 to 60 as x increases (Fig. 4(a)). In the Ba3ZnTa2_xNbx09 system the composition $Ba_3ZnTa_{1.2}sNb_{0.75}O_9$ has the highest e_r (18.6) at 100 kHz.

The grain size in these samples sintered at 1573 K was found to be in the range 2-3 [xm and, hence, the low dielectric constant can be attributed to the small grain size. The small grain size may be due to volatility of zinc, which makes pore shrinkage difficult [6,11] leading to small grain size and density. The absence of ordering of the B and B^1 sites, as indicated from PXRD, could also lead to low values for the dielectric constant. It may be noted that e_r for BagZnTa^c, is about 30 in the 10-12 GHz range of frequency [3] for

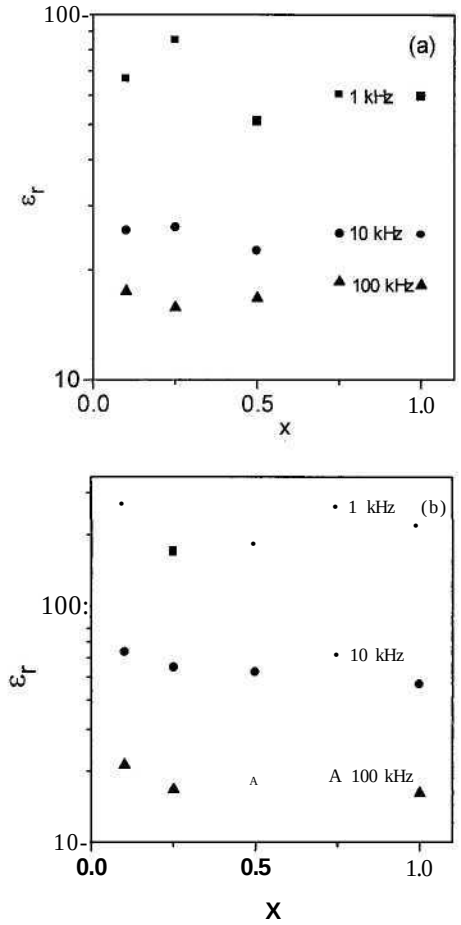

Fig. 4. Plot of the variation of the dielectric constant (e_r) with composition (x) in the (a) $Ba_3ZnTa2\_xNb_xO_9$ and (b) $Ba_3MgTa_{2\_x}Nb_xO_9$.

samples sintered above 1723 K, and the dielectric constant at lower frequencies should be higher than or comparable to those at GHz frequencies.

The dielectric properties measured as a function of frequency for members of $Ba_3MgTa2\_xNb_x0_9$ family are shown in Fig. 5. These samples were sintered at 1573 K for 12 h (see Experimental section for details). The dielectric constant decreases with increase in frequency for all the members under study. With increasing niobium concentration the dielectric constant decreases systematically except for the composition x = 0.75 as shown in Fig. 4(b). Poor reactivity of MgO at lower temperatures is one of the factors that leads to low density and, hence, low dielectric constant. The e_r varies between 16 and 20 at 100 kHz, depending on the Nb concentration. For comparison, we measured the e_r and D of one of the samples sintered only up to 1273 K for about 48 h. The e_r was 19.3 while the D was about 0.20 at 100 kHz. The corresponding sample after 1573 K sintering showed an e_r of 20.27 and a D of 0.68. Thus, it appears that a marginal change occurs in the dielectric constant by increasing the sintering temperature though there is a much larger increase in the dielectric loss.

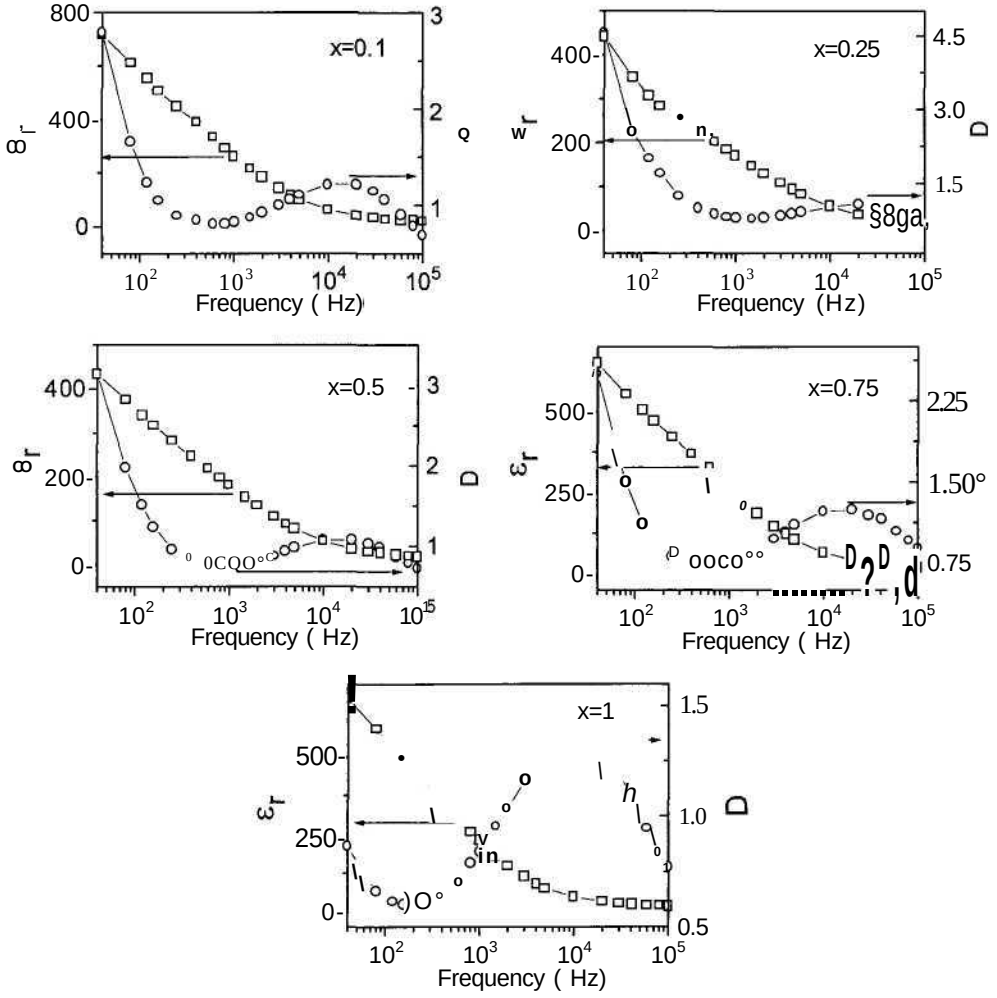

Fig. 5. Plot of the variation of the dielectric constant (e_r) and dielectric loss (D) with frequency for the five compositions studied in the $Ba_3MgTa2_{-x}Nb_xO_9$ system.

From SEM studies, the grain size in our samples sintered at a 1573 K was found to be in the range 1-3 [xm. It is evident that there is an increase in the grain size in the 1573 K sintered samples, implying that the dielectric constant can be further improved by sintering the ceramic at much higher temperatures. BagMgTa^c, sintered at 1823-1873 K, has an e_r of about 30 at 11-12 GHz [6]. The composition with x = 0.25 showed a maximum value of dielectric constant of 20 (at 100 kHz).

4. Conclusions

Various members of Ba3ZnTa2_$_x$Nb$_x$0$_9$ and Ba3MgTa$_{2_x}$Nb$_x$0$_9$ were synthesized by the conventional solid state method. Even after sintering the powders at 1573 K, all the

compounds crystallized in a cubic phase, as determined by PXRD. Members of $Ba3MgTa2_{-x}Nb_x0_9$ showed a minor (5%) amount of $Ba_5Ta_4O_{15}$ impurity phase. $Ba_3ZnTa_{1.2}sNb_{0.75}O_9$ sintered at 1573 K showed maximum e_r = 18.6 (at 100 kHz), while for the $Ba_3MgTa2_{-x}Nb_xO_9$ family, a maximum dielectric constant of 20 was obtained for x = 0.25 at the same frequency.

Acknowledgments

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