

# Synthesis and dielectric properties of pyrochlore solid solutions in the $\text{Bi}_2\text{O}_3\text{-ZnO-Nb}_2\text{O}_5\text{-TiO}_2$ system

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Phase studies of solid solutions based on  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Ti}_{1.5}\text{Nb}_{0.5})\text{O}_7$  revealed extended regions of pyrochlore formation in the  $\text{Bi}_2\text{O}_3\text{-ZnO-TiO}_2\text{-Nb}_2\text{O}_5$  system. At room temperature and 1 MHz  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Ti}_{1.5}\text{Nb}_{0.5})\text{O}_7$  has a high permittivity ( $\kappa' = 200$ ), low dielectric loss ( $\tan \delta < 1 \cdot 10^{-4}$ ) and a temperature coefficient of the permittivity,  $\tau_\kappa = -1300$  ppm/K. Pyrochlore solid solutions based on  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Ti}_{1.5}\text{Nb}_{0.5})\text{O}_7$  can be formed with  $(\text{Bi}_{2-x}\text{Zn}_x)(\text{Ti}_{2-x}\text{Nb}_x)\text{O}_7$  ( $0.35 \leq x \leq 1.0$ ) and with  $(\text{Bi}_{1.5}\text{Zn}_{0.5-y/3}\text{Ti}_{1.5+y}\text{Nb}_{0.5-2y/3})\text{O}_7$  ( $-1.5 \leq y \leq 0.75$ ). Investigations of the dielectric characteristics showed that the high temperature dependence of the permittivity of  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Ti}_{1.5}\text{Nb}_{0.5})\text{O}_7$  can be significantly modified by changing the composition of the pyrochlore within these regions of solid solubility. Below room temperature several of these compositions also exhibit a diffuse frequency dependent maximum in their permittivity characteristic of a transition to a relaxor type ferroelectric state. A third region of high permittivity pyrochlores with  $(\text{Bi}_{1.5+2z}\text{Zn}_{0.25-z}\text{Ti}_{2.25-z})\text{O}_7$  ( $0.0 \leq z < 0.15$ ) was also identified in the  $\text{Bi}_2\text{O}_3\text{-ZnO-TiO}_2$  sub system. © 1999 Kluwer Academic Publishers

## 1. Introduction

Recent studies of the dielectric properties of a series of Bi-based pyrochlores have demonstrated that they may be suited toward applications as co-fired dielectric components. Of particular note are members of the  $\text{Bi}_2(\text{M}'\text{M}'')\text{O}_7$  and  $\text{Bi}_2(\text{M}'_{2/3}\text{M}''_{4/3})\text{O}_7$  families of pyrochlores with  $\text{M}' = \text{Zn, Mg, Ni, Sc, In, and Cu}$ ;  $\text{M}'' = \text{Nb, Ta}$ . For these systems compounds such as  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  exhibit permittivities ( $\kappa'$ ) of 170 with quite low dielectric losses ( $\tan \delta = 4 \cdot 10^{-4}$ ). In an attempt to understand the correlations between the bulk chemistry, structure, and dielectric properties of these systems we have examined how their properties respond to selected cation substitutions. In a previous paper we reported on the relationship between the sizes of the cations in the pyrochlores and the temperature dependence of their permittivity. In this paper we examine the formation of pyrochlores in the  $\text{Bi}_2\text{O}_3\text{-ZnO-Nb}_2\text{O}_5\text{-TiO}_2$  system and report the dielectric properties of a series of new solid solution systems.

Stoichiometric pyrochlores have the general formula  $\text{A}_2\text{B}_2\text{O}_7$ . The structure is composed of two different types of cation coordination polyhedra; the A-site positions are eight coordinate and are typically occupied by larger cations, while smaller sized cations favor the six-coordinate B-site positions. The structure can accommodate a wide range of different chemical substituents and many different examples

of pyrochlores have been reported in the literature. For the Bi-based systems, in which the larger  $\text{Bi}^{3+}$  cations preferentially occupy the A-site positions, pyrochlores with permittivities of approximately 20 and modest dielectric losses ( $\tan \delta = 7 - 19 \cdot 10^{-4}$ ) were reported in the  $\text{Bi}_2\text{O}_3\text{-Sb}_2\text{O}_5\text{-MO}$  ( $\text{M} = \text{Cd, Zn}$ ) systems [1]. For these  $\text{M}_{2-2x}\text{Bi}_{3x}\text{Sb}_{2-x}\text{O}_7$  solid solutions the changes in stoichiometry could be used to control and adjust the temperature coefficient of the permittivity ( $\tau_\kappa$ ). Significantly higher permittivities were reported for the  $\text{Bi}_2(\text{M}'\text{M}'')\text{O}_7$  and  $\text{Bi}_2(\text{M}'_{2/3}\text{M}''_{4/3})\text{O}_7$  systems ( $\text{M}' = \text{Zn, Mg, Ni, Sc, In, Cu}$  and  $\text{M}'' = \text{Nb, Ta}$ ) [2]. For example, in the  $\text{Bi}_2\text{O}_3\text{-ZnO-Nb}_2\text{O}_5$  system two stoichiometric pyrochlores, cubic  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  and orthorhombic  $\text{Bi}_2(\text{Zn}_{2/3}\text{Nb}_{4/3})\text{O}_7$ , were reported with  $\kappa' = 170$  and 90, and  $\tau_\kappa = -400$  ppm/K and 150 ppm/K, respectively [3]. Because intermediate compositions could be prepared with an equilibrium coexistence of both phases ceramics with close to zero  $\tau_\kappa$  could also be prepared. In a recent study it was demonstrated that the temperature coefficients of these systems can also be tuned by introducing cation substituents on to the A (e.g. Gd) and B-site (e.g. Ti, Zr) positions [4].

Because only a relatively small number of high permittivity Bi pyrochlores have been investigated, we have focused on identifying new compositions that exhibit promising dielectric properties. We have shown

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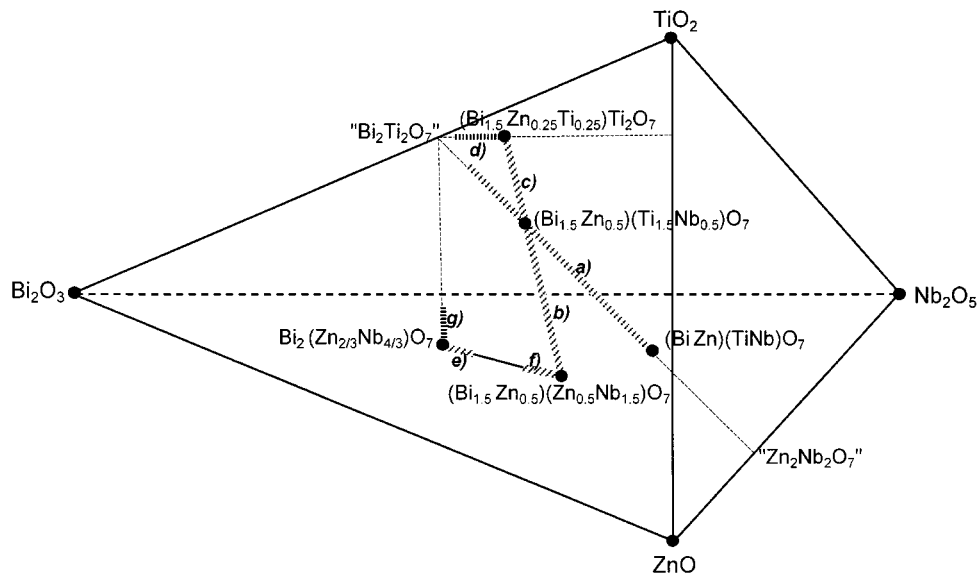


Figure 1 Schematic representation of the pyrochlore solid solutions in the  $\text{Bi}_2\text{O}_3\text{-ZnO-Nb}_2\text{O}_5\text{-TiO}_2$  quaternary system: a)  $(\text{Bi}_{1-x}\text{Zn}_x)(\text{Ti}_{2-x}\text{Nb}_x)\text{O}_7$ ; b)  $(\text{Bi}_{1.5}\text{Zn}_{0.5-y/3}\text{Ti}_{1.5+y}\text{Nb}_{0.5-2y/3})\text{O}_7$  for  $0.0 \leq y \leq 0.75$ ; c)  $(\text{Bi}_{1.5}\text{Zn}_{0.5-y/3}\text{Ti}_{1.5+y}\text{Nb}_{0.5-2y/3})\text{O}_7$  for  $-1.5 \leq y \leq 0.0$ ; d)  $(\text{Bi}_{1.5+2z}\text{Zn}_{0.25-z}\text{Ti}_{2.25-z})\text{O}_7$ ; e)  $\text{Bi}_{2-h}\text{Zn}_{2/3+2h/3}\text{Nb}_{4/3+h/3}\text{O}_7$ , [3]; f)  $(\text{Bi}_{1.5+j}\text{Zn}_{0.5-j})(\text{Zn}_{0.5+j/3}\text{Nb}_{1.5-j/3})\text{O}_7$ , [3]; g)  $\text{Bi}_2(\text{Zn}_{2/3-i/3}\text{Nb}_{4/3-2i/3}\text{Ti}_i)\text{O}_7$ , [4].

that the cubic pyrochlore  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  can accommodate a range of dopants of various ionic sizes [4] that permit considerable tuning of the temperature coefficient of the permittivity. In certain cases these compositions could be sintered to full-density ceramics at 1000 °C. In that study we also reported on the preparation of a Ti-substituted pyrochlore  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Ti}_{1.5}\text{Nb}_{0.5})\text{O}_7$  with  $\kappa' = 200$  and a low dielectric loss ( $\tan \delta = 5 \times 10^{-4}$ ). In this paper this composition is used as a starting point for an investigation of the formation of pyrochlore solid solutions in the  $\text{Bi}_2\text{O}_3\text{-ZnO-TiO}_2\text{-Nb}_2\text{O}_5$  system. A schematic diagram of this system is shown in Fig. 1, this includes the regions of pyrochlore formation reported previously for the  $\text{Bi}_2\text{O}_3\text{-ZnO-Nb}_2\text{O}_5$  system (lines f, e) and the limited range of solubility of Ti in orthorhombic  $\text{Bi}_2(\text{Zn}_{2/3}\text{Nb}_{4/3})\text{O}_7$  (line g). The newly discovered regions of pyrochlore formation and their associated dielectric properties are reported below.

## 2. Experimental procedure

All of the compositions in the  $\text{Bi}_2\text{O}_3\text{-ZnO-Nb}_2\text{O}_5\text{-TiO}_2$  system were prepared using solid state reaction techniques. Stoichiometric mixtures of high purity (>99.9%) reagent-grade oxides were homogenized and pre-reacted at 650 °C for two hours. At that stage  $\text{Bi}_2\text{O}_3$  reacts with the other oxides present in the mixture to form less volatile compounds that permit additional firing at higher temperature with minimal loss of Bi. The pre-reacted powder was re-fired at temperatures ranging from 900 to 1100 °C with an intermediate cooling and grinding to achieve equilibrium. The powders were then uniaxially pressed into pellets at 150 MPa. Approximately  $9 \times 1.5$  mm sized pellets were sintered at temperatures between 1000 and 1150 °C. The density of all the samples was determined to be greater than 95% of the theoretical value.

The progress of the solid state reactions was monitored by powder X-ray diffraction using a Rigaku

Geigerflex D-Max-B X-ray diffractometer with  $\text{CuK}\alpha$  radiation. Lattice parameters were calculated by the least-squares method from data collected at a scan rate of 0.5°/min over the range  $10 < 2\theta < 70$ . Powdered Ag was used as an internal standard. Scanning electron microscope (SEM) imaging and energy dispersive X-ray (EDX) microanalyses of the ceramics were carried out with a JEOL JMS 6400 scanning electron microscope equipped with an Oxford Instruments spectrometer.

The dielectric measurements were made at frequencies from 1 kHz to 1 MHz on silver-plated pellets using a high precision LCR meter (HP 4824A). The temperature dependence of the dielectric properties was measured from -170 to 100 °C by placing the ceramics in an environmental chamber (Delta Design, Delta 9023) and monitoring the temperature with a copper-constantan (T-type) thermocouple. The temperature coefficients of the permittivity ( $\tau_\kappa$ ) were determined from the change in the permittivity over the temperature range -20–80 °C.

## 3. Results and discussion

### 3.1. Synthesis and characterization

#### of $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Ti}_{1.5}\text{Nb}_{0.5})\text{O}_7$

Single phase samples of  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Ti}_{1.5}\text{Nb}_{0.5})\text{O}_7$  were formed by firing the pre-reacted oxide mixture at 950 °C for three hours. The X-ray pattern was indexed in terms of a face-centered cubic pyrochlore cell with  $a = 10.360(2)$  Å (Table I). Although no direct investigations were made to identify the individual site occupancies of the different cations in  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Ti}_{1.5}\text{Nb}_{0.5})\text{O}_7$ , previous investigations of closely related Bi pyrochlores and consideration of the ionic radii of the different cations support a description in which the larger Bi and Zn cations are located in the A-site position and the smaller Ti and Nb cations occupy the B-site sub-lattice.

TABLE I X-ray diffraction data for  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Ti}_{1.5}\text{Nb}_{0.5})\text{O}_7$ 

$h$	$k$	$l$	$d_{\text{calc}}$	$d_{\text{obs}}$	$I_{\text{obs}}$
1	1	1	5.979	5.993	15
3	1	1	3.122	3.124	13
2	2	2	2.990	2.991	100
4	0	0	2.589	2.589	34
3	3	1	2.376	2.376	18
5	1	1	1.993	1.992	5
3	3	3	1.993	—	—
4	4	4	1.831	1.831	37
5	3	1	1.751	1.751	4
4	4	2	1.726	1.725	1
6	2	0	1.637	1.637	1
6	2	2	1.561	1.562	28
4	4	4	1.495	1.495	7

The dielectric properties of  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Ti}_{1.5}\text{Nb}_{0.5})\text{O}_7$  were measured on high density ceramics that were prepared by sintering the pressed single phase powders at  $1100^\circ\text{C}$  for 1 h. At 1 MHz  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Ti}_{1.5}\text{Nb}_{0.5})\text{O}_7$  exhibits a high permittivity ( $\kappa' = 200$ ), and a low dielectric loss ( $\tan \delta < 1 \cdot 10^{-4}$ ). However, the temperature coefficient of the permittivity is very high ( $\tau_\kappa = -1300$  ppm/K). In an attempt to prepare high permittivity, low loss ceramics with a lower  $\tau_\kappa$ , a systematic search was made for new pyrochlore solid solutions based on  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Ti}_{1.5}\text{Nb}_{0.5})\text{O}_7$ . By exploring different types of chemical substitutions, e.g.  $[\text{Bi}^{3+} + \text{Ti}^{4+} = \text{Zn}^{2+} + \text{Nb}^{5+}]$ ,  $[\text{Ti}^{4+} = 1/3\text{Zn}^{2+} + 2/3\text{Nb}^{5+}]$ , and  $[2\text{Bi}^{3+} = \text{Zn}^{2+} + \text{Ti}^{4+}]$ , three new pyrochlore forming regions of solid solubility were identified. These systems, which are identified in the schematic

phase diagram in Fig. 1, and their associated dielectric properties are described below.

### 3.2. $(\text{Bi}_{2-x}\text{Zn}_x)(\text{Ti}_{2-x}\text{Nb}_x)\text{O}_7$ solid solutions

$(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Ti}_{1.5}\text{Nb}_{0.5})\text{O}_7$  was found to be one member of a solid solution system in which Bi and Ti can be substituted by Zn and Nb ( $\text{Bi}^{3+} + \text{Ti}^{4+} = \text{Zn}^{2+} + \text{Nb}^{5+}$ ). This region of solid solubility (line “a” in Fig. 1) can be described by the general formula  $(\text{Bi}_{2-x}\text{Zn}_x)(\text{Ti}_{2-x}\text{Nb}_x)\text{O}_7$  and extends toward two end-members,  $\text{Bi}_2\text{Ti}_2\text{O}_7$  and  $\text{Zn}_2\text{Nb}_2\text{O}_7$ , which themselves cannot be prepared with the pyrochlore structure by standard solid state methods. In these end-members the ratio of the radii of the A and B site cations is either too large ( $\text{Bi}_2\text{Ti}_2\text{O}_7$ ) or too small ( $\text{Zn}_2\text{Nb}_2\text{O}_7$ ) to lie in the field of stability identified for the formation of the pyrochlore structure [5]. However, stable  $(\text{Bi}_{2-x}\text{Zn}_x)(\text{Ti}_{2-x}\text{Nb}_x)\text{O}_7$  pyrochlores with radius ratios that lie within the stability field could be prepared with  $0.35 \leq x \leq 1.0$ . The X-ray patterns of compositions within and just outside this range are shown in Fig. 2. The cell parameter of the pyrochlores varies linearly with composition inside the solid solubility field and ranges from  $a = 10.371(3)$  Å for  $(\text{Bi}_{1.65}\text{Zn}_{0.35})(\text{Ti}_{1.65}\text{Nb}_{0.35})\text{O}_7$  to  $a = 10.330(2)$  Å for  $(\text{BiZn})(\text{TiNb})\text{O}_7$  (Fig. 3). For  $x < 0.35$  the additional phases were identified as  $\text{Bi}_3\text{TiNbO}_9$ ,  $\text{ZnTiO}_3$ , and  $\text{TiO}_2$ . After exceeding the solid solubility limit at the high  $x$  end ( $> 1.0$ ) the secondary phases were  $\text{ZnNb}_2\text{O}_6$ ,  $\text{Zn}_2\text{TiO}_4$ , and  $\text{BiNbO}_4$ .

The permittivities of the  $(\text{Bi}_{2-x}\text{Zn}_x)(\text{Ti}_{2-x}\text{Nb}_x)\text{O}_7$  ceramics show an essentially linear dependence with

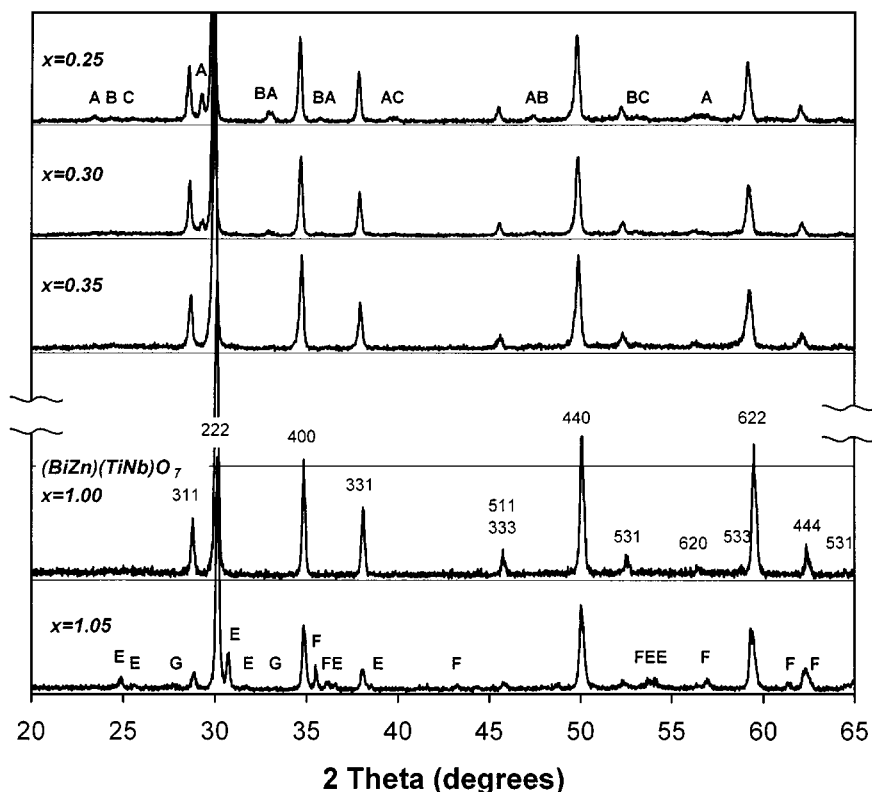


Figure 2 X-ray diffraction patterns of  $(\text{Bi}_{2-x}\text{Zn}_x)(\text{Ti}_{2-x}\text{Nb}_x)\text{O}_7$  with different  $x$ : A =  $\text{Bi}_3\text{TiNbO}_9$ ; B =  $\text{ZnTiO}_3$ ; C =  $\text{TiO}_2$ ; E =  $\text{ZnNb}_2\text{O}_6$ ; F =  $\text{Zn}_2\text{TiO}_4$ ; G =  $\text{BiNbO}_4$ .

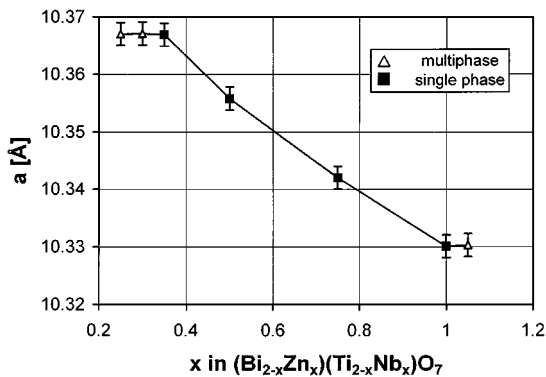


Figure 3 Cell parameters for the  $(\text{Bi}_{2-x}\text{Zn}_x)(\text{Ti}_{2-x}\text{Nb}_x)\text{O}_7$  system.

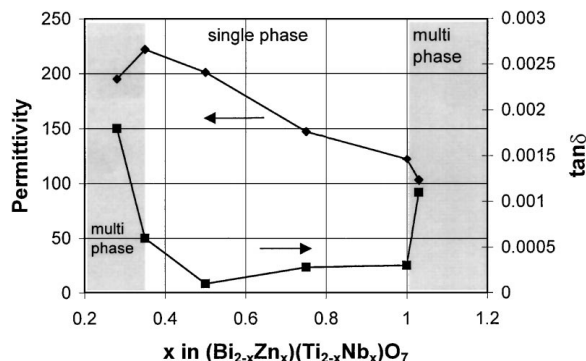


Figure 4 Permittivity and dielectric losses for  $(\text{Bi}_{2-x}\text{Zn}_x)(\text{Ti}_{2-x}\text{Nb}_x)\text{O}_7$  ceramics at 1 MHz.

composition (Fig. 4). At room temperature the highest permittivity is exhibited by the low- $x$  end member ( $x = 0.35$ ,  $\kappa' = 222$ ). For the higher  $x$  compositions, where the concentration of the highly polarizable Ti and Bi ions is decreased, the permittivity decreases to 122 for  $x = 1.0$ . The dielectric losses are low across the entire region of solid solubility and only increase above  $\tan \delta = 3 \cdot 10^{-4}$  (at 1 MHz) for the low- $x$  end member. The increase may reflect the presence of trace amounts of the secondary phases; however, these were not observed in either the X-ray or SEM studies of the  $(\text{Bi}_{1.65}\text{Zn}_{0.35})(\text{Ti}_{1.65}\text{Nb}_{0.35})\text{O}_7$  ( $x = 0.35$ ) ceramics. The temperature coefficient of the permittivity also varies systematically with  $x$  and ranges from  $\tau_\kappa = -1330$  ppm/K for  $x = 0.35$ , to  $-870$  ppm/K for  $x = 1.0$ .

### 3.3. $\text{Bi}_{1.5}\text{Zn}_{0.5-y/3}\text{Ti}_{1.5+y}\text{Nb}_{0.5-2y/3}\text{O}_7$ solid solutions

The coupled substitution of Ti by Zn and Nb ( $\text{Ti}^{4+} = 1/3\text{Zn}^{2+} + 2/3\text{Nb}^{5+}$ ) in  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Ti}_{1.5}\text{Nb}_{0.5})\text{O}_7$  also produced extensive ranges of pyrochlore solid solution formation. For this mechanism of substitution the composition of the solid solutions can be described by the general formula  $\text{Bi}_{1.5}\text{Zn}_{0.5-y/3}\text{Ti}_{1.5+y}\text{Nb}_{0.5-2y/3}\text{O}_7$ . For positive values of  $y$  single phase Ti-rich cubic pyrochlores could be formed up to a  $y = 0.75$  end-member,  $\text{Bi}_{1.5}\text{Zn}_{0.25}\text{Ti}_{1.25}\text{O}_7$ , in the  $\text{Bi}_2\text{O}_3$ -ZnO- $\text{TiO}_2$  ternary system (region c in Fig. 1). For negative values of  $y$  the Ti-deficient solid solutions extend toward the  $y = -1.5$ ,  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$ , end-member previously reported in the  $\text{Bi}_2\text{O}_3$ -ZnO- $\text{Nb}_2\text{O}_5$

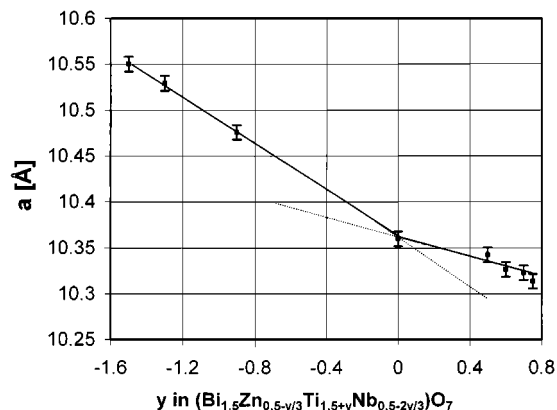


Figure 5 Cell parameters of the  $(\text{Bi}_{1.5}\text{Zn}_{0.5-y/3}\text{Ti}_{1.5+y}\text{Nb}_{0.5-2y/3})\text{O}_7$  system for positive and negative  $y$ .

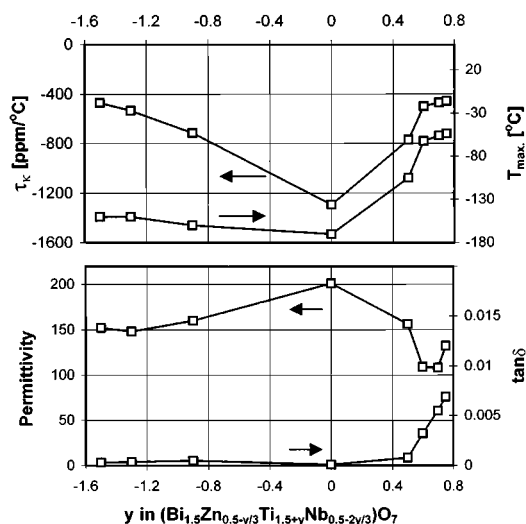


Figure 6 Variation of the room temperature permittivity ( $\kappa'$ ), temperature coefficient ( $\tau_\kappa$ ), dielectric loss ( $\tan \delta$  at 1 MHz), and the temperature of the permittivity maximum ( $T_{\max}$ ) as a function of composition in the  $(\text{Bi}_{1.5}\text{Zn}_{0.5-y/3}\text{Ti}_{1.5+y}\text{Nb}_{0.5-2y/3})\text{O}_7$  system.

ternary system (region b in Fig. 1). The variation of the lattice parameters for these solid solutions are shown in Fig. 5 for  $-1.5 \leq y \leq 0.75$ . In accordance with the relative ionic sizes of  $\text{Ti}^{4+}$  ( $= 0.605 \text{ \AA}$ ) and  $[1/3\text{Zn}^{2+} + 2/3\text{Nb}^{5+}]$  ( $= 0.67 \text{ \AA}$ ) the cell parameters decrease with the introduction of Ti (positive values of  $y$ ) and increase with the replacement of Ti (negative values of  $y$ ). However, the cell parameters are not linear across the entire system and a change in the variation with composition at  $y = 0$  provides evidence for an alteration in the mechanism of the substitution for positive and negative values of  $y$ .

Additional evidence for a change in the substitution mechanism was obtained from the variation of the dielectric properties across the region of solid solubility, see Fig. 6. At room temperature the permittivity of samples with  $y$  between 0.0 and  $-1.5$  systematically decrease as Ti is removed from  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Ti}_{1.5}\text{Nb}_{0.5})\text{O}_7$ ; for example,  $y = 0$ ,  $\kappa' = 200$ ;  $y = -1.5$ ,  $\kappa' = 152$ . However, the permittivity also decreases when additional Ti is introduced into  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Ti}_{1.5}\text{Nb}_{0.5})\text{O}_7$ ; for example,  $y = 0.6$ ,  $\kappa' = 109$ . The two sides of the system also showed

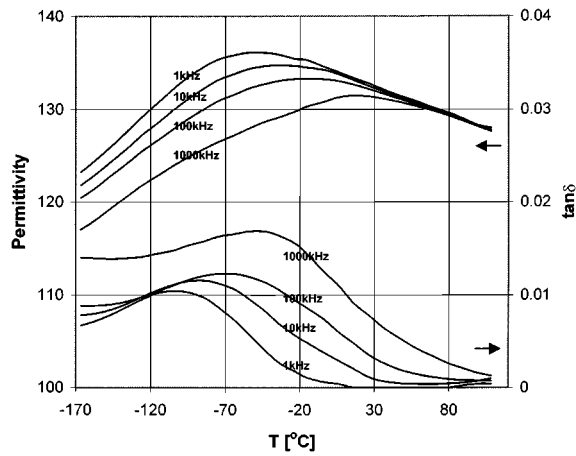


Figure 7 Permittivity and dielectric losses of  $(\text{Bi}_{1.5}\text{Zn}_{0.25}\text{Ti}_{2.25})\text{O}_7$  as a function of temperature and frequency.

opposite trends in the variation of the temperature coefficient of the permittivity with  $y$  (Fig. 6). For  $y$  negative  $\tau_\kappa$  increases from  $-1300$  ppm/K for  $y = 0.0$  to  $-470$  ppm/K for  $x = -1.5$ ; however for positive  $y$  the additional Ti increases the temperature coefficient ( $y = 0.75$ ,  $\tau_\kappa = -460$  ppm/K).

Additional differences in the two sides of this solid solution were observed in the temperature and frequency dependence of the dielectric properties. Data collected from a sample with  $y = 0.75$  from  $-170$  and  $100^\circ\text{C}$  at frequencies between  $1$  kHz and  $1$  MHz are shown in Fig. 7. Below room temperature the real and imaginary parts of the permittivity of this sample exhibit a diffuse frequency dependent maximum. This behavior is characteristic of a relaxor-type ferroelectric response, a feature that has been noted previously for other related Bi pyrochlore systems [2, 6]. Data collected from an entire range of the  $\text{Bi}_{1.5}\text{Zn}_{0.5-y/3}\text{Ti}_{1.5+y}\text{Nb}_{0.5-2y/3}\text{O}_7$  solid solutions indicated that for negative values of  $y$  the temperature of the permittivity maximum ( $\sim -150^\circ\text{C}$  at  $1$  kHz) is quite insensitive to changes in composition. However, for the positive  $y$ , Ti-rich compositions the position of the permittivity maximum shifts to higher temperatures; for example for  $y = 0.75$   $T_{\text{max}} = -45^\circ\text{C}$  at  $1$  kHz. Although additional data on the temperature dependent properties of this system will be reported elsewhere, for the purposes of this paper it is important to note that the variation of the properties with composition are again quite different in the Ti-rich (positive  $y$ ) and Ti-deficient (negative  $y$ ) regions of the solid solution system.

The different behavior of the two regions of this solid solution is also reflected by the dielectric losses at room temperature. For the members with negative  $y$  the dielectric loss at  $1$  MHz is quite low ( $\tan \delta < 5 \cdot 10^{-4}$ ) and relatively independent of composition. For the Ti-rich portion of the solid solution the loss increases as the temperature of the permittivity maximum approaches room temperature. For example in the end-member composition  $(\text{Bi}_{1.5}\text{Zn}_{0.25}\text{Ti}_{2.25})\text{O}_7$  ( $y = 0.75$ ) where  $\kappa' = 132$ ,  $\tan \delta = 7 \cdot 10^{-3}$  at  $1$  MHz.

The differences in the variations of the lattice parameter, permittivity, dielectric loss, and frequency

dispersion for positive and negative values of  $y$  can be interpreted in terms of the site occupancies of the cations in the pyrochlore solid solutions. As noted earlier, from consideration of the sizes of the different cations in  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Ti}_{1.5}\text{Nb}_{0.5})\text{O}_7$  Ti would be expected to have a strong preference for the smaller six-coordinate B-site position in the pyrochlore structure. For the Ti-deficient, negative  $y$  side of the  $\text{Bi}_{1.5}\text{Zn}_{0.5-y/3}\text{Ti}_{1.5+y}\text{Nb}_{0.5-2y/3}\text{O}_7$  solid solution system the introduction of Zn and Nb can be accomplished without affecting the preference of Ti for this position. However, for the Ti-rich compositions with  $0.0 \leq y \leq 0.75$ , the site distributions in the solid solution must change. One possible mode of substitution in this range could involve the introduction of additional Ti onto the B-site to replace the Nb cations, and partial substitution onto the A-site position for the Zn cations, i.e. formation of a solid solution with  $(\text{Bi}_{1.5}\text{Zn}_{0.5-y/3}\text{Ti}_{y/3})(\text{Ti}_{1.5+2y/3}\text{Nb}_{0.5-2y/3})\text{O}_7$ . An alternate mechanism, in which the Ti cations remain partitioned on the B-sites and the Nb cations are partially re-located on the A positions could also be possible up to  $y = 0.5$  where the solid solution would have a composition  $(\text{Bi}_{1.5}\text{Zn}_{1/3}\text{Nb}_{1/6})\text{Ti}_2\text{O}_7$ . However, because the region of solid solubility extends to  $y = 0.75$  even this mechanism would require some additional Ti to be located on the A-site positions. Without a series of detailed structural studies it is not possible to discriminate between these two mechanisms for the Ti-rich region. However in either case it is clear that the mechanism of substitution is different to that for solid solutions with negative  $y$ , and that the change in the site occupancies induces significant alterations in the dielectric response.

### 3.4. $(\text{Bi}_{1.5+2z}\text{Zn}_{0.25-z}\text{Ti}_{2.25-z})\text{O}_7$ solid solutions

Investigations of the coupled substitution of Zn and Ti by Bi ( $2\text{Bi}^{3+} = \text{Zn}^{2+} + \text{Ti}^{4+}$ ) in the Ti-rich,  $\text{Bi}_{1.5}\text{Zn}_{0.25}\text{Ti}_{2.25}\text{O}_7$  end member of the  $\text{Bi}_{1.5}\text{Zn}_{0.5-y/3}\text{Ti}_{1.5+y}\text{Nb}_{0.5-2y/3}\text{O}_7$  solid solution revealed an additional region of pyrochlore formation (region d in Fig. 1). This region of solid solubility extended from  $\text{Bi}_{1.5}\text{Zn}_{0.25}\text{Ti}_{2.25}\text{O}_7$  toward a hypothetical  $\text{Bi}_2\text{Ti}_2\text{O}_7$  end-member in the  $\text{Bi}_2\text{O}_3$ - $\text{TiO}_2$  system. As expected given the thermodynamic instability of the pyrochlore form of  $\text{Bi}_2\text{Ti}_2\text{O}_7$ , these solid solutions, which can be described as  $(\text{Bi}_{1.5+2z}\text{Zn}_{0.25-z}\text{Ti}_{2.25-z})\text{O}_7$  had a relatively limited range of homogeneity and could only be formed for  $0.0 \leq z < 0.15$  (Fig. 8). Samples with higher  $z$  contained additional peaks from  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ; according to the phase relations a small amount of a Ti-rich phase, most probably  $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ , should also be present. Samples outside the solubility limit with lower  $z$  contained second phases of  $\text{Zn}_2\text{TiO}_4$  and  $\text{TiO}_2$ .

As expected given the much larger size of the Bi cation the cell parameters of  $(\text{Bi}_{1.5+2z}\text{Zn}_{0.25-z}\text{Ti}_{2.25-z})\text{O}_7$  show a large change with  $z$  (Fig. 9). Although the region of solid solution is quite narrow the additional Bi cations also have a significant effect on the permittivity maxima associated with the low temperature anomaly described above.

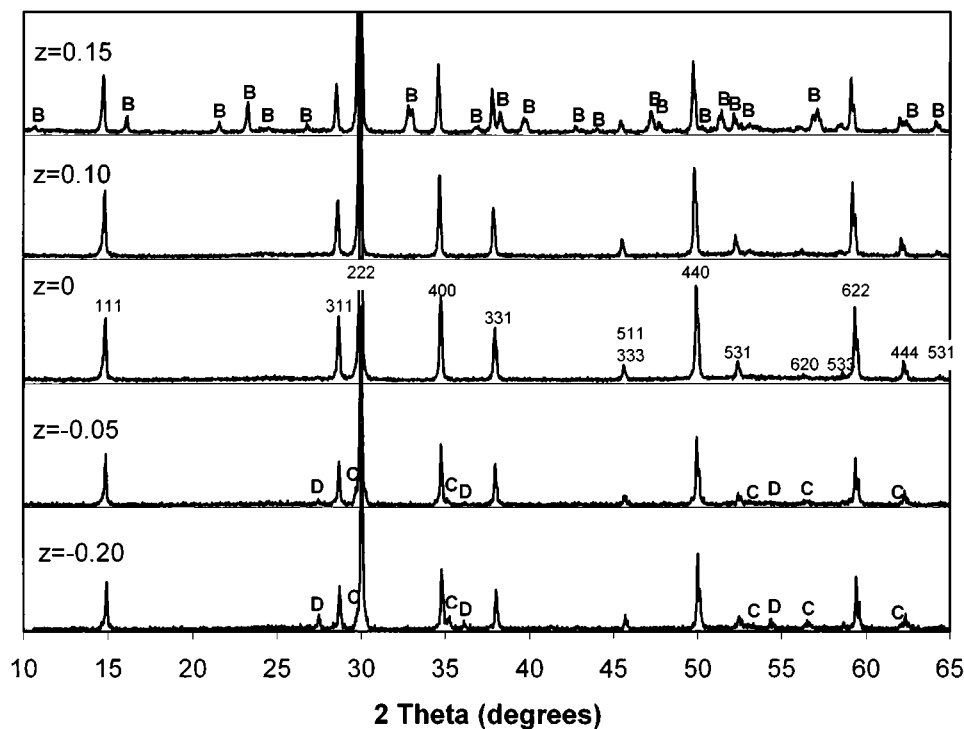


Figure 8 X-ray diffraction patterns of the samples in the  $(\text{Bi}_{1.5+2z}\text{Zn}_{0.25-z}\text{Ti}_{2.25-z})\text{O}_7$  system: B =  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ; C =  $\text{Zn}_2\text{TiO}_4$ ; D =  $\text{TiO}_2$ .

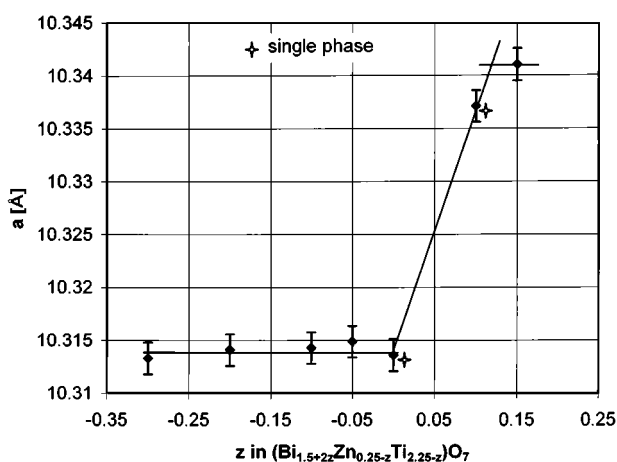


Figure 9 Cell parameters for the  $(\text{Bi}_{1.5+2z}\text{Zn}_{0.25-z}\text{Ti}_{2.25-z})\text{O}_7$  system.

For  $z=0.1$  the maximum occurs at  $-16^\circ\text{C}$ , this should be compared to  $-49^\circ\text{C}$  for  $z=0$ . Because of the proximity of this transition, the room temperature dielectric losses in this system are high and frequency dependent (for  $z=0$  see Fig. 7). The magnitude of the room temperature permittivity decreases with  $z$ ; for example,  $z=0.15$   $\kappa' = 92$ ;  $z=0$ ,  $\kappa' = 133$ ).

#### 4. Conclusions

Dense ceramics of the pyrochlore  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Ti}_{1.5}\text{Nb}_{0.5})\text{O}_7$  can be prepared at  $1100^\circ\text{C}$  and exhibit a high permittivity ( $\kappa' = 200$ ) and low dielectric loss ( $\tan \delta < 1 \cdot 10^{-4}$ ) at 1 MHz and room temperature. The temperature dependence of the permittivity of this compound,  $\tau_\kappa = -1300$  ppm/K, can be significantly modified through the formation of pyrochlore solid solutions in the  $\text{Bi}_2\text{O}_3$ - $\text{ZnO}$ - $\text{TiO}_2$ - $\text{Nb}_2\text{O}_5$  system. Three different regions of solid solubility were identified:

$(\text{Bi}_{2-x}\text{Zn}_x)(\text{Ti}_{2-x}\text{Nb}_x)\text{O}_7$  with  $0.35 \leq x \leq 1.0$ ;  $\text{Bi}_{1.5}\text{Zn}_{0.5-y/3}\text{Ti}_{1.5+y}\text{Nb}_{0.5-2y/3}\text{O}_7$  with  $-1.5 \leq y \leq 0.75$  and;  $(\text{Bi}_{1.5+2z}\text{Zn}_{0.25-z}\text{Ti}_{2.25-z})\text{O}_7$  with  $0.0 \leq z < 0.15$ . For the  $(\text{Bi}_{2-x}\text{Zn}_x)(\text{Ti}_{2-x}\text{Nb}_x)\text{O}_7$  system the replacement of Ti and Bi by Zn and Nb reduced the permittivity and a maximum value ( $\kappa' = 222$ ) was observed for the  $x=0.35$  end-member.  $\tau_\kappa$  showed a linear change across the system and ranging from  $-1300$  ppm/K for  $x=0.35$  to  $-870$  ppm/K for  $x=1.0$ . The structure and properties of the  $\text{Bi}_{1.5}\text{Zn}_{0.5-y/3}\text{Ti}_{1.5+y}\text{Nb}_{0.5-2y/3}\text{O}_7$  solid solutions showed different behavior for positive and negative values of  $y$ . In the  $y$  positive region ( $0.0 \leq y \leq 0.75$ ) the introduction of additional Ti decreases  $\kappa'$  and increases  $\tau_\kappa$ , while for  $y$  negative ( $-1.5 \leq y \leq 0.0$ ) the replacement of Ti decreases  $\kappa'$  and increases  $\tau_\kappa$ . Below room temperature the permittivities exhibit a frequency dependent maximum which shifts to higher temperature for higher Ti compositions. Similar transitions were observed in the  $(\text{Bi}_{1.5+2z}\text{Zn}_{0.25-z}\text{Ti}_{2.25-z})\text{O}_7$  solid solutions.

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