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Effect of ionic substitution on the structural, dielectric and electrical properties of bismuth zinc niobate ceramics

A. F. Qasrawi^{a,b,*}, Hussein A. Abu Je'ib^b and A. Mergen^c

^aGroup of Physics, Faculty of Engineering, Atilim University, 06836 Ankara, Turkey ^bDepartment of Physics, Arab-American University, Jenin, West Bank, Palestine ^cMetallurgical and Materials Engineering Dept., Marmara University, 34722 Istanbul, Turkey

The effects of tin substitution on the structural, dielectric and electrical properties of the $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ pyrochlore ceramics have been investigated. Tin atoms was substituted in the A ($Bi_{1.5}Zn_{0.46}$)-site instead of zinc and in the B (($Zn_{0.46}Nb_{1.5}$) -site instead of niobium in accordance to the chemical formulae $Bi_{1.5}Zn_{0.92}Nb_{1.5x}Sn_xO_{6.92x/2}$ and ($Bi_{1.5x/3}Zn_{0.463x/2}Sn_x$)(Nb_{1.5}Zn_{0.46})O_{6.92}, for $0.00 \le x \le 0.40$ and $0.00 \le x \le 0.60$, respectively. A relative single phase formation of the structures was possible for x values less than 0.25 and less than 0.10. Pronounced tunability in the dielectric constant values associated with very low dielectric loss are obtainable by Sn substitution. Furthermore, a frequency invariant but linearly varying temperature dependent dielectric constant is observed. The electrical conductivity decreased by two and one order of magnitude for the A and B-site substitutions, respectively. The temperature-dependent conductivity analysis in the temperature region of 300-500 K, reflected the existence of shallow and deep impurity energy levels being created by the doping process.

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Introduction

Pyrochlore lattice structural materials such as $A_2B_2O_7$ and $A_2B_2X_6Z$ compounds have shown significant promise as ideal candidates for applications ranging from electronic materials and solid electrolytes, to heating elements, high temperature electrodes and fixation of radioactive waste. This versatility depends on the fact that the pyrochlore crystal structure allows a wide variety of ionic substitutions at both the A, B sites as the B element can be a transition metal, with variable oxidation state, and the A element can be a rare earth or an element, with inert lone pairs; At the same time they satisfy other requirements such as physical stability, chemical or thermal compatibility with other materials involved in the design [1, 3].

Pyrochlore compounds can accommodate various cations in the A- and B-sites due to their large stability field which impart various properties to the pyrochlores. If it is assumed that the Zn cation in the $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ pyrochlore is distributed evenly through A- and B-sites, the chemical formula of bismuth-zinc-niobium (BZN) pyrochlore can then be stated as $(Bi_{1.5}Zn_{0.46})(Zn_{0.46}Nb_{1.5})O_{6.92}$ which is an A and B-site and oxygen deficient pyrochlore [3]. Such types of ceramics are observed to exhibit different

physical properties depending on the type of ions implanted them. Namely, Ti doping alters the dielectric relaxation temperature [4], vanadium behaves as a sintering aid [5] and Gd [6] highly affects the dielectric properties of the BZN pyrochlore.

Previously we have determined the energy band gap, the dispersive optical parameters [7], the structural and dielectric [8] properties of the pure $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ ceramics and the effect of Ta doping on the structure, dielectric and electrical properties of the pyrochlore. In this study we will report the Sn (with 6 and 8 coordination number) doping effects on the structural, dielectric and electrical properties of the $Bi_{1.5}Zn_{0.92}Nb_{1.5}Xsn_xO_{6.92-x/2}$ and $(Bi_{1.5-x/3}Zn_{0.46-3x/2}Sn_x)(Nb_{1.5}Zn_{0.46})O_{6.92}$ pyrochlore ceramics. The main difference in the physical properties established by the type of substitution will be examined. Furthermore, the transport properties of the Sn doped microwave ceramics will be investigated by means of electrical conductivity measurements.

Experimental procedure

Sn doped BZN ceramic powders having the composition $Bi_{1.5}Zn_{0.92}Nb_{1.5-x}Sn_xO_{6.92-x/2}$ and $(Bi_{1.5-x/3}Zn_{0.46-3x/2}Sn_x)$ (Nb_{1.5}Zn_{0.46})O_{6.92}, were prepared by the conventional high temperature solid state reaction technique. A detailed experimental description of the preparation and characterizations of the samples have been previously reported [7-9].

^{*}Corresponding author:

Tel +90-312-5868329

Fax: +90-312-5868091

E-mail atef_qasrawi@atilim edu tr

Results and Discussion

Structural analysis

As the ionic radius of tin (Sn) metal which have a 6 coordination number, Sn_{6-coord}, is the same as the ionic radius of niobium (Nb) (0.69 Å) and because the ionic radius of Sn with a 8 coordination number $Sn_{8-coord.}$ (0.81 Å) is less than the ionic radius of Zn (8 coordination number) ion (0.91 Å), the $Sn_{6-coord}$ was doped into the B-site of BZN pyrochlore in place of Nb and Sn_{8-coord} was doped into the A-site at ratios between x = 0.00-0.60 and x = 0.00-0.40 in accordance to the formulae $Bi_{1.5}Zn_{0.92}Nb_{1.5-x}Sn_xO_{6.92-x/2}$ and $(Bi_{1.5-x/2})$ $_{3}Zn_{0.46-3x/2}Sn_{x})(Nb_{1.5}Zn_{0.46})O_{6.92}$, respectively Fig. 1 (a) and (b) displays the respective X-ray diffraction patterns. For the replacement of Nb by Sn presented as Sn(Nb) in Fig. 1 (a), a single phase observation was possible for $x \le 0.25$ only. For x values less than 0.25, the reflected X-ray patterns, presented in Fig. 1 (a), did not show any secondary phase in the structure of the BZN, indicating that replacement of Nb by Sn forms a complete substitutional solid solution. When x is greater than 0.25, a ZnO (second) phase (card number: JCPDS Kart No: 36-1451) started to form (Fig. 1). For the substitution of Zn by $Sn_{8-coord}$ presented as Sn(Zn) in Fig. 1 (b), a single phase observation was possible for $x \le 0.10$ only. For $0.13 \le x \le 0.20$ a second phase, BiNbO₄ (card number: JCPDS 16-295), appeared in the XRD patterns and for $0.30 \le x \le 0.40$, ZnNb₂O₆ and SnO₂ phases appeared in the spectrum. The appearance of multiphases in the BZN pyrochlore ceramics has also been reported in the literature. It has

(a)		1		o : ZnO P: Pyro	chlore			
<u> </u>			<u> </u>			l		Sn(Nb) 0.60
			<u> </u>					Sn(Nb) 0,30
			l			l		Sn(Nb) 0,25
								Sn(Nb) 0,20
								Sn(Nb) 0,10
P		Р	P ↓	P		P J	۶.	Sn(Nb) 0,06
0	20	30)	40 20 (a)		50	60	
(b)	o * +	No**	*:BiN	lbO4 o:	ZnNb ₂ O	**	ochlore	Sn(Zn) 0.40
	* *0* +	Ue**	** *		*. *	** *.		Sn(Zn) 0.30
	* **	J**	.**. **		**	** *.		Sn(Zn) 0.20
					*.	* .		Sn(Zn) 0.15
P		~	*	*P	P			Sn(Zn) 0.13 Sn(Zn) 0.10
0	20	30	40	<u> </u>	50		7	70
				20 (b)				

Fig. 1. X-ray diffraction patterns (a) for $Bi_{1.5}Zn_{0.92}Nb_{1.5-x}Sn_xO_{6.92-x/2}$ and (b) for $(Bi_{1.5-x/3}Zn_{0.46x/2}Sn_x)(Nb_{1.5}Zn_{0.46})O_{6.92}$ ceramics.

been reported that the pure $Bi_{1.5}Zn_{0.92}Nb_1O_{6.92}$ is always composed of a single phase while $Bi_{1.5}ZnNb_{1.5}O_7$ pyrochlore contains a very small amount of ZnO phase [8]. Consistent results were also reported by Levin et al. [10] who have analyzed the structure of $Bi_{1.5}ZnNb_{1.5}O_7$ pyrochlore and found that the cubic pyrochlore includes a small amount of ZnO. Wu et al. [2] investigated the microstructures of $Bi_{1.5}ZnNb_{1.5}O_7$ and $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ pyrochlores and proved that $Bi_{1.5}ZnNb_{1.5}O_7$ was not composed of a single phase pyrochlore but instead, it consists of an unusual structure of $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ and ZnO which is distributed evenly in the grains and at the boundaries.

For the purpose of electrical and dielectric measurements Sn doped BZN ceramics were sintered to obtain high density pellets. The sintering temperatures (T_s) and the densities of Sn doped BZN ceramics are given in Table 1. The table includes the density measured by Archimedes method (ρ_B) and the theoretical (ρ_{th}) one which was calculated from the X-ray diffraction data using the calculated lattice constants. All the samples were restricted to have a relative density (ρ_r) greater than 97%. The samples which exhibited a low relative density were improved by raising the sintering temperature. The highest relative density of 99.9% displayed in Table 1- relates to replacement of Nb by 0.10 Sn in the B-site, the next is 99.43% obtained by replacement of Zn by 0.06 Sn in the A-sites of the pyrochlore.

Dielectric analysis

The effects of Sn(Nb) and Sn(Zn) doping ratios on the dielectric constant (ϵ) of the singe phased Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92} pyrochlore ceramics are presented in Table 1. As seen from the table, the value of the dielectric constant of the pure sample at room temperature is 178. It increases to 266 and decreases to 167 for 0.06 Sn(Nb) and Sn(Zn), doping ratios respectively. It also decreases from 266 to 207 for Sn(Nb) and increases from 167 to 187, for Sn(Zn) when the Sn content is raised from 0.06 to 0.10. The presented data indicates a pronounced effect of site substitution on the dielectric properties. Namely, a high tunability of the dielectric constant is obtained by the doping ratio and type selection.

Table 1 displays the Sn content effect on the room temperature dielectric loss $(tan(\delta))$ being recorded at a frequency (f) of 0.1 MHz for BZN pyrochlore ceramics. The room temperature dielectric loss values are mostly of the order of ~10⁻⁴. As the table reflects most of the dielectric loss values are of the same order of magnitude regardless of the Sn doping type or ratio. This order of magnitude is relatively low for all the samples under investigation. This property makes the Sn doped ceramics attractive for application in telecommunication electronics.

Fig. 2(a) and (b), reflects the room temperature



Fig. 2. The frequency dependence of a) the relative dielectric constant and b) the dielectric loss for Sn doped BZN pyrochlores.



Fig. 3. The temperature effect on the ε -*f* dependence for a) x = 0.06 Sn(Nb) b) x = 0.06 Sn(Zn) c) x = 0.10 Sn(Nb) and d) x = 0.10 Sn(Zn).

frequency (f) dependence of dielectric constant for the samples doped with 0.06 and 0.10 and dielectric loss $(\tan(\delta))$ for the samples doped with 0.06 Sn for the Bi_{1.5}Zn_{0.92}Nb_{1.5-x}Sn_xO_{6.92-x/2} and for (Bi_{1.5-x/3}Zn_{0.46-x/2}Sn_x)(Nb_{1.5}Zn_{0.46})O_{6.92}, respectively. At any particular doping ratio, the dielectric constant value is the same

regardless of the applied AC signal frequency. On the other hand, the dielectric loss shown in Fig. 2 (b) reflected a very strong dependency on applied AC signal frequency. While the dielectric loss of the sample doped Sn(Nb) slightly increases with increasing frequency, the Sn(Zn) doping shown a sharp decrease in $\tan(\delta)$ with increasing f.

Fig. 3 (a)-(d) illustrates the dielectric constants of the samples under investigation being recorded at different temperatures (T) in the temperature range of 298-473 K. At all temperatures for the sample which contains 0.06 Sn(Nb), the dielectric constant values are observed to be frequency independent. At any particular temperature, the dielectric constant value is the same regardless of the applied frequency. The samples which are doped with 0.06 and 0.10 Sn(Zn) and 0.10 Sn(Nb), (Fig. 3 (b), (c) and (d), respectively), reflected a very weak frequency dependence of the dielectric constant. In general, increasing the temperature decreases the value of the dielectric constant. As for example, for one of the presented samples (x = 0.10 of Sn(Nb)), at 1.5 MHz, the dielectric constant decreases from 208 to \sim 191 as the temperature is raised from 298 to 473 K, respectively. The temperature coefficient of dielectric constant, α_{e} , which was calculated from the relation $\alpha_{\varepsilon} = (\varepsilon_{T2} - \varepsilon_{T1})/(\varepsilon_{T1}(T_2 - T_1))$ with T_1 and T_2 being 298 and 393 K, respectively, and displayed in Table 1, was found to increase from -647 in pure BZN to -493 for x = 0.06 Sn(Nb) and reaches -432 ppmK⁻¹ for x = 0.10 Sn(Nb). For a Sn(Zn) doping ratio of 0.06 and 0.10 α_{ϵ} is -331 and -353, respectively.

The decrease in the value of the dielectric constant with increasing temperature may be attributed to the contribution of more than one type of polarization, electronic, ionic, dipolar and space charge polarization. The nature of the variation of the dielectric constant as a function of temperature and frequency determines which type of contribution is dominant [11]. Since the dielectric constant is frequency independent as shown in Fig. 3, it indicates no role of the applied electric

Table 1. Synthesis, dielectric and electrical parameters of Sn doped Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92} ceramics.

Parameter	Pure	$Sn(Nb) \\ x = 0.06$	$\frac{\text{Sn(Nb)}}{\text{x} = 0.10}$	Sn(Zn) x = 0.06	Sn(Zn) x = 0.10					
$\rho_{th} (g/cm^3)$	7.11	7.06	7.06	7.01	6.96					
$\rho_B (g/cm^3)$	6.67	6.95	7.05	6.97	6.83					
$ ho_r$ (%)	93.81	98.5	99.90	99.43	97.96					
T_s (°C)	1000	1025	1025	1025	1025					
ε (0.1 MHz)	178	266	207	167	182					
$\tan(\delta) (0.1 \text{ MHz})$	8.00×10^{-4}	12.54×10^{-4}	3.24×10^{-4}	$7.36 imes 10^{-4}$	8.32×10^{-4}					
$\alpha_{\varepsilon} (ppm/{}^{o}C)$	-674	-493	-432	-331	-353					
$\sigma \left(\Omega \text{ cm} \right)^{-1}$	5.08×10^{-10}	8.3×10^{-11}	1.1×10^{-11}	7.3×10^{-12}	6.9×10^{-12}					
$E_{\sigma} (T < 400 \text{ K}) (eV)$	0.022	0.124	0.793 (T > 350 K)							
$E_{\sigma} (T < 400 \text{ K}) (eV)$	0.415	1.371	1.474	1.989	1.978					



Fig. 4. a) The temperature dependence of the dielectric loss for sample doped with 0.06 Sn(Zn). b) The σ -T dependence.

field on the electronic polarization processes. In this region the decrease of the dielectric constant with temperature may be mainly due to the contribution of the same type of polarization.

Fig. 4(a) reflects an illustrative example of the dependence of the dielectric loss on temperature for the Sn(Zn) with x = 0.06 doping ratio. As seen from the plots of the figure, the value of $tan(\delta)$ increases with increasing temperature. The increase in the dielectric loss with increasing temperature was also observed for $SrBi_2V_xNb_{2-x}O_9$ ceramics [12]. The behavior of loss values was attributed to the intrinsic defect formation at higher temperatures. The formation of defects in the ceramics structure was assigned to the expected bismuth and/ or $[Bi_2O_2]^{-2}$ evaporation at high temperatures. For this reason, the samples may have possessed vacancies generating charge carriers [13]. The introduction of V in place of niobium is suggested to ease the release of the charge carriers and therefore the doped samples would show a higher loss at higher temperatures. Similar behavior of the $tan(\delta)$ -T dependence which show a maximum loss at particular temperatures was observed for Sn doped Ba $(Ti_{1-x}Sn_x)O_3$ [14]. The phenomena was attributed to the existence of the non-homogeneous polar regions in the samples.

The values of the dielectric constant determined here lay in the preferable range for microwave detection [3, 15, 16] The variation of the dielectric constant of bismuth-zinc-niobium pyrochlore ceramics with Sn content, the low dielectric loss of the dielectric constant, the relatively low sintering temperature, the dielectric constant-frequency stability, the linear variation of the dielectric constant with temperature, and the small light weight of these ceramics make them suitable and attractive multifunctional electronic components that can be implanted in wireless communication technology.

Electrical conductivity analysis

The DC electrical conductivity was measured by the Hall bar technique. The values of the electrical



Fig. 5. The $\ln(\sigma)$ -T⁻¹ in the high temperature region. The solid lines represent the slopes of the curves.

conductivities (σ) recorded around room temperature are displayed in Table 1. Generally, the electrical conductivities of the samples are very low. While the pure sample exhibits conductivity value of the order of 10⁻¹⁰ (Ω cm⁻¹), the Sn doped samples exhibited a bit lower conductivity values. The difference between doped and pure samples is approximately one order of magnitude for Sn(Nb) and two orders of magnitude for Sn(Zn) indicating that the electrical conductivity depends on the ionic radius and metal substitution type.

Fig. 4(b) illustrates the variation of dc electrical conductivity with temperature. As seen from the figure, for the samples under investigation, the conductivity increases with increasing temperature. The variation of the electrical conductivity with temperature follows different rates in different temperature regions. Except for the sample which contains 0.10 Sn(Nb), for both pure and doped samples in the temperature region of 300-395 K, the σ -T variation is weak. In the temperature region of 400-500 K, the dependence of conductivity on temperature is very high for both pure and doped samples. Regardless of the temperature range, the thermally activated electrical conductivity of the pure and doped samples follows the relation, σ $\alpha \exp(-E_{\sigma}/kT)$ where E_{σ} is the conductivity activation energy. The linear slopes -shown by solid lines in Fig. 5- of the plots of the $\ln(\sigma) \cdot T^{-1}$ allowed the determination of the conductivity activation energies as 0.022 and 0.124, 0.793 eV, below 400 K for the pure, 0.06 and 0.10 doped Sn(Nb) (not shown in Fig. 5) samples and 0.415 and 1.371 eV, 1.474 and 1.989 and 1.978 above 400 K, for the pure and 0.06, 0.10 Sn(Nb) doped and 0.06 and 0.10 Sn(Zn) doped samples, respectively.

The existence of the energy levels in the pure samples may be attributed to the formation of intrinsic defects. On the other hand, the values of the conductivity activation energies being 0.124, 0.793 and 1.371 eV are mainly due to the Sn(Nb) substitution in the pure samples. The values reflect the existence of deep impurity levels in the energy gap of the BZN pyrochlore [7]. The value of the activation energies being $\sim 2.0 \text{ eV}$ for Sn(Zn) is much greater than that determined as ~1.4 for Sn(Nb) substitutions. This difference in the values may be attributed to the ionic radius. Because the radius of $Sn_{6-coord}$. is equal to that of Nb, while the radius of $Sn_{8-coord}$ (0.81 Å) is less than that of Zn (0.91 Å) very large potential barriers are expected to be created at the grain boundaries of the pyrochlore. The constant electrical conductivity with increasing temperature which was observed for the sample which contains Sn in the temperature region of 300-395 K, may indicate that the electrical conductivity is not dominated by the bulk ceramic material, but by the resistance of the ceramic- surface contacts in the material. This behavior could have happed due to the increased lattice imperfections associated with the growth of the ZnO phase which becomes pronounced for x values of 0.30 for Sn(Nb) and 0.13 for Sn(Zn).

Conclusions

The structural, dielectric and electrical properties of the $Bi_{1.5}Zn_{0.92}Nb_1O_{6.92}$ pyrochlore ceramics are altered by the substitution of tin in place of niobium at the Bsite and in place of zinc in the A-site of the pyrochlore ceramics. The single phase formation of the ceramics was possible for tin contents of 0.25 in the B-site and 0.10 in the A-site. The metallic substitution significantly changed the dielectric constant and its temperature coefficient and lowered the electrical conductivity. The temperature dependence of the frequency dependent dielectric constant and the DC electrical conductivity are highly attenuated by the doping type and ratio.

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