

Comparative Phase Equilibria in the $\text{Bi}_2\text{O}_3\text{-MO}_x\text{-Nb}_2\text{O}_5$ Systems ($\text{MO}_x = \text{Mn}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{Co}_3\text{O}_4, \text{ZnO}$)

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ABSTRACT: Phase equilibrium studies of the title systems all reveal the formation of non-stoichiometric, displacively disordered pyrochlore phases. Formation of other ternary phases in these systems is limited. Initial screening of the dielectric properties of the Mn, Fe, and Co pyrochlores at 100 KHz indicated lossy behavior and dielectric constants on the order of 150.

Key words: phase equilibrium, pyrochlore, $\text{Bi}_2\text{O}_3\text{-MO}_x\text{-Nb}_2\text{O}_5$ (M = Mn, Fe, Co, Zn), dielectric constant

1. INTRODUCTION

Pyrochlore phases ($\text{A}_2\text{B}_2\text{O}_6\text{O}'$) form in a wide variety of chemical systems and are known to exhibit many different exploitable "electroceramic" properties including ferroelectricity, ionic conductivity, metallic conductivity, semiconductivity, superconductivity, ferromagnetism, antiferromagnetism, and spin-glass behavior [1].

Pyrochlores found in the Bi-Zn-Nb-O system can be used to prepare temperature-stable dielectric ceramics potentially useful as embedded capacitors or other dielectric elements [2-3]. These materials are two-phase mixtures of the two ternary compounds, pyrochlore and zirconolite, that form in the $\text{Bi}_2\text{O}_3\text{-ZnO-Nb}_2\text{O}_5$ system – no other compounds were found in the phase diagram study [1]. The zirconolite [4] and pyrochlore [5] crystal structures have been characterized in detail.

Neutron powder diffraction studies of the pyrochlore $\text{Bi}_{1.5}\text{Zn}_{0.92}\text{Nb}_{1.5}\text{O}_{6.92}$ [5] revealed static displacive disorder in the $\text{A}_2\text{O}'$ portion of the structure and concluded a structural formula that featured the unusual mixture of small Zn^{2+} ions (radius 0.64 Å [6]) with considerably larger Bi^{3+} ions (radius 1.17 Å) on the 8-coordinated A sites. Diagnostically, this disorder was indicated by observation of weak reflections; e.g., with Miller indices 442, which are forbidden in the ideal pyrochlore arrangement. These reflections were accounted for by moving the A and O' ions to lower-symmetry crystallographic positions – though the cubic space group remained unchanged ($Fd\bar{3}m$, $a = 10.5616(1)$ Å). The combined displacements of the A (0.39 Å) and O' (0.46 Å) ions changes the coordination number of the A cations from 8 to (5 + 3), thus permitting the smaller Zn^{2+} ion to achieve a chemically reasonable environment, with fewer nearest oxygens, via local correlations of the displaced ions, as subsequently confirmed by a detailed study of diffuse scattering [7]. Vibrational spectroscopic

studies suggested that the glass-like dielectric behavior observed for $\text{Bi}_{1.5}\text{Zn}_{0.92}\text{Nb}_{1.5}\text{O}_{6.92}$ is caused by this displacive disorder [8]. The unusual structural behavior in this pyrochlore therefore appears to play a key role in its electronic properties.

Phase equilibria studies of the analogous systems with Mn, Fe, and Co instead of Zn were carried out to elucidate the location and nature of pyrochlore phases as well as the formation of any other ternary compounds with the combination of both dielectric (Bi, Nb) and magnetic (Mn, Fe, Co) ions.

2. EXPERIMENTAL METHODS

52 and 68 polycrystalline specimens (3-4 g each) were prepared to determine the Bi-Mn-Nb-O and Bi-Fe-Nb-O phase diagrams, respectively. Synthesis was carried out in air by solid-state reactions using Bi_2O_3 (99.999%), MnCO_3 (reagent grade, pre-analyzed by TGA) or Fe_2O_3 (reagent grade), and Nb_2O_5 (99.999%). Prior to each heating, each sample was mixed by grinding with an agate mortar and pestle for 15 min, pelletized, and placed on sacrificial powder of the same composition on Pt foil supported by alumina ceramic. After an initial overnight calcine at 800 °C (below the m.p. of Bi_2O_3 , 825 °C) multiple 4-hour heatings (with intermediate grinding and re-pelletizing) were carried out at 885 °C – 925 °C. (Exceptions were low-melting specimens with Bi contents above 90 % mole fraction $\text{BiO}_{1.5}$, which were not heated above 700 °C). Samples were furnace-cooled to ≈ 700 °C and then air-quenched on the bench-top. Typically, three to five heatings were required to attain equilibrium, which was presumed when no further changes could be detected in the weakest peaks observed in the X-ray powder diffraction patterns. Single pyrochlore-type crystals were readily grown in both systems by slow-cooling neat melts enclosed

in welded platinum capsules.

Phase assemblages were ascertained using the disappearing phase method and X-ray diffraction data obtained with a powder diffractometer equipped with incident Soller slits, a theta-compensating slit and graphite monochromator, and a scintillation detector. Samples were mounted in welded glass slides. Patterns were collected at ambient temperatures using $\text{CuK}\alpha$ radiation over the range $3^\circ 2\theta$ to $70^\circ 2\theta$ with a $0.02^\circ 2\theta$ step size and a 2 s count time.

Dielectric constants were evaluated by measuring the capacitance at 100 kHz of sintered disks of single-phase pyrochlore specimens. An LCR meter was used with an applied signal of 0.8 V; samples were metallized with fired-on thick-film silver paint. Pyrochlores in the Bi-Mn-Nb-O, Bi-Fe-Nb-O, and Bi-Co-Nb-O systems exhibited relative permittivities on the order of 150 and were highly lossy at 100 kHz.

3. RESULTS

Preliminary results for the Bi-Mn-Nb-O phase diagram are given in Fig. 1. Pyrochlore was the only ternary phase observed to form in this system and is seen to form stable mixtures with six phases in the perimeter binary systems.

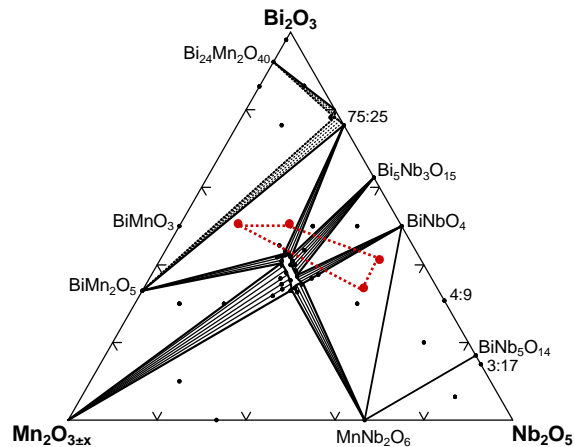


Fig. 1. Phase diagram determined for the Bi-Mn-Nb-O system in air with maximum synthesis temperatures of 885 °C. The central dotted lines outline the compositions for “traditional” pyrochlores (with only Bi on the A-sites and Mn/Nb mixtures on the B-sites).

Preliminary results for the Bi-Fe-Nb-O phase diagram are shown in Fig. 2. In addition to pyrochlore, three other phases were found to form, one with an Aurivillius-type structure and two with layer structures related to that of the phase $\text{Bi}_8\text{Nb}_{18}\text{O}_{57}$ – studies of these compounds will be described elsewhere. The pyrochlore phase is seen to form stable mixtures with 8 other phases in the system (Fig. 2). The large width of the pyrochlore field illustrates its tolerance of a wide Fe/Nb range compared to the Mn system, which in turn occurs with a larger Bi concentration range (Fig. 1). Both the Mn and Fe pyrochlore fields are significantly larger than that of the analogous Zn system [1].

Preliminary studies of the Bi-Co-Nb-O phase diagram, which will be described elsewhere, suggest that, as for the analogous Mn system, pyrochlore is the only ternary phase that forms. The location and shape of the pyrochlore field

in the Co system resembles more those in the Zn system, rather than those shown in Figs. 1 and 2 for the Mn and Fe systems.

Further studies of the Bi-Mn-Nb-O, Bi-Fe-Nb-O, and Bi-Co-Nb-O pyrochlore phases are in progress to determine oxidation states (especially for Co and Mn), characterize single crystals, and further evaluate magnetic and dielectric properties.

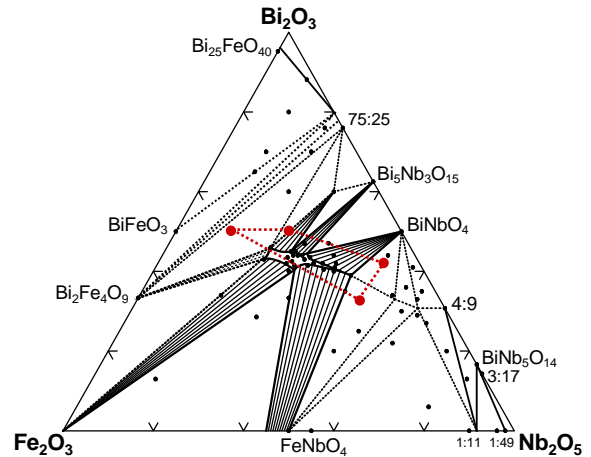


Fig. 2. Phase diagram determined for the Bi-Fe-Nb-O system in air with maximum synthesis temperatures of 925 °C. The central dotted lines outline the compositions for “traditional” pyrochlores (with only Bi on the A-sites and Fe/Nb mixtures on the B-sites).

In both the Bi-Mn-Nb-O and Bi-Fe-Nb-O phase diagrams, similar to the Bi_2O_3 -ZnO- Nb_2O_5 system [1], the pyrochlore single-phase fields occur at substantially lower Bi concentrations than the conventional formulas, and at compositions requiring the mixing of B-type Mn and Fe cations on the A-sites with Bi^{3+} . Furthermore, all X-ray powder diffraction patterns for pyrochlore and pyrochlore-containing specimens in these studies exhibited clearly observable 442 reflections. We conclude that, as for the Bi-Zn-Nb-O system, the occurrence of displacive disorder in the $\text{A}_2\text{O}'$ network is required for the formation of pyrochlore in the Bi-Mn-Nb-O and Bi-Fe-Nb-O chemical systems. We refer to these as misplaced-displacive cubic pyrochlores [1] – pyrochlores which exhibit misplacement of traditionally octahedral B-site cations onto the larger A-sites, accompanied by displacive disorder in the $\text{A}_2\text{O}'$ substructure to facilitate lower coordination numbers for the smaller species.

4. CONCLUSIONS

Phase equilibrium studies of the Bi-M-Nb-O (M = Zn, Mn, Fe, Co) systems have confirmed that all pyrochlore phases that form, regardless of the 3d metal, are displacively disordered. Furthermore, all systems feature pyrochlores at compositions requiring the mixing of small B-type ions (Zn, Mn, Fe, Co) with large Bi^{3+} ions on the A-sites. In the Bi-Zn-Nb-O system [1], the location of the pyrochlore field indicates that this behavior is required thermodynamically for the formation of this crystal structure – pyrochlore does not form at any composition predicted by conventional crystal chemical rules (i.e. at compositions with only Bi on the A-sites and Zn,Nb confined to B-sites).

These studies provide further evidence that the pyrochlore structure can accommodate small B-type metals on the large A-sites via displacive disorder. Therefore, solid state chemists are no longer restricted to the formula $A_2B_2O_6O'$ in the preparation of pyrochlore-type compounds with yet unknown, potentially useful properties. We suggest that many compounds can now be synthesized and/or modified by deliberate combinations of large and small metal ions on the A-sites. Since large A cations and smaller B-type cations tend to be electronically dissimilar, electrical and magnetic properties should be strongly affected by mixing them in the A_2O' network [9]. Ionic conductivity properties should also depend strongly on the occurrence of B cations, vacancies, and displacive disorder in the A_2O' network. We challenge the theoretical community to help us understand why some chemical systems only form so-called misplaced-displacive cubic pyrochlore phases, even though conventional crystal chemistry suggests that normal pyrochlores should form.

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