Supplementary Information

Effect of R-site Element on Crystalline Phase and Thermal Stability of Fe Substituted Mn Mullite-type Oxides: $R_2(Mn_{1-x}Fe_x)_{4}O_{10-\delta}$ (R = Y, Sm or Bi; $x = 0, 0.5, 1$)

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Fig. S1. (a) Crystal structure of mullite-type oxides. Atoms are labeled with their Wyckoff symbols. (b) Edge-shared MO$_5$ square pyramids in O10-type structure. (c) Vertex-sharing MO$_4$ tetrahedral in O9-type structure. Green, blue, brown, and red balls represent R, Mn, Fe, and O atoms, respectively.

Table S1. U values used in this work for oxide systems and the energy adjustments between previous work and this work.

<table>
<thead>
<tr>
<th>Element</th>
<th>$U_{\text{eff}}$ (eV)</th>
<th>$\Delta E_M$ (eV)</th>
<th>$\Delta E_M$ (eV)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>4.0</td>
<td>2.0</td>
<td>1.7</td>
</tr>
<tr>
<td>Mn</td>
<td>3.9</td>
<td>1.8</td>
<td>1.7</td>
</tr>
</tbody>
</table>

$^a$Ref. 1
**Fig. S2.** Rietveld refinement plot of (a, b) R = Y; (c, d) R = Sm for 50% Fe/50% Mn and 100% Fe, respectively in the reactants. The blue, red, and grey lines represent the experimental, calculated, and difference patterns, respectively. Phase compositions and lattice parameters for the mullite-type compounds are summarized in Table S2 and S3, respectively. $\lambda_{K\alpha1} = 0.15406$ nm wavelength was used in the refinement.

**Fig. S3.** Rietveld refinement plot of Bi$_2$Fe$_4$O$_9$. The blue, red, and grey lines represent the experimental, calculated, and difference patterns, respectively. Phase compositions and lattice parameters for the mullite-type compounds are summarized in Table S2 and S3, respectively. $\lambda_{K\alpha1} = 0.15406$ nm wavelength was used in the refinement.
<table>
<thead>
<tr>
<th>R-site</th>
<th>M-site</th>
<th>Phase Composition</th>
<th>% Phase Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>100% Mn</td>
<td>(Y_2\text{Mn}<em>4\text{O}</em>{10})</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>50% Fe/50% Mn</td>
<td>(Y_2\text{Mn}<em>{1.88(2)}\text{Fe}</em>{1.87(2)}\text{O}_{10})</td>
<td>55.3(5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Y\text{FeO}_3)</td>
<td>20.9(4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\text{Mn}_2\text{O}_3)</td>
<td>16.4(6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Y\text{Mn}_3\text{O}_3)</td>
<td>7.4(1)</td>
</tr>
<tr>
<td></td>
<td>100% Fe</td>
<td>(Y\text{FeO}_3)</td>
<td>56.6(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\text{Fe}_2\text{O}_3)</td>
<td>27.4(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Y_3\text{Fe}<em>5\text{O}</em>{12})</td>
<td>10.5(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Y_2\text{O}_3)</td>
<td>5.5(1)</td>
</tr>
<tr>
<td>Sm</td>
<td>100% Mn</td>
<td>(\text{Sm}_2\text{Mn}<em>4\text{O}</em>{10})</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>50% Fe/50% Mn</td>
<td>(\text{Sm}<em>2\text{Mn}</em>{2.22(3)}\text{Fe}<em>{2.00(4)}\text{O}</em>{10})</td>
<td>18.2(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\text{SmFeO}_3)</td>
<td>47.0(5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\text{Mn}_2\text{O}_3)</td>
<td>34.8(5)</td>
</tr>
<tr>
<td></td>
<td>100% Fe</td>
<td>(\text{SmFeO}_3)</td>
<td>72.1(4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\text{Fe}_2\text{O}_3)</td>
<td>27.9(4)</td>
</tr>
<tr>
<td>Bi</td>
<td>100% Mn</td>
<td>(\text{Bi}_2\text{Mn}<em>4\text{O}</em>{10})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50% Fe/50% Mn</td>
<td>(\text{Bi}<em>2\text{Mn}</em>{2.23(4)}\text{Fe}<em>{2.00(2)}\text{O}</em>{10})</td>
<td>54.4(4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\text{Bi}<em>2\text{Fe}</em>{4.00(4)}\text{O}_9)</td>
<td>41.8(4)</td>
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<tr>
<td></td>
<td></td>
<td>(\text{Mn}_2\text{O}_3)</td>
<td>3.8(3)</td>
</tr>
<tr>
<td></td>
<td>100% Fe</td>
<td>(\text{Bi}<em>2\text{Fe}</em>{4.16(1)}\text{O}_9)</td>
<td>95.1(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\text{Bi}_2\text{O}_3)</td>
<td>4.0(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\text{BiFeO}_3)</td>
<td>0.9(1)</td>
</tr>
</tbody>
</table>
Table S3. Rietveld refined and simulated lattice parameters and Fe ground state occupation sites in the single unit cell for R\textsubscript{2}(Mn\textsubscript{1-x}Fe\textsubscript{x})\textsubscript{4}O\textsubscript{10-δ} (R = Y, Sm, Bi).

<table>
<thead>
<tr>
<th>R = Y</th>
<th>Experimental (nm)</th>
<th>Theoretical (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>100% Mn\textsuperscript{4+}</td>
<td>0.72667(6)</td>
<td>0.84732(6)</td>
</tr>
<tr>
<td>50%Fe/50%Mn</td>
<td>0.72801(10)</td>
<td>0.84625(12)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>R = Sm</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Mn\textsuperscript{4+}</td>
<td>0.74296(4)</td>
<td>0.85802(5)</td>
<td>0.56908(3)</td>
<td>0.751</td>
<td>0.866</td>
<td>0.578</td>
</tr>
<tr>
<td>50%Fe/50%Mn</td>
<td>0.74190(20)</td>
<td>0.85680(20)</td>
<td>0.56837(15)</td>
<td>0.749</td>
<td>0.870</td>
<td>0.578</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>R = Bi</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Mn\textsuperscript{4+}</td>
<td>0.75652(2)</td>
<td>0.85370(2)</td>
<td>0.57635(1)</td>
<td>0.759</td>
<td>0.864</td>
<td>0.584</td>
</tr>
<tr>
<td>50%Fe/50%Mn</td>
<td>0.76066(8)</td>
<td>0.84996(10)</td>
<td>0.58019(6)</td>
<td>0.758</td>
<td>0.873</td>
<td>0.583</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Ref. 1

Figure S4 shows the density of states (DOS) for unstable Bi\textsubscript{2}Fe\textsubscript{4}O\textsubscript{10} \textit{(O10)} and stable Bi\textsubscript{2}Fe\textsubscript{4}O\textsubscript{9} \textit{(O9)} compounds with 100% Fe substitution. According to crystal field theory, Fe d-electrons in octahedral (4\textit{f}) and polyhedral (4\textit{h}) sites follow high spin 3d\textsuperscript{5} state.\textsuperscript{2} In \textit{O10-type} structure (Fig. S4a), the increase in Fe concentration (x ≥ 0.6) forces Fe into the 4\textit{f} octahedral sites resulting in significant Jahn-Teller distortion; the 4\textit{g} and 2\textit{g} states of Fe in 4\textit{f} octahedra show further splitting into five different recognizable states, including an empty state in the middle of the band gap (labeled as 2\textit{g} \textsuperscript{*} and 4\textit{g} \textsuperscript{*} in Fig. S4a). This new empty state indicates an increase in the oxidation state of Fe greater than 3\textsuperscript{+}, which leads to Fe instability. Moreover, the empty state results in the removal of an additional electron from the half-filled d shell along with an increase in the minority spin caused by an increase in bonded electrons. This is energetically unfavorable per Hund’s Rule and Fe’s strong exchange interaction\textsuperscript{3} resulting in decreased stability of \textit{O10-type} structure (Fig. 6). Contrary to the distorted Fe octahedral occupation in \textit{O10-type} structures, Fe in pyramidal sites (Fig. S4b) show no clear evidence for serious Jahn-Teller distortion and therefore does not decrease the system stability. For \textit{O9-type} structure, there is no over oxidation of Fe in the substituted octahedral (Fig. S4c) or tetrahedral sites (Fig. S4d), thus no 4\textit{g} or 2\textit{g} states below the Fermi level. Since \textit{O9-type} structures have 3\textsuperscript{+} octahedral and tetrahedral sites, we see stable Fe substitution into both locations resulting in a DOS similar to that found in the \textit{O10-type}
pyramidal sites. This exchange interaction induced separation of occupied majority spin states from unoccupied minority spin states gives Fe its most stable configuration with a half-filled d-shell allowing for O9-type formation.

**Fig. S4.** Density of states for (a, b) Bi$_2$Fe$_4$O$_{10}$ (O10) and (c, d) Bi$_2$Fe$_4$O$_9$ (O9). States of Fe d-electrons in (a) 4f octahedral and (b) 4h pyramid sites in Bi$_2$Fe$_4$O$_{10}$, respectively. (c) 4f octahedral and (d) 4h tetrahedral sites in Bi$_2$Fe$_4$O$_9$, respectively. Red and blue represents majority and minority spins, respectively. (*Total DOS was divided by 5 to clearly illustrate Fe p-DOS.*).

In contrast to Fe, Mn compound shows a lower stability in O9-type structures (Fig. S5a). In Bi$_2$Mn$_4$O$_9$ O9-type structure, octahedral chains show high d orbital electron density right below the Fermi level (Fig. S5a, black arrow). This indicates that Mn atoms are still highly reactive. On the other hand, in O10-type structure DOS for the 4f octahedral site (Fig. S5b) shows an electron density decrease (Fig. S5b, black arrow) while the non-bonding states (Fig. S5b, green arrow) increase above Fermi level. This is due to the higher oxidation state of Mn to 4+, resulting in lower reactivity from Mn atoms and no Jahn-Teller distortion, hence a more stable structure. Because Mn$^{3+}$ is known to have stable first order Jahn-Teller distortion,$^4$ having
Mn$^{3+}$ ion in the 4$f$ octahedral site of O9-type will destabilize the structure as Mn$^{3+}$ would attempt to elongate the z direction. Consequently, these Mn$^{3+}$ substituted octahedral sites exhibit small amounts of second order Jahn-Teller distortion in the a-b plane attempting to compensate for lack of first order Jahn-Teller distortion, decreasing stability of O9-type Mn compound. Mn$^{3+}$ is also unstable when placed in a tetrahedral site in the O9-type structure; in the tetrahedral site, the formation energy is 0.8 eV lower than that of Mn substituted octahedral sites due to lack of Jahn-Teller distortion. Thus, it is difficult to form pure Mn compounds with O9-type structure. These results clearly show that the pure Fe compound can never form stable Bi$_2$Fe$_4$O$_{10}$ O10-type structure and the pure Mn compound can never form stable Bi$_2$Mn$_4$O$_9$ O9-type structure.

![Density of states for 4f octahedral Mn d-shell electrons](image)

**Fig. S5.** Density of states for 4$f$ octahedral Mn d-shell electrons in (a) Bi$_2$Mn$_4$O$_9$ O9-type and (b) Bi$_2$Mn$_4$O$_{10}$ O10-type. The black arrows show high d orbital electron density right below the Fermi level. The green arrow shows the formation of additional non-bonding states representing the higher oxidation state of Mn. Red and blue represents majority and minority spins, respectively.
**Fig. S6.** (a) Zoom in view of TGA (black) and DSC (red) curves showing the decomposition region for R = Y for 50% Fe and 50% Mn in the reactants. (b) XRD pattern of as-synthesized (black) and decomposed (red) samples, respectively. Respective reference diffraction data are shown.

**References**


