

Structure and dielectric properties of $\text{Bi}_2(\text{MNb})\text{O}_7$ ($M = \text{Fe}^{3+}, \text{In}^{3+}$) pyrochlores

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In this work, we investigate the local structure and associated dielectric properties of a family of Bi-based pyrochlore phases, namely $\text{Bi}_2(\text{MNb})\text{O}_7$ ($M = \text{Fe}^{3+}$ and In^{3+}) with a 1:1 $M:\text{Nb}$ ratio on the pyrochlore B sites. At 1 MHz and room temperature, the dielectric constant of $\text{Bi}_2(\text{FeNb})\text{O}_7$ (BFN) was found to be 100 while its dielectric loss was 0.007. For $\text{Bi}_2(\text{InNb})\text{O}_7$ (BIN), under the same conditions, the corresponding dielectric constant was 133 and the dielectric loss 0.002, respectively. These results suggest this family of Bi-pyrochlore phases have potential for application as dielectric materials as well as expanding the options available to adjust the physical properties of current Bi-containing pyrochlore phases. A composite $\text{Bi}_2\text{Fe}_{0.5}\text{In}_{0.5}\text{NbO}_7$ (BFIN) intermediate was also synthesized to optimize associated dielectric properties.

1. Introduction

Dielectric ceramics with high relative permittivities, low dielectric losses, low temperature coefficients of permittivity and which can be sintered at relatively low temperatures are of great interest for use as microwave dielectric resonators, oscillators and filters [1-3]. Bi-based, $A_2B_2O_7$ or $O'A_2B_2O_6$, pyrochlore related systems such as $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ (BZN) and $\text{Bi}_2(\text{Zn}_{2/3}\text{Nb}_{4/3})\text{O}_7$ [4] are well known for their relatively low-firing temperatures, high dielectric constants and low dielectric losses. They are also, however, known to be strongly displacively disordered, particularly on the $O'A_2$ sub-structure.

In the case of $\text{Bi}_2(M^{\text{III}}\text{Nb}^{\text{V}})\text{O}_7$ pyrochlore systems, the mechanism underlying displacive disorder is distinctly different to that of BZN and BZN-related pyrochlores. The focus of the current paper is upon the $\text{Bi}_2(M^{\text{III}}\text{Nb}^{\text{V}})\text{O}_7$, $M = \text{In}$ and Fe , pyrochlore systems and the interaction between local displacive disorder and dielectric properties. Electron diffraction is used to search for evidence of correlated displacive disorder.

2. Experimental

$\text{Bi}_2\text{FeNbO}_7$ (BFN), $\text{Bi}_2\text{InNbO}_7$ (BIN), and $\text{Bi}_2\text{Fe}_{0.5}\text{In}_{0.5}\text{NbO}_7$ (BFIN) were prepared by solid-state reaction via thoroughly mixing high purity Bi_2O_3 (Merck), Fe_2O_3 (Atomergic), In_2O_3 (Merck) and Nb_2O_5 (Aldrich) and then annealing at 1000 or 1050 °C for 2 h for crystallization.

All the resultant samples were found to be quite dense. The measured density of the BFN sample was 7.65g/cm^3 , corresponding to 99% of theoretical density while that of the BIN sample was 7.80g/cm^3 (97%), and the BFIN was 7.45g/cm^3 (95%). Both sides of the resultant pellets were polished and then brushed with silver conductive paste followed by heat treatment at 550 °C for 30 minutes 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.

TEM investigation was carried out in a Philips EM 430 TEM on crushed grains of the samples dispersed onto holey carbon coated copper grids.

3. Results

In a recent diffraction investigation of BIN and BFN [5, 6], we reported preliminary electron diffraction evidence for β -cristobalite type orientational disorder of the $O'Bi_4$ tetrahedral sub-structure. The lack of correlation in the sense of this tetrahedral edge rotation from one $\langle 110 \rangle$ column to the next ensures that such displacive shifts give rise only to structured diffuse scattering rather than additional satellite reflections as shown in Fig. 1. A highly structured, diffuse intensity distribution was observed in the form of transverse polarized, $\{110\}^*$ sheets of diffuse intensity, perpendicular to each of the six $\langle 110 \rangle$ directions of real space along with $\langle 111 \rangle^*$ rods of diffuse intensity where three of the $\{110\}^*$ sheets of diffuse intensity intersect. $\{110\}^*$ sheets of diffuse intensity in reciprocal space imply correlated $\langle 110 \rangle$ columns of displacements in real space [7, 8]. Such displacive disordering is characteristic of both BIN and BFN. The magnitude and extent of this displacive disordering potentially makes a significant contribution to the measured dielectric loss of these materials.

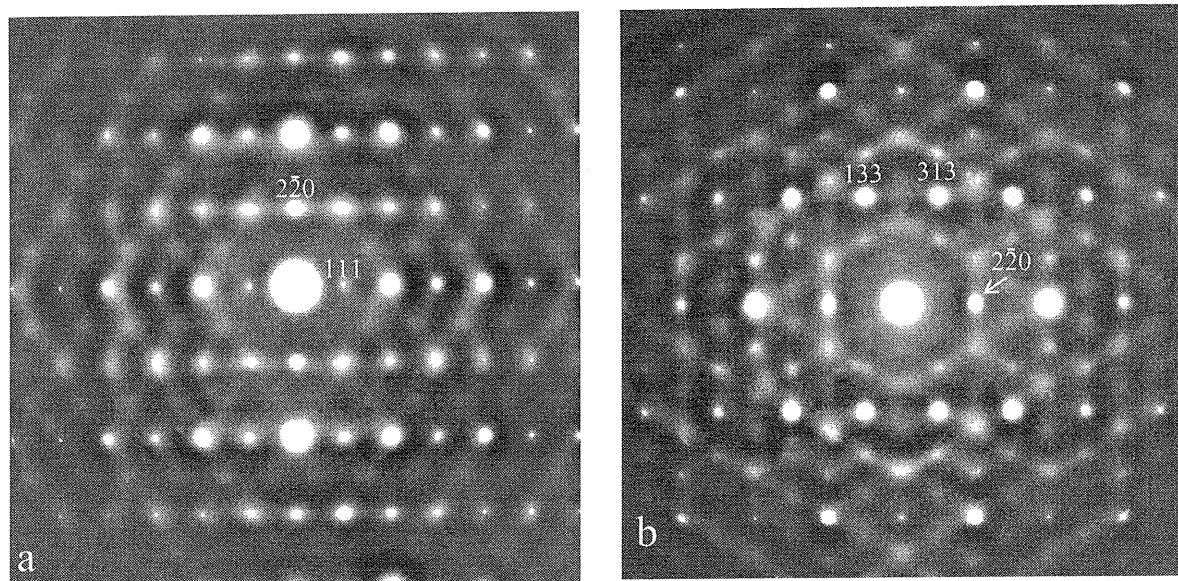


Fig.1 Typical (a) $\langle 11\bar{2} \rangle$, (b) $\langle 33\bar{4} \rangle$ zone axis electron diffraction patterns of BFN.

Figure 2 shows the measured dielectric frequency spectra for these three compounds. BFN, BIN and BFIN were found to be good dielectric materials, indeed comparable with BZN and $Bi_2Zn_{2/3}Nb_{4/3}O_7$ [4]. The dielectric constant of BFN was found to be 100 while its dielectric loss was found to be 0.007 when measured at a frequency of 1 MHz at room temperature. The correspondingly numbers for BIN are 133 and 0.002 and 107 and 0.004 for BFIN. In the case of BIN, this is in good agreement with a previous result obtained by Cann *et al* [9].

From Fig. 2, the measured high dielectric constant and low dielectric loss of BIN was found to be essentially frequency independent over the measured frequency range (from 40 Hz to 1 MHz). By contrast, the dielectric constant and dielectric loss of BFN and BFIN slowly but continuously decreased with increasing frequency. BFN and BFIN show a slightly higher dielectric loss by comparison with BIN. This may be associated with the fact that BFN exhibits both strong $\langle 111 \rangle^*$ diffuse rods and $\{110\}^*$ diffuse sheets while $\langle 111 \rangle^*$ diffuse rods predominate in the case of BIN (see *ref.* [6]). This suggests that the highly correlated $\langle 111 \rangle$ tetrahedral edge rotations of the type responsible for the observed $\langle 111 \rangle^*$ diffuse rods, have intrinsically lower dielectric loss than Bi-pyrochlores for which the $\langle 110 \rangle$ tetrahedral edge rotations responsible for the $\{110\}^*$ diffuse sheets predominate.

BIN and BFN are iso-structural and exhibit a very similar type of displacive disorder. Their measured dielectric losses are similar, in particular in the higher frequency range as shown in Fig. 2. As a result, one can design the composite BFIN to optimize the associated dielectric properties *i.e* dielectric constant, dielectric loss and temperature coefficient of capacitance. As an example, a 50:50 BFIN sample was successfully synthesized. It has thereby been shown that the dielectric constant of such composite materials can be tuned without sacrificing their low dielectric loss. Further more detailed investigation of the dielectric properties of these composite materials is in progress.

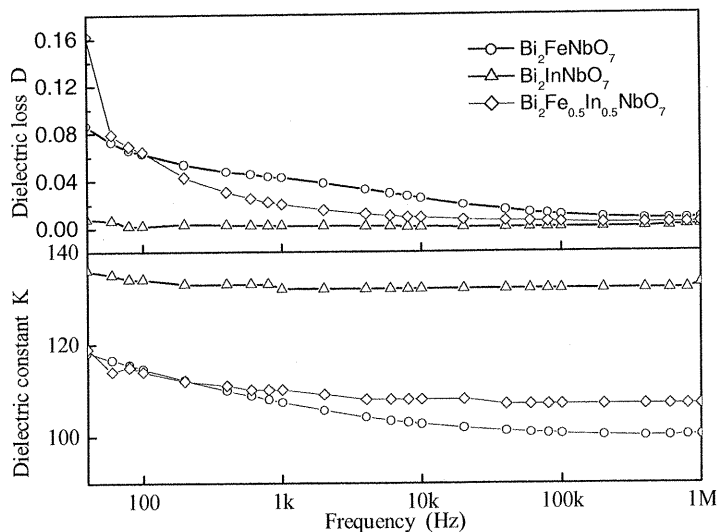


Fig. 2. Dielectric spectra of BIN, BFN and BFIN

4 Conclusions

Displacive disorder associated with deleterious dielectric loss properties have been observed in the TEM. The correlation between local structure and dielectric properties was investigated in this work. A composite BFIN material was also synthesized in an attempt to optimize dielectric properties.

Acknowledgments

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