Synthesis and microwave dielectric properties of $Sr_3Zn_{1-x}Mg_xNb_2O_9$ phases

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(Refereed)
Received 18 July 2001; received in revised form 29 September 2001; accepted 19 November 2001

Abstract

Oxides of the type, $Sr_3Zn_{1-x}Mg_xNb_2O_9$ ($0 \leq x \leq 1$) have been obtained by the ceramic method. These oxides crystallize in the hexagonal cell corresponding to ordered triple perovskites. Sintered disks show nearly frequency-independent dielectric constant for all the compositions. Compositions sintered at 1425°C yield dielectric constant of 20–22 at ~6 GHz, with quality factor ranging from 1300 to 1500. $Sr_3Zn_{0.5}Mg_{0.5}Nb_2O_9$ shows a very low temperature coefficient of resonant frequency (τ_f) of +4 ppm/°C.

Keywords: A. Ceramics; A. Electronic materials; A. Oxides; C. X-ray diffraction; D. Dielectric properties

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1. Introduction

In perovskite compounds of the formula $A(B_{1/3}B'_{2/3})O_3$ an ordered phase with 1:2 regular arrangement of the B and B′ ions often exists. The structure of the ordered phase has been assigned by Galasso and Pyle [1]. Some of the compounds with an ordered configuration of B and B′ ions on the octahedral sites having a low dielectric loss are used as dielectric resonators. The dielectric resonator has the advantages of compactness and ease of matching to microwave-integrated circuits. The desired ceramic characteristics for use as microwave resonators include a suitable dielectric constant ε (20–40), high unloaded Q (>3000) and low-temperature coefficient of the resonant frequency (τ_f) 0 + 10 ppm/°C.

In the past 15 years, a number of ceramics have been developed [2–4] as microwave dielectric resonators like $BaZn_{1/3}Nb_{2/3}O_3$, $BaMg_{1/3}Nb_{2/3}O_3$ and $BaZn_{1/3}Ta_{2/3}O_3$. Substitution of the Ba-site with Sr has been attempted earlier to form solid solutions and their dielectric properties have also been investigated. For example, the system $Ba(Mg_{1/3}Ta_{2/3})O_3$–$Sr(Mg_{1/3}Ta_{2/3})O_3$ [5] and $Ba(Zn_{1/3}Nb_{2/3})O_3$–$Sr(Zn_{1/3}Nb_{2/3})O_3$ [6], have been systematically explored to obtain new materials with better dielectric properties. $Sr(Mg_{1/3}Nb_{2/3})O_3$ was reported to be hexagonally ordered around 1650°C [7].

In this paper, we describe the structural and dielectric properties of solid solutions of the type $Sr(Zn_{1-x}Mg_x)_{1/3}Nb_{2/3}O_3$, where the effect of B-site substitution has been investigated in the Sr-based perovskite oxide.

2. Experimental

The starting materials were $SrCO_3$, MgO, ZnO and Nb_2O_5 powders. They were mixed and milled with a mortar and pestle. The mixed powders were then calcined at 1000°C for 30 h with intermittent grinding. The calcined powders were mixed with 5% of polyvinylalcohol (PVA) and made into disks. The disks were then sintered at 1000°C for 48 h, 1200°C for 12 h and finally at 1300°C for 12 h. For measurement at GHz frequencies the samples were further sintered at 1425°C for 6 h. The powders were studied by powder X-ray diffraction (XRD) (Bruker D8—Advance diffractometer). Particle size of the sintered materials were measured using a Scanning Electron Microscope (Cambridge 360). The density of the sintered disks was measured by Archimedes method. The as-sintered samples were coated with “Al” in vacuum to measure the dielectric constant and loss tangent in the low frequency range (50 Hz–500 kHz) using a LCR meter (HP 4284L). Dielectric properties at GHz frequencies were measured using a Network Analyzer (Hewlett-Packard 8510B) and a reflection transmission unit (Hewlett-Packard 8510B). The apparatus was controlled using a Hewlett-Packard 9000, 300 series computer. The ε_r was calculated from the TE_{011} resonance mode of the end-shorted sample placed between two conducting plates, using the method of Hakki and Coleman [8] and modified by Courtney [9]. The Q-factor was measured by the microstripline method of Khanna and Garault [10]. The coefficient of temperature variation of resonant frequency was measured by noting the temperature variation of resonant frequency of the TE_{011} mode in the transmission configuration over a range of temperature 23–80°C.

3. Results and discussion

The entire range of compounds in the $Sr_3ZnNb_2O_9$–$Sr_3MgNb_2O_9$ system crystallize in a cubic structure when calcined at 1000°C. The lattice parameter (a) of these

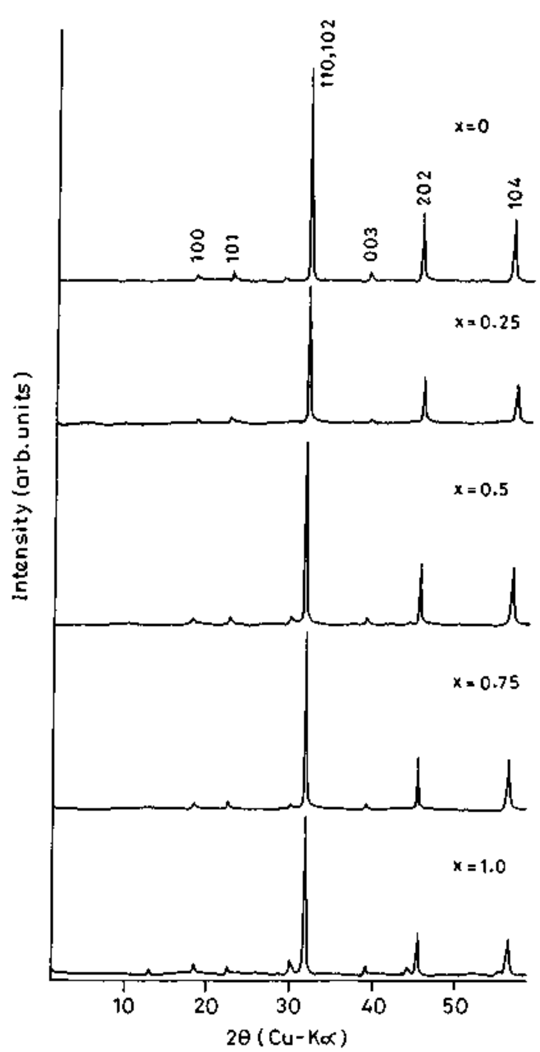

Fig. 1. Powder X-ray diffraction patterns of $Sr_3Zn_{1-x}Mg_xNb_2O_9$ system sintered at 1300°C.

Table 1
Lattice parameters (Å) for the oxides of the type $Sr_3Zn_{1-x}Mg_xNb_2O_9$

Composition	a_{cubic}[a]	Ordered phase (hexagonal)[b]	
		a	c
$Sr_3ZnNb_2O_9$	4.0067(2)	5.646(6)	6.907(3)
$Sr_3Zn_{0.75}Mg_{0.25}Nb_2O_9$	4.0058(3)	5.653(5)	6.913(3)
$Sr_3Zn_{0.5}Mg_{0.5}Nb_2O_9$	4.0059(3)	5.653(5)	6.918(3)
$Sr_3Zn_{0.25}Mg_{0.75}Nb_2O_9$	4.0048(1)	5.653(3)	6.919(2)
$Sr_3MgNb_2O_9$	4.0006(4)	5.643(4)	6.909(2)

[a] 1000°C/30 h.

[b] 1000°C/30 h/1000°C/48 h/1200°C/24 h/1300°C/12 h.

compounds is ~4.001 Å. Powder XRD of the 1300°C sintered samples show the hexagonally ordered phase (Fig. 1) for all the oxides. All the reflections could be indexed satisfactorily in the hexagonal cell with $a \sim 5.65$ Å and $c \sim 6.91$ Å. However, the XRD patterns show a small amount of (~5%) $Sr_5Nb_4O_{15}$ phase as

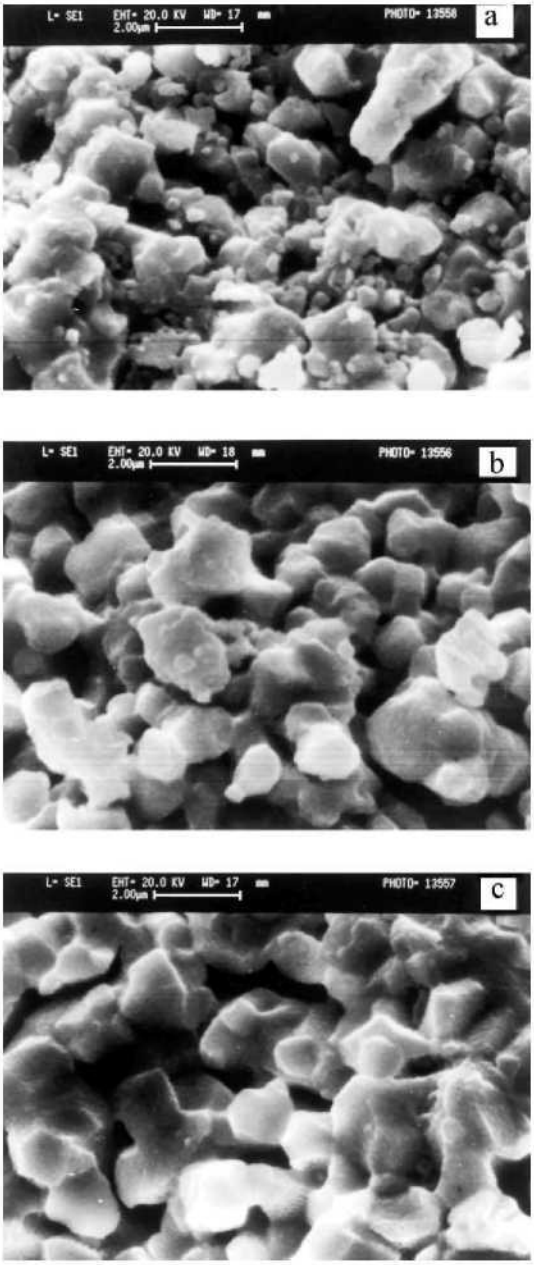

Fig. 2. Scanning electron micrographs of oxides of the $Sr_3Zn_{1-x}Mg_xNb_2O_9$ system sintered at 1425°C for (a) $x = 0.25$; (b) $x = 0.50$; (c) $x = 0.75$.

impurity. The lattice parameters and other X-ray data are summarized in Table 1. $Sr_3ZnNb_2O_9$ is earlier reported to be hexagonally ordered with $a = 5.66$ Å, $c = 6.95$ Å [6]. These values are slightly higher than what we obtained (Table 1). There is a very small decrease in the lattice parameters as we substitute Mg in Zn sites

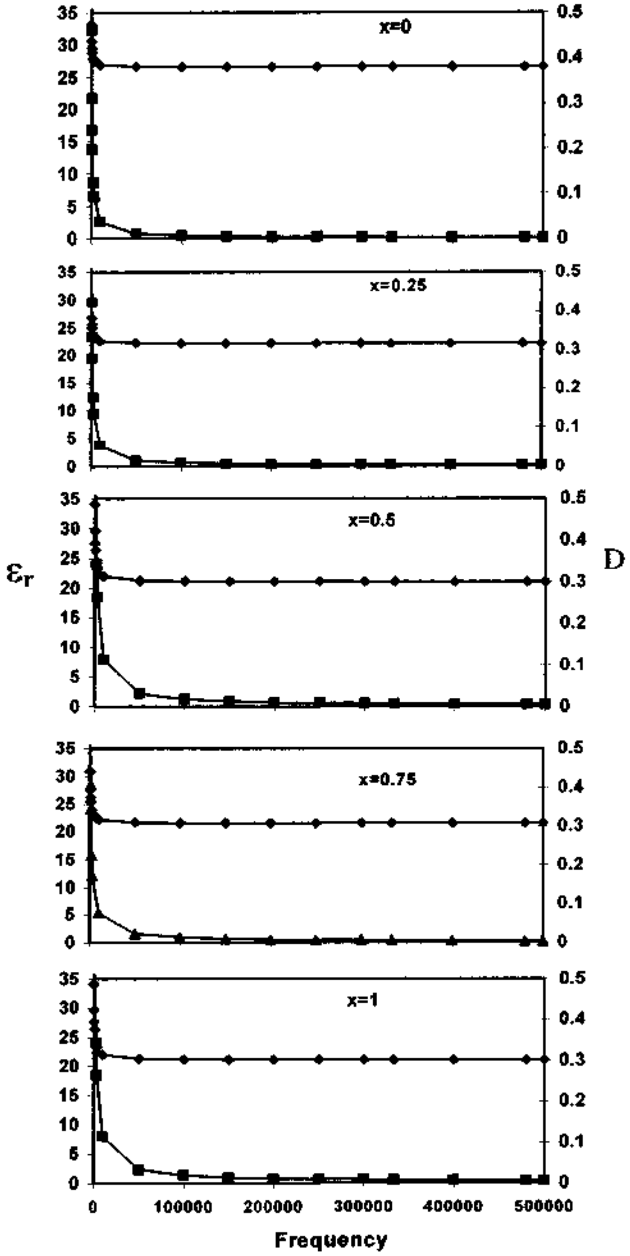

Fig. 3. Variation of dielectric constant (ε_r) and dielectric loss (D) with frequency for $Sr_3Zn_{1-x}Mg_xNb_2O_9$ system in the 50 Hz–500 kHz region.

Table 2
Dielectric properties for $Sr_3Zn_{1-x}Mg_xNb_2O_9$ at GHz frequencies

Composition	ε_r	$Q \times f$ (f in GHz)	τ_f (ppm/°C)
$Sr_3ZnNb_2O_9$	20.69	$1300 \times 5.8197 = 7565$	−27.43
$Sr_3Zn_{0.75}Mg_{0.25}Nb_2O_9$	19.96	$1429 \times 5.9750 = 8538$	−15.7
$Sr_3Zn_{0.5}Mg_{0.5}Nb_2O_9$	22.31	$1521 \times 5.3665 = 8162$	+4.38
$Sr_3Zn_{0.25}Mg_{0.75}Nb_2O_9$	21.55	$1168 \times 5.7525 = 6718$	−10.23

ε_r: dielectric constant; Q: quality factor; τ_f: temperature coefficient of resonant frequency.

and is observable at high "Mg" concentrations. This is understood easily since the ionic radii [11] of Mg^{2+}(VI) is 0.720 and that of Zn^{2+}(VI) is 0.740.

The scanning electron micrograph of the samples sintered at 1425°C are shown in Fig. 2. The average grain size (calculated by the linear intercept method) is around 1 μm for $x = 0.25$. We see a distribution of grain sizes. However, for $x = 0.5$ and 0.75, the grains are more regular and compact. The average grain size also increases to 1.8 and 2.2 μm for $x = 0.5$ and 0.75 compositions, respectively.

The room temperature dielectric properties on sintered pellets (1300°C) show frequency stable (Fig. 3) dielectric constant around 20–27 for all the compositions in the 100 Hz–500 kHz range. The dielectric loss was ~0.001 for all compositions. Both the dielectric constant and the dielectric loss remained almost constant in the entire frequency range measured. There have been earlier reports [6] of dielectric properties of SZN and SMN, where the dielectric constant is reported to be 37–40, respectively at 100 kHz. However, no detail of the X-ray studies are given to ensure absence of impurities. In addition, the variation of the dielectric constant with frequency has also not been studied earlier [6].

We have also studied the dielectric properties at microwave frequencies (5.4–5.9 GHz) for disks sintered at 1425°C. The observed dielectric constant and quality factor for various members of the solid solution are shown in Table 2. The density of these samples were ~97% of the theoretical density. The dielectric constant varies between 20 and 22 for various members of the $Sr_3Zn_{1-x}Mg_xNb_2O_9$ family. The $x = 0.5$ composition, $Sr_3(Zn_{0.5}Mg_{0.5})Nb_2O_9$, has the highest dielectric constant of 22.3. All the samples have low loss or a high Q. The $Q \times f$ values are listed in Table 2. The temperature coefficient of resonant frequency (τ_f) is quite low, varying between −27 and +4.3 ppm/°C for different compositions. The $x = 0.5$ composition has the best dielectric properties among the compositions studied with the highest ε, lowest loss and lowest τ_f value of +4.38 ppm/°C. Thus, our studies show the possibility of fine tuning the properties by suitable substitution in the course of which materials with nearly zero τ_f can be obtained.

4. Conclusions

The detailed structural studies using powder XRD and the dielectric properties at low frequency (50 Hz–500 kHz) and at high frequency (5–6 GHz) was investigated for the $Sr_3Zn_{1-x}Mg_xNb_2O_9$ system. All the oxides are hexagonally ordered after sintering at 1300°C. These oxides have extremely stable dielectric constant in the 100 Hz–500 kHz frequency range. From microwave (5.4 GHz) measurement it is found that the $x = 0.5$ composition has a very small temperature coefficient of the resonant frequency (τ_f) of +4.3 ppm/°C. It has a relatively high dielectric constant of 22.3 and a Q of 1521. This composition has characteristics required for use as a dielectric resonator at microwave frequencies.

Acknowledgment

Financial assistance from BRNS, Govt. of India is gratefully acknowledged.

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