

# Local crystal chemistry, structured diffuse scattering and the dielectric properties of $(\text{Bi}_{1-x}\text{Y}_x)_2(\text{M}^{\text{III}}\text{Nb}^{\text{V}})\text{O}_7$ ( $M = \text{Fe}^{3+}, \text{In}^{3+}$ ) Bi-pyrochlores

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## Abstract

Electron diffraction is used to investigate the large amplitude displacive disorder characteristic of the  $\text{Bi}_2(\text{M}^{\text{III}}\text{Nb}^{\text{V}})\text{O}_7$  Bi-pyrochlores,  $\text{Bi}_2\text{InNbO}_7$  and  $\text{Bi}_2\text{FeNbO}_7$ , as well as of their *A* site substituted  $\text{Bi}_{1.5}\text{Y}_{0.5}\text{InNbO}_7$  and  $\text{Bi}_{1.5}\text{Y}_{0.5}\text{FeNbO}_7$  variants. Highly structured diffuse distributions in the form of  $\{110\}^*$  sheets of diffuse intensity perpendicular to the six  $\langle 110 \rangle$  directions of real space along with  $\langle 111 \rangle^*$  rods of diffuse intensity perpendicular to the four  $\{111\}$  real space planes are observed. The existence of this structured diffuse scattering is interpreted in terms of large amplitude,  $\beta$ -cristobalite-type tetrahedral rotations of the  $O'A_2$  tetrahedral framework sub-structure of the ideal pyrochlore structure type. Bond valence sum calculations are used to understand the local crystal chemistry responsible for such displacive disorder. The frequency-dependent dielectric properties of  $\text{Bi}_2\text{InNbO}_7$  and  $\text{Bi}_2\text{FeNbO}_7$  are also investigated along with the effect upon them of *A* site doping with Y.

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**Keywords:** Structured diffuse scattering; Electron diffraction investigation of; Bi-pyrochlores; Displacive disorder therein

## 1. Introduction

The ever-expanding global market for wireless communication devices provides a strong incentive to search for new, and/or improved, microwave dielectric materials. In particular, dielectric ceramics which have high relative permittivities, low dielectric losses as well as low-temperature coefficients of permittivity are of great interest for use as microwave dielectric resonators, oscillators and filters [1–3]. Materials of this type whose dielectric properties are furthermore tuneable under the action of an applied electric or magnetic field and which can be sintered at relatively low temperatures are of even greater interest [4–6]. Potential applications include use as co-fired multi-layer ceramic capacitors (MLCC), tunable filters, phase shifters, electrically steerable antennas, etc. Amongst the limited range of current candidate materials, Bi-based pyrochlore systems, such as, e.g.,  $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$  (BZN),

$\text{Bi}_2(\text{Zn}_{2/3}\text{Nb}_{4/3})\text{O}_7$  and related systems,  $\text{Bi}_2(\text{M}^{\text{III}}\text{Nb}^{\text{V}})\text{O}_7$ , etc. [5–9], show great potential.

Of such Bi-based,  $A_2B_2O_7$  or  $O'A_2 \cdot B_2O_6$ , pyrochlore systems (see Fig. 1), many are known to be strongly displacively disordered, particularly on the  $O'A_2$  sub-structure (see e.g., [10–15] and references contained therein). Indeed, after careful consideration, Vanderah et al. [15] have recently even gone so far as to conclude that “... the occurrence of displacive disorder in the  $O'A_2$  network is required for the formation of pyrochlore ...” in many such Bi-pyrochlore systems. It has frequently been found, for example, that Bi ions when placed on the  $16d$  ideal *A* site positions of the pyrochlore structure type exhibit anomalously large atomic displacement parameters (adp's) [10–14]. Indeed the adp's have often been so large that the structure has been found to be rather better modelled by displacing the Bi/*A* site ions perpendicular to the local three-fold  $O'-\text{Bi}-O'$  axes by up to  $\sim 0.5 \text{ \AA}$  or so into  $96g$  or  $96h$  sites (see, e.g., Fig. 1 of [12] and Refs. [10–15]). Formally, the Bi and other *A* site ions are then able to occupy any one of up to 6 equivalent such displacively disordered local positions (see, e.g., Fig. 1 of [12]).

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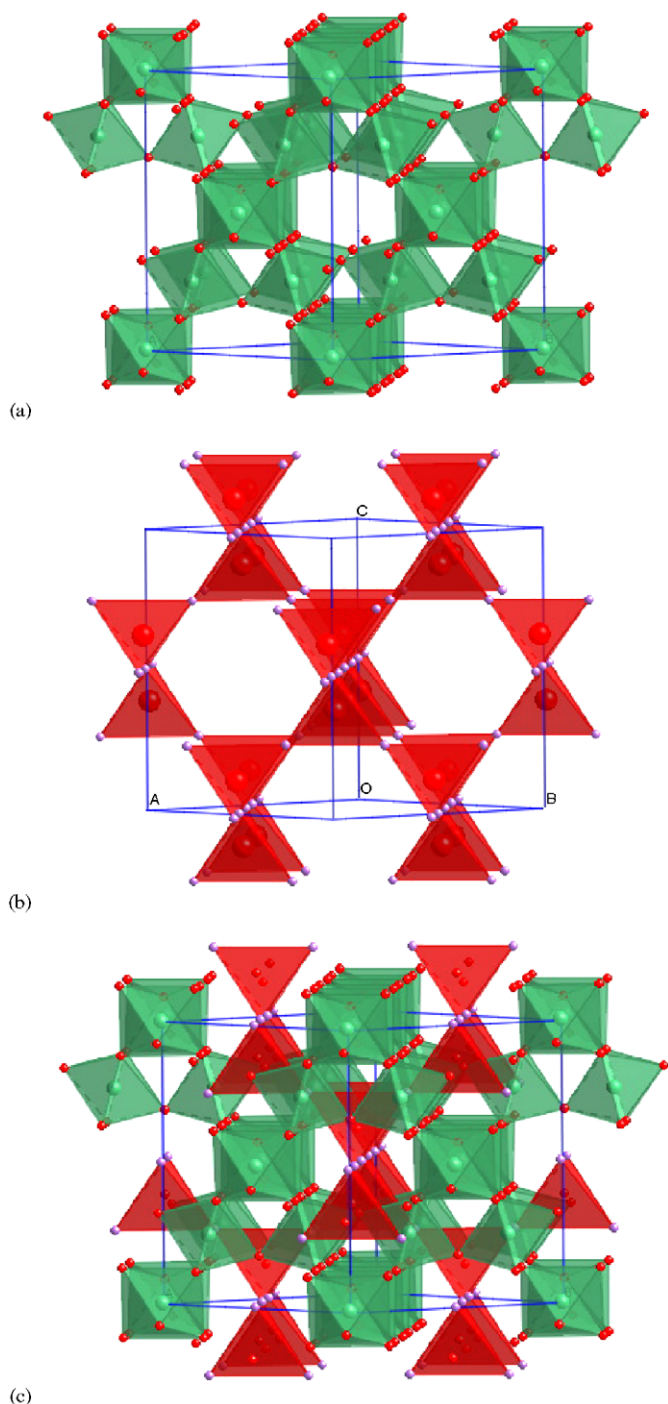


Fig. 1. The (a)  $B_2O_6$  octahedral framework sub-structure and (b)  $O'A_2$  tetrahedral framework sub-structure of the (c) ideal pyrochlore  $O'A_2 \cdot B_2O_6$  or  $A_2B_2O_7$  structure-type projected along a direction close to  $\langle 110 \rangle$ .

This displacive disorder (in particular, "... the local hopping of atoms in the  $O'$  and  $A$  site positions among several local potential minima ...") [16] is commonly reported to be associated with anomalous low-temperature glass-like dielectric behaviour and, in particular, with a low-temperature peak in the dielectric loss which moves systematically to higher temperatures upon increasing

frequency [16–19]. As this has the potential to rule out the use of such materials at microwave frequencies, it becomes very important to investigate the local crystal chemistry underlying this displacive disorder in order to obtain insight into its effect upon the dielectric properties of Bi-based pyrochlore systems. In recent papers, the observation of a characteristic, highly structured diffuse intensity distribution via electron diffraction and its interpretation in terms of highly correlated compositional and displacive disorder [19,20] has been used to make significant progress towards attaining this insight in the particular case of BZN and BZN-related pyrochlores.

In the case of the  $Bi_2(M^{III}Nb^V)O_7$  pyrochlore systems, however, the mechanism underlying displacive disorder appears to be distinctly different to that of BZN and BZN-related pyrochlores. The focus of the current paper is therefore upon the  $Bi_2(M^{III}Nb^V)O_7$ ,  $M = \text{In}$  and  $\text{Fe}$ , pyrochlore systems and the interaction between their local crystal structure and dielectric properties. Electron diffraction is again used to search for evidence of correlated disorder. The effect upon structure as well as dielectric properties of partial substitution of the  $Bi^{3+}$  ions on the pyrochlore  $A$  sites with  $Y^{3+}$  ions is also investigated.

## 2. Experimental

Samples of nominal stoichiometry  $Bi_2FeNbO_7$  (BFN),  $Bi_{1.5}Y_{0.5}FeNbO_7$  (BYFN),  $Bi_2InNbO_7$  (BIN), and  $Bi_{1.5}Y_{0.5}InNbO_7$  (BYIN) were prepared by solid-state reaction via thoroughly mixing high purity  $Bi_2O_3$  (Merck),  $Fe_2O_3$  (Atomerigic),  $Y_2O_3$  (ROC/RIC),  $In_2O_3$  (Merck) and  $Nb_2O_5$  (Aldrich). The raw materials were dried at  $120^\circ\text{C}$  for 24 h to remove adsorbed water before mixing. The resultant powders were then ground in an agate mortar under acetone for 30 min, pressed into pellets and then annealed at temperatures from  $900$  to  $1100^\circ\text{C}$  for periods ranging from 2 to 48 h. The XRD and electron diffraction patterns of the samples annealed for 2 and 48 h did not differ significantly. Taking into consideration the crystallizability and density of samples, the optimized final annealing process was determined to be  $1000^\circ\text{C}$  for 2 h for BFN,  $1050^\circ\text{C}$  for 2 h for BYFN, and  $1100^\circ\text{C}$  for 48 h for the In-containing samples.

All the resultant annealed samples were found to be quite dense (important for dielectric properties measurements). The measured density of the  $Bi_2FeNbO_7$  sample, for example, was  $7.65\text{ g/cm}^3$ , corresponding to 99% of theoretical density while that of  $Bi_2InNbO_7$  was  $7.80\text{ g/cm}^3$ , corresponding to 97% of theoretical density. Both sides of the resultant pellets were also polished and then brushed with silver conductive paste followed by heat treatment at  $550^\circ\text{C}$  for 30 min in order to ensure good electrical contact. Frequency-dependent dielectric spectra were then collected at room temperature using a high precision LCR meter (Agilent 4284A) from 40 Hz to 1 MHz.

XRD data were collected using a Guinier–Hägg camera with  $\text{CuK}\alpha_1$  radiation to determine phase purity. Silicon

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