Subsolidus phase equilibria and properties in the system 

\( \text{Bi}_2\text{O}_3:\text{Mn}_2\text{O}_3_{\pm x}:\text{Nb}_2\text{O}_5 \)


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Abstract

Subsolidus phase relations have been determined for the Bi–Mn–Nb–O system in air (750–900 °C). Phases containing Mn\(^{2+}\), Mn\(^{3+}\), and Mn\(^{4+}\) were all observed. Ternary compound formation was limited to pyrochlore \((A_2B_2O_6O_0)\), which formed a substantial solid solution region at Bi-deficient stoichiometries (relative to Bi\(_2\)(Mn,Nb)\(_2\)O\(_7\)) suggesting that \(\sim 14\% - 30\%\) of the A-sites are occupied by Mn (likely Mn\(^{2+}\)). X-ray powder diffraction data confirmed that all Bi–Mn–Nb–O pyrochlores form with structural displacements, as found for the analogous pyrochlores with Mn replaced by Zn, Fe, or Co. A structural refinement of the pyrochlore \(0.4000:0.3000:0.3000\) Bi\(_2\)O\(_3\):Mn\(_2\)O\(_3\):Nb\(_2\)O\(_5\) using neutron powder diffraction data is reported with the A and O\(_0\) atoms displaced (0.36 and 0.33 Å, respectively) from ideal positions to 96g sites, and with Mn\(^{2+}\) on A-sites and Mn\(^{3+}\) on B-sites \((\text{Bi}_{1.6}\text{Mn}_{0.4}\text{(Mn}_{0.8}\text{Nb}_{1.2})\text{O}_7, Fd\bar{3}m (\#227), a = 10.478(1) Å)\); evidence of A or O\(_0\) vacancies was not found. The displacive disorder is crystallographically analogous to that reported for \(\text{Bi}_{1.5}\text{Zn}_{0.92}\text{Nb}_{1.5}\text{O}_{6.92}\), which has a similar concentration of small B-type ions on the A-sites. EELS spectra for this pyrochlore were consistent with an Mn oxidation between 2+ and 3+. Bi–Mn–Nb–O pyrochlores exhibited overall paramagnetic behavior with negative Curie–Weiss temperature intercepts, slight superparamagnetic effects, and depressed observed moments compared to high-spin, spin-only values. At 300 K and 1 MHz the relative dielectric permittivity of \(\text{Bi}_{1.600}\text{Mn}_{1.200}\text{Nb}_{1.200}\text{O}_7\) was \(\approx 128\) with \(\tan \delta = 0.05\); however, at lower frequencies the sample was conductive which is consistent with the presence of mixed-valent Mn. Low-temperature dielectric relaxation such as that observed for \(\text{Bi}_{1.5}\text{Zn}_{0.92}\text{Nb}_{1.5}\text{O}_{6.92}\) and other bismuth-based pyrochlores was not observed. Bi–Mn–Nb–O pyrochlores were readily obtained as single crystals and also as textured thin films using pulsed laser deposition.

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Keywords: Pyrochlore; Displacive disorder; Bismuth manganese niobates; Bi–Mn–Nb–O; Phase equilibria; Phase diagram; Dielectric properties; Magnetic properties

1. Introduction

Considerable practical and fundamental interest exists in materials in which interactions occur between electric and magnetic dipoles; e.g., multiferroic materials, which exhibit the unusual coexistence of ferroelectricity and ferromagnetism as well as coupling between their order parameters [1–4]. So-called multifunctional magnetoelectric materials exhibit magnetic behavior that can be manipulated by electric fields, and vice versa [5,6]. Such materials, with high dielectric permittivity and high magnetic permeability, could serve as both inductors and capacitors in resonant circuits, and could enable entirely new applications such as multiple-state memory elements, electric-field-controlled ferromagnetic resonance devices, and transducers with magnetically modulated piezoelectricity [3,7–10]. The factors underlying the occurrence of these properties are not understood—only a few multiferroic compounds are known [3,11], including BiMn\(_2\O\(_3\) [12,13] and several other complex manganates [14–17]. Efforts continue to find new compounds [10,18] with robust, technically exploitable
magnetoelectric responses. The present study of the B$_2$O$_3$–Mn$_2$O$_3$$_{1-x}$–Nb$_2$O$_5$ system was undertaken to elucidate the phase equilibria of BiMnO$_3$ in the ternary system, and to reveal compound formation among strongly polarizable and magnetic cations.

2. Experimental methods

Fifty-two polycrystalline specimens (3–4 g each) were prepared in air by solid-state reactions using B$_2$O$_3$ (99.999%), “MnCO$_3$” (99.99%, pre-analyzed by thermogravimetric decomposition in air to Mn$_2$O$_4$), and Nb$_2$O$_5$ (99.999%). Prior to each heating, each sample was mixed by grinding with an agate mortar and pestle for 15 min, pelletedized, and placed on a bed of sacrificial powder of the same composition supported on alumina ceramic. After an initial overnight calcine at 800°C (below the m.p. of B$_2$O$_3$, 825°C) multiple 1–3 d heatings (with intermediate grinding and re-pelletizing) were carried out at 885–900°C.$^2$ Samples were furnace-cooled to ~700°C and then air-quenched on the bench-top. Metastable melting in non-equilibrated ternary specimens, an initial problem owing to large differences in the melting points of B$_2$O$_3$, Mn$_2$O$_3$, and Nb$_2$O$_5$, was avoided by soaking samples at 885°C for 2–3 d for the second heating, followed by a third overnight heating at 900°C. Equilibrium was presumed when no further changes could be detected in the weakest peaks observed in the X-ray powder diffraction patterns. A eutectic in the ternary system may occur near 50:25:25 Bi$_2$O$_3$–Mn$_2$O$_3$–Nb$_2$O$_5$, which formed liquid at 925°C. Bi$_2$O$_3$ volatilization was observed above the solidus by thermogravimetric analysis, but was not detectable in the subsolidus study.

Pyrochlore-type crystals were easily obtained by heating a single-phase polycrystalline specimen (composition 40:30:30 B$_2$O$_3$:Mn$_2$O$_3$$_{1-x}$–Nb$_2$O$_5$) in a Pt capsule (sealed by welding) to 1300°C, followed by slow cooling (5°C/h) to below the freezing point (~1175°C). The crystals were obtained as brown-black shards and exhibited conchoidal fracture. The refined unit cell parameter obtained for a powdered sample of the crystals ($a = 10.495(1)$ Å) was larger than that of the starting material ($a = 10.478(1)$ Å), suggesting higher Bi-content in the crystals. Pyrochlore films were readily deposited by pulsed laser deposition (248 nm KrF EXCIMER, 10 Hz, 10 J/cm$^2$, background pressure 24 Pa O$_2$) from a target disk prepared by sintering (1050°C, 8 h) single-phase pyrochlore powder (composition 40:30:30 B$_2$O$_3$:Mn$_2$O$_3$$_{1-x}$–Nb$_2$O$_5$). Films grew at high deposition rates (~0.4 nm/s) on Si- and Pt-coated Si substrates. Crystalline, highly {111} textured films were obtained by either cold deposition in vacuum, followed by annealing for 10 min at 700°C, or by deposition at 600°C in 17 Pa O$_2$.

Phase assemblages were ascertained using the disappearing phase method [19,20] and X-ray powder diffraction data obtained with a Philips$^3$ diffractometer equipped with incident Soller slits, a θ-compensating slit and graphite monochromator, and a scintillation detector. Samples were mounted in well glass slides. Patterns were collected at ambient temperatures using CuK$_\alpha$ radiation over the range 3–70° 2θ with a 0.02° 2θ step size and a 2 s count time. Intensity data measured as relative peak heights above background were obtained using the DATA SCAN software package, and processed using JADE. For unit cell refinements, observed 2θ line positions were first corrected using SRM 660, LaB$_6$ [21], as an external calibrant. Lattice parameters were refined using JADE (2θ values, CuK$_\alpha_1$ = 1.540593 Å). Single pyrochlore-type crystals were characterized by the precession camera method (Zr-filtered MoK$_\alpha$ radiation) to assess quality, cell parameter, and space group.

Neutron powder diffraction data were collected using the BT-1 32-detector neutron powder diffractometer at the NIST Center for Neutron Research, NBSR. The specimen (10 g) was loaded in a vanadium container of length 50 mm and diameter 12.4 mm. A Cu(311) monochromator with a 90° take-off angle, $\lambda = 1.5402(2)$ Å, and in-pile collimation of 15 min of arc were used. Data were collected under ambient conditions and at 12 K, over the range of 3–168° 2θ with a step size of 0.05°. The instrument is described at the website http://www.ncnr.nist.gov/.

The oxidation state of Mn in selected samples was evaluated by electron energy loss spectroscopy (EELS) using polycrystalline specimens which were crushed in acetone and dispersed on lacey carbon-coated grids. EELS measurements of the Mn–L$_{2,3}$ edge were conducted in a JEOL-3010 UHR (300 kV) transmission electron microscope (TEM) equipped with a LaB$_6$ electron source, Gatan Imaging Filter (GIF), and a slow-scan charge-coupled device (CCD) camera. The EELS spectra were recorded with the TEM operated in the diffraction mode using a 0.6 nm GIF entrance aperture, energy dispersion of 0.1 eV/channel, and 30 s integration time (under the chosen conditions, the full-width at half-maximum of the zero-loss peak was 1.7 eV). Mn$_3$O$_4$ (Mn$^{3+/2+}$) and MnNb$_2$O$_6$ (Mn$^{2+}$) were analyzed as reference samples. For each sample, 10 spectra were collected from distinct particulars. The averaged background-subtracted spectra were processed to remove the effect of plural inelastic scattering using a Fourier-ratio deconvolution method [22]. Since all spectra were collected from sufficiently thin areas, the effect of this deconvolution was rather small.

$^2$Exceptions: specimens with Bi contents >70 mol% were not heated above 750°C (to avoid melting and decomposition of sillenite-type phases), and those with Bi contents ≤20 mol% were heated at higher final temperatures, 975–1200°C, to achieve equilibrium more quickly.

$^3$Certain commercial equipment and software are identified in order to adequately specify the experimental procedure; recommendation or endorsement by the National Institute of Standards and Technology is not therein implied.
Magnetic properties were characterized using a Quantum Design SQUID magnetometer and single-phase polycrystalline samples. Magnetization was measured as a function of temperature between 2 and 300 K after cooling in the absence of an applied field (zero-field cooled, ZFC) and after cooling in a magnetic field (field-cooled, FC) of 50 kG. In addition, measurements at 4.2 K and at ambient temperature were carried out to determine the field dependence of the magnetization in applied fields between 0 and 50 kG.

Dielectric properties were evaluated using sintered (1050 °C, 4 h) pellets (∼13 mm diameter, ∼1 mm thick) of single-phase specimens which were polished to obtain planar surfaces. Density was determined geometrically. Gold electrodes (∼75 nm thick) were sputtered onto the pellet surfaces to form parallel plate capacitors. Capacitance and dielectric loss were measured using an Agilent 4284 LCR meter at frequencies varying from 10 kHz to 1 MHz. Reported permittivity data have been corrected to theoretical density. Although the sample temperature was varied between 110 and 450 K using a programmable 9023 Delta Design controller, data is reported only up to 300 K due to the high conductivity observed. Typical uncertainties in the permittivity data are on the order of 5% and are dominated by the geometric estimates of porosity.

3. Results and discussion

3.1. Phase formation

The results of the phase equilibrium study are presented in Fig. 1. Previously reported diagrams for the binary peristerite systems [23] were mostly confirmed in the present study. In the Mn–Nb–O system only the Mn²⁺ compound manganocolumbite, MnNb₂O₆, was observed to form. In the Bi–Mn–O system two compounds formed, sillenite-type Bi₁₂MnO₂₀ (Mn⁴⁺) [24] and Bi₂Mn₄O₁₀, which contains ordered Mn³⁺ and Mn⁴⁺ in pyramidal and octahedral coordination, respectively [25,26]. The high-pressure (3–6 GPa/700 °C) perovskite-related BiMnO₃ phase [27–29] was not observed in the study of the ternary system; this compound decomposes at 600 °C when heated under ambient pressure [30], and was not stabilized in the presence of Nb₂O₅. The binary Bi–Nb–O phases observed were in general agreement with the comprehensive study reported by Roth [31] except for the high-Bi₂O₃ (∼0.75 mol fraction) region, represented in Fig. 1 as a “fluorite” solid solution extending from 75:25 Bi₂O₃:Nb₂O₅ (Bi₃Nb₂O₇) to 93:7 Bi₂O₃:Nb₂O₅ and dissolving /C₂₄ 7 mol% Mn₂O₃ as shown. This region of the Bi₂O₃:Nb₂O₅ system has received considerable attention as it forms a series of structurally complex, modulated...
superstructures [32–36] with variable and potentially useful dielectric properties [33,37–39]. Reported differences in the detailed phase relations in this region likely arise from kinetic effects, variations in synthesis (especially cooling methods), and/or differences in characterization methods (e.g., X-ray or electron diffraction). For example, the present study, in agreement with early studies [31], did not find a sillenite-type compound at the composition Bi12Nb0.29O20. This specimen was a mixture of monoclinic Bi2O3 and the fluorite-type solid solution after repeated heatings at 700 °C for a total of 414 h; however, a different heat treatment may have resulted in the metastable body-centered cubic form of Bi2O3 (sillenite-type) [40] instead of the monoclinic polymorph.

Ternary phase formation in the Bi2O3·Mn2O3·3·1.5·Nb2O5 system was found to be limited to pyrochlore, which forms an appreciable solid solution region (Fig. 1). During synthesis, the pyrochlore phase formed early in partially reacted samples and was readily purified within the single-phase region, suggesting high thermodynamic stability. Numerous descriptions can be found for the pyrochlore crystal structure, VIII A2B2O7, which is unusual in that it can be considered as two relatively independent interpenetrating networks: B6O12 octahedra sharing all vertices, and [O6A4] tetrahedra in an anti-cristobalite-type arrangement [41–44]. The structural formula is often written as (A2O3)(B2O6) or A2B6O12O’ to emphasize this interesting structural character. The larger A-cations are 8-fold ( = 6 + 2) coordinated by six oxygens in puckered rings formed by the B6O12 network plus two O’ oxygens above and below in the A2O’ network. The structure inherently facilitates non-stoichiometry as the A2O’ network can be partially occupied, or in some cases completely absent; furthermore, numerous non-oxide and halide pyrochlores are known. In addition to extensive compositional ranges, pyrochlores exhibit a remarkable variety of exploitable physical properties, hence the considerable technical importance of this class of solids [43,45–47].

Bi–Mn–Nb–O pyrochlores have been previously reported to form at the stoichiometries Bi2Mn3Nb2O11+y, Bi2Mn3Nb2O11+y [48], Bi3Mn6Nb2O11+y [49], and Bi1.5MnNb2O7 [50]; however, under the conditions of the present study none of these compositions fall in the pyrochlore single-phase field: Composition Bi1.5MnNb2O7 formed mostly pyrochlore with a small amount of Mn2O3, Bi1.5MnNb2O7 forms a two-phase region of pyrochlore and a considerable amount of Bi2O3/Mn2O4, Bi1.5Mn2NbO2 formed a three-phase mixture as described in Fig. 1, and Bi1.5MnNb2O7 formed a mixture of pyrochlore and Bi2O3. As shown on the diagram (Fig. 1), Bi–Mn–Nb–O pyrochlores form thermodynamically stable mixtures with the Bi1.5Mn2O7 solid solution, Bi1.5Mn2O7, Bi1.5Mn2O7, Mn2O3, Mn2O3, Mn2O3, and Bi2Mn2O10. Compositions, nominal formulas, and refined unit cell parameters for single-phase Bi–Mn–Nb–O pyrochlores prepared in the present study are given in Table 1; all specimens were black in color. The trends in unit cell parameters suggest that cell volume increases markedly with both Bi and vacancy concentration.

Observe, indexed X-ray powder diffraction data for the pyrochlore 0.4000:0.3000:0.3000 Bi2O3·Mn2O3·3·1.5·Nb2O5 are given in Table 2. As noted previously [43], the 442 reflection, forbidden for an ideal pyrochlore structure, was readily observed in this pattern and in all patterns of pyrochlore and pyrochlore-containing specimens prepared in this study. The 442 reflection was also observed in precession photos of single crystals. Similar to the Bi–Zn–Nb–O pyrochlores [43,51], the presence of this diagnostic reflection indicates the presence of displacements off ideal crystallographic sites. The consistent observation of this reflection indicates that all Bi–M–Nb–O pyrochlores exhibit site displacements (either static or dynamic). Furthermore, the stoichiometric location of the pyrochlore phase field, as also found for the analogous Bi–M–Nb–O systems (M = Zn [43], Fe [52], Co [53], occurs at substantially lower Bi concentrations than conventional formulations placing only Bi on the A-sites and the smaller M/Nb cations on the B-sites. The pyrochlore field includes compositions with “excess” B-cations that require mixing of some Mn on the A-sites and Mn Nb2O5 and Mn2O3/Mn3O4, and Bi2Mn4O10. Compositions, nominal formulas, and refined unit cell parameters for single-phase Bi–M–Nb–O pyrochlores prepared in the present study are given in Table 1; all specimens were black in color. The trends in unit cell parameters suggest that cell volume increases markedly with both Bi and vacancy concentration.

<table>
<thead>
<tr>
<th>Bi2O3·Mn2O3·3·1.5·Nb2O5</th>
<th>Nominal Formula (Mn3+)</th>
<th>a (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4250:0.3000:0.2750</td>
<td>Bi1.676□0.056Mn1.183Nb0.084O7-xy</td>
<td>10.482(1)</td>
</tr>
<tr>
<td>0.4200:0.2900:0.2900</td>
<td>Bi1.64□0.089Mn1.134Nb0.134O7-xy</td>
<td>10.499(1)</td>
</tr>
<tr>
<td>0.4100:0.3150:0.2750</td>
<td>Bi1.617□0.056Mn1.242Nb0.084O7-xy</td>
<td>10.466(1)</td>
</tr>
<tr>
<td>0.4000:0.3000:0.3000</td>
<td>Bi1.55□0.111Mn1.167Nb0.167O7-xy</td>
<td>10.478(1)</td>
</tr>
<tr>
<td>0.3600:0.3200:0.3200</td>
<td>Bi1.38□0.154Mn1.23Nb0.235O7-xy</td>
<td>10.451(1)</td>
</tr>
</tbody>
</table>

These compositions correspond to the points within the six-sided pyrochlore region shown in Fig. 1. For purposes of comparison, the formulas have been normalized to seven oxygens (full occupancy of the O’ site) and assume Mn3+ (x = 0). Although the metal ratios given here are precise, the actual populations on the A and B sites depend on the O’ occupancy factor and Mn oxidation state(s), which are uncertain and which may vary in each pyrochlore.

*Estimated by assuming an average Mn oxidation state of 2.75+ and full occupancy of the O’ site; the latter assumption results in maximum estimates for Mn4+ site concentrations and minimum estimates for A-site vacancy concentrations.


3.2. Oxidation state of Mn

In the present study conducted in air, compounds with di-, tri-, and tetravalent Mn were all obtained; e.g., light tan MnNb2O6 (Mn2+), black Bi2MnO20 (Mn4+), and black Bi2Mn3O10 (Mn3+/4+). Both Mn3O4 (Mn3+, bixbyite) and Mn2O3 (Mn2+, hausmannite) were observed in equilibrated mixtures prepared in the phase diagram study (MnO was not observed). The oxidation state of Mn in the pyrochlore phase Bi1.556Mn1.167Nb1.167O7 was inferred from the observed relative intensities of the L3 and L2 lines in the EELS spectra. For transition metals (Bi2O3:Mn2O3 di-, tri-, and tetravalent Mn were all obtained; e.g., light tan Mn3O4 and MnNb2O6 yields a valence state of Mn that was observed to increase dramatically with a decrease in Mn valence from 4 to 2 [56]. Comparison of the Mn–L2,3 spectra (Fig. 2) recorded from the pyrochlore sample to those for Mn3O4 (Mn2+/3+, hausmannite) and Mn2O3 (Mn2+/Mn3+, ramsdellite) gives that the valence of Mn is between 2+ and 3+ in the pyrochlore phase. Linear interpolation of the L3/L2 intensity ratios between the corresponding valences for Mn3O4 and MnNb2O6 yields a valence state of ~2.2 for Mn in the pyrochlore phase (a double-step background function was used to extract the L3 and L2 intensities, as described in Ref. [56]). This value is considered approximate since the coordination environment of Mn in the pyrochlore A-sites is expected to be considerably different from that in the reference compounds. Overall, the EELS results and the deep black colors of the Bi–Mn–Nb–O pyrochlores are both consistent with the presence of mixed-valent 2+/3+ Mn.

3.3. Structural refinement of the pyrochlore phase

The highly symmetrical ideal pyrochlore structure A2B2O6O7 crystallizes in space group Fd3m with A and B cations on two special positions (16d, 16c) and oxygens on two sites, 48f (O) and 8b (O0). Numerous pyrochlores [43] have been reported for the defect pyrochlores Tl2Nb2O6 and Tl2Ta2O6 [59,60]. Bi2Ti2O7 [61], Bi2–xCrTaO7–y [62], and Bi2Sn2O7 [63,64]. Another study of Tl2Nb2O6+x phases concluded that, in agreement with NMR results, the 1 0.4000:0.3000:0.3000 Bi2O3:Mn2O3:Nb2O5. Displaceable disorder in the A2O network has been reported for numerous pyrochlores [43]. For Bi2–xM1Ru2O7–y (M = Cu, Co; x = 0; 0.4), the disorder was attributed to the lone pairs on Bi3+ [57]. Pyrochlores in the Sn32–x(M2–xSn4+)O7–x–y/2 (M = Nb5+ or Ta5+) series were found to have both cation and anion vacancies as well as static displacements of O [58]. Static disorder has also been reported for the defect pyrochlores Tl2Nb2O6 and Tl2Ta2O6 [59,60]. Bi2Ti2O7 [61], Bi2–xCrTaO7–y [62], and Bi2Sn2O7 [63,64]. Another study of Tl2Nb2O6+x phases concluded that, in agreement with NMR results, the forbidden reflections were better accounted for by anisotropic thermal (rather than static) displacements [65].
Various models have been used to refine the structures of displacively ordered pyrochlores. In an X-ray single-crystal diffraction study of Tl$_2$Ta$_2$O$_6$, Tl$^+$ ions were displaced from the 16d to the 32e sites, yielding two equivalent half-occupied positions [60]. For Bi$_{2-x}$Ru$_2$O$_{7-y}$ [57], Bi$_{2-y}$Yb$_x$Ru$_2$O$_{7-y}$ [60], and Bi$_{2-y}$Cr$_2$O$_{7-y}$ [62], Bi was displaced to the 96h site, yielding a toroid of six possible equivalent positions. In the structural refinement of Bi$_{1.5}$Zn$_{0.92}$Nb$_{1.5}$O$_{6.92}$ [51] both the A cations and O’ oxygens were displaced to 96g sites, resulting in six equivalent possible positions for the former and 12 for the latter; a study of short-range ordering has also been reported for this pyrochlore [66]. For Bi$_{2-y}$Ru$_2$O$_{7-y}$ [57] the O’ oxygens were displaced from the 8b to the 32e site, distributed across four equivalent positions. Although the displacively disordered sites in the different models are crystallographically distinct, the refinements in general indicate similar magnitudes for the displacements of A and O’ from the ideal positions (on the order of \( \leq 0.5\) Å).

Rietveld refinement results obtained for pyrochlore-type 0.40000:0.30000:0.3000 Bi$_2$O$_3$:Mn$_2$O$_3$:y: Nb$_2$O$_5$ using five different models and neutron powder diffraction data are given in Table 3. Cation ratios were fixed according to the preparative analytical masses; no impurity phases were detectable by X-ray or neutron diffraction; however, the oxidation state of Mn was uncertain. Two approaches were tried, the first assumed the presence of only Mn$^{3+}$ (Bi$_{1.5}$Mn$_{0.33}$ (Mn$_{0.83}$Nb$_{1.167}$)O$_7$) and the second placed larger Mn$^{3+}$ on the A-site and smaller Mn$^{3+}$ on the B-site (Bi$_{1.6}$Mn$_{0.33}$ (Mn$_{0.83}$Nb$_{1.167}$)O$_7$); in both cases, the B- and O’-sites were assumed to be fully occupied. In all initial refinements, the composition with mixed Mn$^{2+}$/3+ gave better fits, as found in other neutron powder diffraction studies of Mn-containing pyrochlores which found high-spin Mn$^{3+}$ on the A-site [67] and high-spin Mn$^{3+}$ on the B-site [68]. Cation occupancies were therefore fixed according to the formula Bi$_{1.6}$Mn$_{0.33}$ (Mn$_{0.83}$ Nb$_{1.167}$)O$_7$. The anomalously large thermal parameters obtained for the A- and O’-sites in Model 1 (ideal pyrochlore structure), when combined with the observation of 442-type reflections in the powder diffraction patterns, confirm the presence of displacements. In Models 2 and 3 the A-site cations were displaced onto the 96h and 96g sites, respectively, resulting in substantially improved fits and slightly better fit statistics for Model 3; however, the O’ thermal parameters remained large. Models 4 and 5 retained A-site cations on the 96g sites and displaced O’ to the 32e ((x, x, x) with \( x \sim 0.36 \) or 96g ((x, x, z) with \( z \sim 0.35 \) and \( z \sim 0.37 \)) sites, respectively. These models returned similar fit statistics, but the smaller O’-thermal parameter obtained with Model 5 suggests that its position is best described on the 96g site.

Final refinement results for pyrochlore-type 0.40000:0.30000:0.3000 Bi$_2$O$_3$:Mn$_2$O$_3$:y: Nb$_2$O$_5$ at 12 K and 293 K using Model 5 are given in Table 4; the difference profiles are shown in Fig. 3. The similar results obtained at the two temperatures suggest that the displacements are static in nature. The site occupancy obtained for O’ does not differ significantly from the fully occupied value of 1/12

### Table 3

<table>
<thead>
<tr>
<th>Model 1</th>
<th>Model 2</th>
<th>Model 3</th>
<th>Model 4</th>
<th>Model 5</th>
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<td>( a ) (Å)</td>
<td>10.4761(1)</td>
<td>10.47617(9)</td>
<td>10.4761(1)</td>
<td>10.47615(8)</td>
</tr>
<tr>
<td>A-site</td>
<td>16d</td>
<td>96h</td>
<td>96g</td>
<td>96g</td>
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<tr>
<td>Occ. (Bi, Mn)</td>
<td>0.8, 0.2</td>
<td>0.133, 0.033</td>
<td>0.133, 0.033</td>
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<td>( x ) (Bi, Mn)</td>
<td>1/2</td>
<td>0</td>
<td>0.4679(4)</td>
<td>0.4686(4)</td>
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<td>( y ) (Bi, Mn)</td>
<td>1/2</td>
<td>0.2264(1)</td>
<td>0.5094(3)</td>
<td>0.5098(4)</td>
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<td>( z ) (Bi, Mn)</td>
<td>1/2</td>
<td>0.7736(1)</td>
<td>0.5094(3)</td>
<td>0.5098(4)</td>
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<td>( U_{iso} ) (Bi, Mn) (Å$^2$)</td>
<td>6.91(9)</td>
<td>1.69(6)</td>
<td>1.16(9)</td>
<td>1.32(10)</td>
</tr>
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<td>B-site</td>
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<td>16c</td>
<td>16c</td>
<td>16c</td>
</tr>
<tr>
<td>Occ. (Mn, Nb)</td>
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<td>0.4, 0.6</td>
<td>0.4, 0.6</td>
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<tr>
<td>( U_{iso} ) (Mn, Nb) (Å$^2$)</td>
<td>1.89(7)</td>
<td>1.94(5)</td>
<td>1.9(5)</td>
<td>1.9(5)</td>
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<tr>
<td>O-site</td>
<td>48f</td>
<td>48f</td>
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<td>( x ) (O)</td>
<td>0.3205(1)</td>
<td>0.32055(7)</td>
<td>0.32046(7)</td>
<td>0.32037(7)</td>
</tr>
<tr>
<td>( U_{iso} ) (O) (Å$^2$)</td>
<td>2.51(2)</td>
<td>2.35(2)</td>
<td>2.33(2)</td>
<td>2.33(2)</td>
</tr>
<tr>
<td>O’-site</td>
<td>8b</td>
<td>8b</td>
<td>8b</td>
<td>32e</td>
</tr>
<tr>
<td>Occ. (O)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.25</td>
</tr>
<tr>
<td>( x ) (O)</td>
<td>3/8</td>
<td>3/8</td>
<td>3/8</td>
<td>0.539(5)</td>
</tr>
<tr>
<td>( y ) (O)</td>
<td>3/8</td>
<td>3/8</td>
<td>3/8</td>
<td>0.539(5)</td>
</tr>
<tr>
<td>( z ) (O)</td>
<td>3/8</td>
<td>3/8</td>
<td>3/8</td>
<td>0.539(5)</td>
</tr>
<tr>
<td>( U_{iso} ) (O) (Å$^2$)</td>
<td>6.0(1)</td>
<td>6.49(9)</td>
<td>6.56(9)</td>
<td>3.5(2)</td>
</tr>
<tr>
<td>( R_w ) (%)</td>
<td>6.09</td>
<td>4.31</td>
<td>4.26</td>
<td>4.23</td>
</tr>
<tr>
<td>( R_p ) (%)</td>
<td>4.57</td>
<td>3.50</td>
<td>3.47</td>
<td>3.45</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>2.66</td>
<td>1.328</td>
<td>1.302</td>
<td>1.279</td>
</tr>
</tbody>
</table>

Atoms retained on special positions in all models are B-site Mn/Nb on 16c (0, 0, 0) and oxygen on 48f (x, 0, 0).
(0.083), suggesting the presence of few or no O vacancies. The refinement results are consistent with a structural formula of Bi\(_{1.6}\)Mn\(_{2+}\)\(_{0.4}\) (Mn\(_{3+}\)\(_{0.8}\)Nb\(_{1.2}\))O\(_7\) for this pyrochlore, with both the A- and B-sites completely filled and with 20% of the A-sites occupied by Mn\(_{2+}\). The displacively disordered crystal structure is illustrated in Fig. 4. The [Mn\(_n\)Nb\(_\ell\)]O\(_6\) octahedra in the B\(_2\)O\(_6\) network are nearly regular, with metal-oxygen distances of 2.009 Å (x6), and O–B–O angles deviating about 3.1° from 90°. The observed bond valence sum of 4.0 v.u. for the B site, calculated using the \(R_0\) parameters for Nb\(_{5+}\) and Mn\(_{3+}\) [69] and the occupancies in Table 4, is in reasonable agreement with the value of 4.2 v.u. expected from the formal valences. The A-site cations and neighboring O' positions are both displacively disordered, therefore calculation of bond valence sums is less meaningful. However, the displaced structure results in a number of considerably shorter A–O and A–O' distances compared to the ideal structure (Model 1): Observed A–O distances range from 2.302 to 3.023 Å (compared to 2.661 Å (x6) in the ideal structure), and observed A–O' distances range from 2.155 to 2.459 Å (compared to 2.287 Å (x2) in the ideal structure). The shorter distances available in the displaced structure can reasonably accommodate the smaller Mn\(_{2+}\) and can also

![Fig. 3. Observed, calculated, and difference neutron diffraction profiles for the pyrochlore 0.4000:0.3000:0.3000 Bi\(_2\)O\(_3\):Mn\(_2\)O\(_3\):Nb\(_2\)O\(_5\) at ambient temperature. Tick marks indicate allowed reflection positions.](image)

![Fig. 4. Crystal structure of the pyrochlore Bi\(_{1.6}\)Mn\(_{2+}\)\(_{0.4}\) (Mn\(_{3+}\)\(_{0.8}\)Nb\(_{1.2}\))O\(_7\) (Table 4) illustrating the displacive disorder of the A\(_2\)O' network. The vertex-linked polyhedra represent the octahedral B\(_2\)O\(_6\) network. The toroids of black spheres represent the six equivalent 96g sites for the A-site Bi/Mn cations, and the cuboctahedral clusters of larger lighter spheres denote the 12 possible displaced positions for the O' oxygens. The final refinement results at 12 K indicate that the A-site cations are displaced 0.361(6) Å from the ideal 16d position, while O' is displaced 0.33(2) Å from the high-symmetry 8b position.](image)

### Table 4

<table>
<thead>
<tr>
<th>Name</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>(U_{eff} (\text{Å}^2) \times 100)</th>
<th>Site</th>
<th>Occ.</th>
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</thead>
<tbody>
<tr>
<td>Bi/Mn</td>
<td>0.4723(6)</td>
<td>0.5145(6)</td>
<td>0.5145(6)</td>
<td>1.39(6)</td>
<td>96g</td>
<td>0.1333/0.0333</td>
</tr>
<tr>
<td>Nb/Mn</td>
<td>0.4718(7)</td>
<td>0.5135(7)</td>
<td>0.5135(7)</td>
<td>1.69(6)</td>
<td>96g</td>
<td>0.1333/0.0333</td>
</tr>
<tr>
<td>O</td>
<td>0.32034(7)</td>
<td>0.125</td>
<td>0.125</td>
<td>1.77(6)</td>
<td>96g</td>
<td>0.1333/0.0333</td>
</tr>
<tr>
<td>O'</td>
<td>0.32068(7)</td>
<td>0.125</td>
<td>0.125</td>
<td>1.98(5)</td>
<td>96g</td>
<td>0.1333/0.0333</td>
</tr>
</tbody>
</table>

The upper and lower entries correspond to 12 and 293 K, respectively. The lattice parameter, cell volume, and final fit statistics at 12 K (293 K) are

<table>
<thead>
<tr>
<th>(a) (Å)</th>
<th>(a) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.47242(8)</td>
<td>10.47616(8)</td>
</tr>
</tbody>
</table>

Volume: 1148.526(15) Å\(^3\) (1149.757(15) Å\(^3\)), \(R_{wp} = 4.10\%\) (3.91\%), \(R_p = 3.30\%\) (3.18\%), \(R(F^2) = 3.68\%\) (3.39\%), \(\chi^2 = 1.23(1.10)\).
improve the bonding for Bi\(^{3+}\) (which would have a bond valence sum of 2.5 v.u. in the ideal structure).

The structural model for Bi\(_{1.6}\)Mn\(_{0.4}\)\((\text{Mn}_{0.8}\text{Nb}_{1.2})\)O\(_7\) (Table 4) is crystallographically analogous to that found for pyrochlore-type Bi\(_{1.5}\)Zn\(_{0.9}\)Nb\(_{1.5}\)O\(_6\)\(_{.9}\) [51], which has a similar concentration of B-type cations on the A-sites (21%). The displacements of the A-cations (0.36 Å) and the O\(^-\) oxygens (0.3 Å) from the ideal positions are similar, albeit slightly smaller than those in the Zn analog (0.39 and 0.46 Å, respectively). In refinements of the analogous Bi–Fe–Nb–O [52] and Bi–Co–Nb–O [53] pyrochlores, the A-site cations were also displaced to the 96g sites but O\(^-\) was displaced differently in each case—possibly a result of different concentrations of B-type ions on the A-sites (<10% and ~18%, respectively). The presence of smaller B-type cations on the A-sites should drive distortions to reduce their effective coordination number and achieve chemically reasonable bond distances; therefore, correlations between A-site occupancies and the details of the O\(^-\) displacements are expected.

### 3.4. Magnetic properties of pyrochlore phases

Magnetic data obtained for three different single-phase Bi–Mn–Nb–O pyrochlore samples indicated qualitatively similar properties. The field dependence of the magnetization confirmed that all samples were overall paramagnetic in nature. The temperature dependence of the magnetic susceptibility, and its inverse, for the pyrochlore with composition 0.3600:0.3200:0.3200 Bi\(_2\)O\(_3\):Mn\(_2\)O\(_3\):\(\pm_{.7}\)Nb\(_2\)O\(_5\) are shown in Fig. 5. Above 100 K the inverse magnetic susceptibility was linear and that range was used to fit the Curie–Weiss law; the results are given in Table 5. For all three compounds, the extrapolation of the linear fits indicated small negative temperature intercepts, suggesting the presence of weak antiferromagnetic cooperative interactions. All of the observed effective magnetic moments calculated from the slopes of the Curie–Weiss fits for a mixture of A-site Mn\(^{2+}\) (3d\(^5\), high spin S = 5/2, 5.92 \(\mu_B\)) and B-site Mn\(^{3+}\) (3d\(^4\), high spin S = 2, 4.90 \(\mu_B\)) are expected given the triangular symmetry of the metal lattices which results in geometric magnetic frustration [71,72].

Pyrochlore compounds are known to exhibit a wide range of cooperative magnetic properties and, for example, are of significant interest as ‘spin-ice’ systems [73–75]. The reported magnetic behavior of the rhombohedrally distorted pyrochlore Mn\(_2\)Sb\(_2\)O\(_7\) [67], with Mn\(^{2+}\) filling the A-sites, is similar to that of the Bi–Mn–Nb–O pyrochlore studied here. Mn\(_2\)Sb\(_2\)O\(_7\) exhibited paramagnetic behavior that obeyed the Curie–Weiss Law which extrapolated to a small negative temperature intercept (−33 K), and indicated a somewhat depressed effective moment (5.76 \(\mu_B\))

![Fig. 5. Temperature dependence of the zero-field-cooled (circles) and field-cooled (triangles) mass susceptibility and inverse mass susceptibility for the pyrochlore 0.3600:0.3200:0.3200 Bi\(_2\)O\(_3\):Mn\(_2\)O\(_3\):\(\pm_{.7}\)Nb\(_2\)O\(_5\) at an applied field of 50 kG. Similar results were obtained with an applied field of 20 kG. The inset shows the field dependence of the magnetization measured at 4.2 K (triangles) and 300 K (squares). (Lines are present to guide the eye.) The slight curvature observed in the low-temperature data suggests the presence of weak superparamagnetic effects. (Units: To convert susceptibility values in emu/g to SI units m\(^3\)/kg, multiply by 4\(\pi\)/10\(^3\). To convert field values in Oe (or G) to SI units A/m, multiply by 10\(^3\)/4\(\pi\). Magnetization values in emu/g are numerically equal to SI units of A/m kg [70].)](image)

#### Table 5

<table>
<thead>
<tr>
<th>Bi(_2)O(_3):Mn(_2)O(<em>3):(\pm</em>{.7})Nb(_2)O(_5)</th>
<th>Formula</th>
<th>(\mu_{\text{eff}})/mol Mn ((\mu_B))</th>
<th>(\theta) (K)</th>
<th>(\mu_{\text{calc}})/mol Mn ((\mu_B))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3600:0.3200:0.3200</td>
<td>Bi(<em>{1.4})Mn(</em>{0.4})(\pm_{.7})(\text{Mn}<em>{0.8})(\text{Nb}</em>{1.2})O(_7)</td>
<td>4.94</td>
<td>−34</td>
<td>5.37</td>
</tr>
<tr>
<td>0.4000:0.3000:0.3000</td>
<td>Bi(<em>{1.4})Mn(</em>{0.4})(\pm_{.7})(\text{Mn}<em>{0.8})(\text{Nb}</em>{1.2})O(_7)</td>
<td>4.95</td>
<td>−35</td>
<td>5.26</td>
</tr>
<tr>
<td>0.4200:0.2900:0.2900</td>
<td>Bi(<em>{1.4})Mn(</em>{0.4})(\pm_{.7})(\text{Mn}<em>{0.8})(\text{Nb}</em>{1.2})O(_7)</td>
<td>4.90</td>
<td>−31</td>
<td>5.20</td>
</tr>
</tbody>
</table>

The effective moments \((\mu_{\text{eff}})/\text{mol Mn}\) and temperature-axis intercepts \((\theta\), K\) were approximated from linear fits of the inverse susceptibility data (ZFC) in the temperature range 100–300 K. The calculated spin-only moments \((\mu_{\text{calc}})/\text{mol Mn}\) assume high-spin states for Mn\(^{2+}\) (3d\(^5\), 5.92 \(\mu_B\)) occupying A-sites and Mn\(^{3+}\) (3d\(^4\), 4.90 \(\mu_B\)) occupying B-sites, in proportions indicated by the formulas.
compared to the spin-only (high-spin) value for Mn\textsuperscript{2+} (5.92 \mu_B).

3.5. Dielectric properties of the pyrochlore phase

The relative permittivity (corrected for porosity) and dielectric loss for the single-phase pyrochlore Bi\textsubscript{1.600}Mn\textsubscript{1.200}Nb\textsubscript{1.200}O\textsubscript{7} (0.4000:0.3000:0.3000 Bi\textsubscript{2}O\textsubscript{3:Mn\textsubscript{2}O\textsubscript{3}:Nb\textsubscript{2}O\textsubscript{5}) as a function of temperature and frequency are shown in Fig. 6. The sample is predominantly conductive at temperatures above 250 K and the onset of conductivity is frequency dependent; these effects likely reflect the presence of mixed-valent Mn\textsuperscript{2+/3+}. Low-temperature dielectric relaxation such as that observed for Bi\textsubscript{1.5}Zn\textsubscript{0.92}Nb\textsubscript{1.5}O\textsubscript{6.92} and other bismuth-based pyrochlores was not observed.

Fig. 6. Relative dielectric permittivity (corrected for porosity) and dielectric loss for the single-phase pyrochlore Bi\textsubscript{1.600}Mn\textsubscript{1.200}Nb\textsubscript{1.200}O\textsubscript{7} (0.4000:0.3000:0.3000 Bi\textsubscript{2}O\textsubscript{3:Mn\textsubscript{2}O\textsubscript{3}:Nb\textsubscript{2}O\textsubscript{5}) at frequencies of 10, 100 kHz, and 1 MHz. The sample is predominantly conductive at temperatures above 250 K and the onset of conductivity is frequency dependent; these effects likely reflect the presence of mixed-valent Mn\textsuperscript{2+/3+}. Low-temperature dielectric relaxation such as that observed for Bi\textsubscript{1.5}Zn\textsubscript{0.92}Nb\textsubscript{1.5}O\textsubscript{6.92} and other bismuth-based pyrochlores was not observed.

### 4. Conclusions

Subsolidus phase relations have been determined for the Bi–Mn–Nb–O system in air using specimens equilibrated at 750–900 °C. Under these conditions, compounds contain- 

ing Mn in the 2+, 3+, and 4+ oxidation states were all observed. Ternary phase formation was limited to pyrochlores, which forms a considerable solid solution region at stoichiometries that are “Bi-deficient” compared to conventional A\textsubscript{2}B\textsubscript{2}O\textsubscript{7}-type formulations with Bi on the A-sites and Mn/Nb on the B-sites. The location of the pyrochlore field suggests that approximately 14–30% of the A-sites can be occupied by Mn (likely Mn\textsuperscript{2+}); analysis of EELS spectra indicated that the oxidation state of Mn in pyrochlore is between 2+ and 3+. All Bi–Mn–Nb–O pyrochlores form with structural displacements, as also found for analogous Bi–M–Nb–O pyrochlores with M = Zn, Fe, and Co. A structural refinement of the pyrochlore Bi\textsubscript{1.600}Mn\textsubscript{0.8} (Mn\textsubscript{3+}0.8Nb\textsubscript{1.2})O\textsubscript{7} using neutron powder diffraction data is reported with the displacive disorder modeled similarly to that in Bi\textsubscript{1.5}Zn\textsubscript{0.92}Nb\textsubscript{1.5}O\textsubscript{6.92}. The results are consistent with a structural formula of Bi\textsubscript{1.6}Mn\textsubscript{0.8} (Mn\textsubscript{3+}0.8Nb\textsubscript{1.2})O\textsubscript{7}, with both the A- and B-sites completely occupied. Bi–Mn–Nb–O pyrochlores exhibited overall paramagnetic behavior with weak antiferromagnetic interactions and the presence of some superparamagnetic effects; observed moments were depressed compared to high-spin, spin-only values calculated for the corresponding Mn\textsuperscript{2+/3+} mixtures. Measurements of relative dielectric permittivity and dielectric loss between 110 and 300 K indicated conductive, frequency-dependent properties consistent with the presence of mixed-valent Mn. In contrast to Bi\textsubscript{1.5}Zn\textsubscript{0.92}Nb\textsubscript{1.5}O\textsubscript{6.92}, no low-temperature dielectric relaxation was observed. Bi–Mn–Nb–O pyrochlores form thermodynamically stable mixtures with Bi\textsubscript{3}NbO\textsubscript{7} solid solution, Bi\textsubscript{5}Nb\textsubscript{3}O\textsubscript{15}, BiNbO\textsubscript{4}, MnNb\textsubscript{2}O\textsubscript{6},
Mn$_2$O$_3$/Mn$_3$O$_4$, and Bi$_2$Mn$_4$O$_{10}$. Crystalline, highly textured Bi–Mn–Nb–O pyrochlore films were readily deposited using pulsed laser deposition.

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References