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Tunable band gap in $\text{Bi}(\text{Fe}_{1-x}\text{Mn}_x)\text{O}_3$ films

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In order to investigate band gap tunability in polar oxides, we measured the optical properties of a series of $\text{Bi}(\text{Fe}_{1-x}\text{Mn}_x)\text{O}_3$ thin films. The absorption response of the mixed metal solid solutions is approximately a linear combination of the characteristics of the two end members, a result that demonstrates straightforward band gap tunability in this system. © 2010 American Institute of Physics. [doi:10.1063/1.3427499]

Iron-based compounds and mixed metal oxides are promising materials for light harvesting applications.¹ One system that has attracted attention in this regard is BiFeO_3 . Recent reports of photoconductivity,² a photovoltaic effect,³ and a 0.8–0.9 V open circuit voltage in a working solar device,⁴ illustrate the potential of a polar oxide as the active photovoltaic material. The light harvesting efficiency in BiFeO_3 is, however, still limited by a variety of factors including carrier lifetimes, recombination rates, and matching the band gap and overall electronic structure with the solar spectrum. Optical spectroscopy is a sensitive and microscopic probe of the nature and size of a band gap, chemical bonding, and hybridization.^{2,5,6} At the same time, it offers a test of band gap tuning methodologies, previewing how chemical substitution or strain might impact the match with the solar spectrum, and by corollary, energy conversion efficiencies of a device.

The rhombohedrally-distorted perovskite BiFeO_3 has attracted attention as a ferroelectric below 1100 K due to Bi displacement and as a G-type antiferromagnet below 640 K. The optical response is relatively well understood, and the 2.7 eV direct band gap can be attributed to majority channel $\text{Fe } 3d \rightarrow \text{O } 2p$ charge transfer excitations.^{2,5,7} On the other hand, BiMnO_3 is ferromagnetic below 105 K with a large saturation magnetization (3.6 μ_B per formula unit) and strong magnetoelectric coupling.^{8,9} First principles calculations predict that gap-forming charge transfer excitations should be observed at much lower energy in BiMnO_3 than in BiFeO_3 .^{10–13} Previous efforts focused on the potential of alloy systems for combining ferroelectricity and ferromagnetism.¹⁴ Although ultimately unsuccessful due to the lack of metal site ordering,¹⁴ mixed metal polar oxides such as $\text{Bi}(\text{Fe}_{1-x}\text{Mn}_x)\text{O}_3$ remain attractive candidates for light harvesting applications, especially if the solid solutions retain their ferroelectric character.

The preparation of single phase epitaxial solid solutions allowed us to investigate the optical properties of $\text{Bi}(\text{Fe}_{1-x}\text{Mn}_x)\text{O}_3$ thin films and compare the results with theoretical predictions. These measurements reveal an absorption band at 1.6 eV that develops with increasing Mn concentration. We assign this near-infrared feature to charge transfer excitations between mixed Mn $3d$ and O $2p$ states. Overall, the optical properties of the $x=0.2, 0.4, 0.6,$ and 0.8 solid solutions retain the basic characteristics of the two end members and are very similar to that expected from simple concentration averaging. We extract a 1.1 eV optical band gap in the BiMnO_3 end member.¹⁵ More broadly, we show that BiFeO_3 presents an excellent starting point for band gap tuning experiments in which metal site substitution can be used to capture the long near infrared tail in the solar spectrum.

Our experiments were carried out on a series of 33 and 50 nm thick $\text{Bi}(\text{Fe}_{1-x}\text{Mn}_x)\text{O}_3$ films grown by reactive molecular-beam epitaxy in an adsorption-controlled regime on SrTiO_3 (001) substrates.^{5,16} Film grown details are reported elsewhere.¹⁵ BiFeO_3 and BiMnO_3 films on DyScO_3 (110) substrates were also employed to extend our measurements to higher energy, a procedure that was especially useful for understanding charge excitations in the BiMnO_3 end member. As shown in Fig. 1, the mixed metal oxide films of interest here are solid solutions rather than phase separated heterostructures. Optical spectra were collected in transmittance mode using a Perkin–Elmer Lambda-900 spectrometer (3000–190 nm; 0.41–6.53 eV). Corresponding substrates were used as references. Absorption was calculated as $\alpha(E) = -(1/d)\ln[\mathcal{T}(E)]$, where d is the film thickness, \mathcal{T} is the measured transmittance, and E is the energy.

Figure 2 displays the 300 K optical absorption spectrum of a series of $\text{Bi}(\text{Fe}_{1-x}\text{Mn}_x)\text{O}_3$ solid solution films including the two end members BiFeO_3 and BiMnO_3 . The optical properties of BiFeO_3 are well documented.^{2,5,7} The 300 K direct charge gap is at 2.7 eV. It is preceded by a small shoulder centered at ~ 2.5 eV, which yields an absorption onset near 2.2 eV. Peaks at 3.2 and 4.5 eV are dipole-allowed charge transfer excitations.^{2,7} With increasing Mn substitution, the 2.7 eV charge gap broadens and begins to redshift

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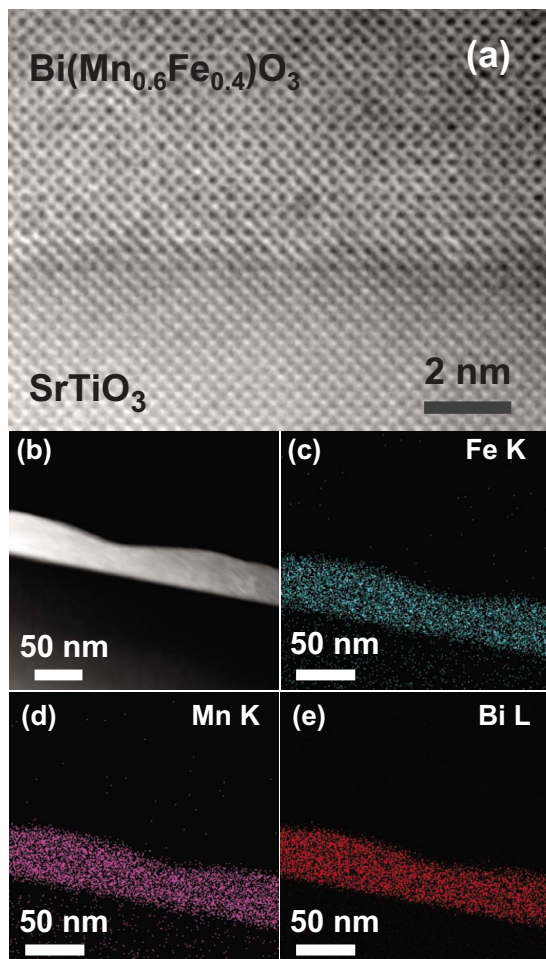


FIG. 1. (Color online) Transmission electron microscopy image of $\text{BiMn}_{0.6}\text{Fe}_{0.4}\text{O}_3$ on SrTiO_3 . (a) High resolution image of the $\text{BiMn}_{0.6}\text{Fe}_{0.4}\text{O}_3/\text{SrTiO}_3$ interface. [(b)–(e)] Bright field image and Fe, Mn, and Bi map of the same region, respectively. Considerable variation in the film thickness is revealed.

(Fig. 3). This trend continues in $\text{Bi}(\text{Fe}_{0.8}\text{Mn}_{0.2})\text{O}_3$ and $\text{Bi}(\text{Fe}_{0.6}\text{Mn}_{0.4})\text{O}_3$. The 2.5 eV shoulder is barely visible in $\text{Bi}(\text{Fe}_{0.8}\text{Mn}_{0.2})\text{O}_3$, and it disappears in films with higher Mn^{3+} concentrations. At the same time, a new structure appears in the near infrared, grows with increasing Mn^{3+} substitution, and eventually develops into the 1.6 eV band in BiMnO_3 . Based upon comparison with electronic structure calculations,^{10–13} the experimental spectrum of chemically similar materials with Mn^{3+} centers in locally distorted octahedral environments such as LaMnO_3 ,^{17–20} and the overall intensity ($\alpha \sim 10^5 \text{ cm}^{-1}$), we assign the near infrared band at $\sim 1.6 \text{ eV}$ to charge transfer excitations between mixed O 2p and Mn 3d states. Plots of $(\alpha E)^2$ versus energy place the charge gap in BiMnO_3 at $\sim 1.1 \pm 0.1 \text{ eV}$ (Fig. 3 inset).^{21,22} Overall, the optical properties of the $\text{Bi}(\text{Fe}_{1-x}\text{Mn}_x)\text{O}_3$ solid solution films appear to be a superposition of the end member spectral responses.

Previous work suggests that $\text{Bi}(\text{Fe}_{1-x}\text{Mn}_x)\text{O}_3$ forms solid solutions over the entire composition range at high pressure,¹⁴ whereas at atmospheric pressure BiMnO_3 is metastable. This is because Fe^{3+} and Mn^{3+} have similar ionic radii and positive ferromagnetic/antiferromagnetic ordered phase enthalpies.²³ Further, introducing Mn into BiFeO_3 is unlikely to create mixed valent Fe centers.^{23,24} Earlier ellipsometry studies of $\text{Bi}(\text{Fe}_{0.5}\text{Mn}_{0.5})\text{O}_3$ thin films show an

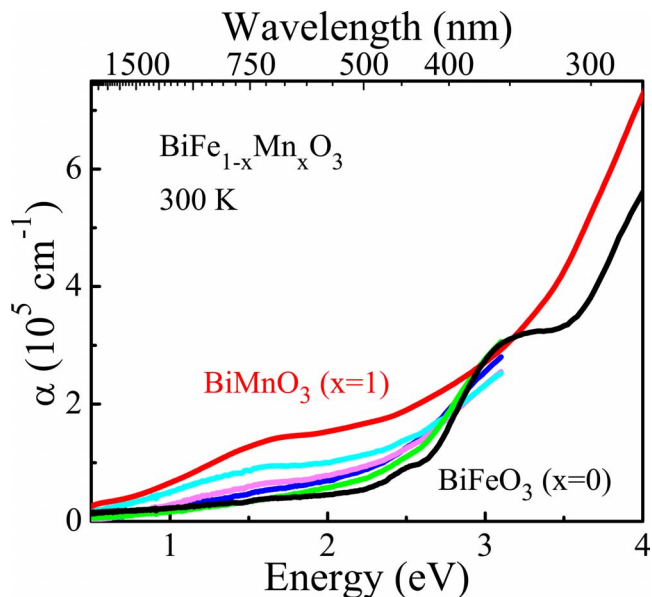


FIG. 2. (Color online) Absorption spectrum of $\text{Bi}(\text{Fe}_{1-x}\text{Mn}_x)\text{O}_3$ thin films at 300 K, where $x=0, 0.2, 0.4, 0.6, 0.8,$ and 1 .

absorption profile that is consistent with our data above 1.2 eV,²³ although an additional peak near 1.1 eV (1100 nm) is attributed to mixed valent Mn states. This feature is not observed in our spectra [Fig. 4(b)], a possible indication of minimal valence mixing of Mn in our materials.

In order to gain additional insight into this system, we compared the measured absorption spectra of the $\text{Bi}(\text{Fe}_{1-x}\text{Mn}_x)\text{O}_3$ films with simulated spectra that were calculated by assuming a linear combination of BiMnO_3 and BiFeO_3 spectra according to the relative Fe and Mn atomic concentrations (Fig. 4). Overall, the measured spectra are very similar to the simulations, with only subtle differences. Two items merit special attention. First, the small shoulder at $\sim 2.5 \text{ eV}$ is broadened and barely visible in the spectrum of the $x=0.2$ film whereas it is still obvious in the simulated spectra at both $x=0.2$ and 0.4 . That the 2.5 eV shoulder degrades faster than expected compared with simple concentration averaging is a possible indication of nonlocal charac-

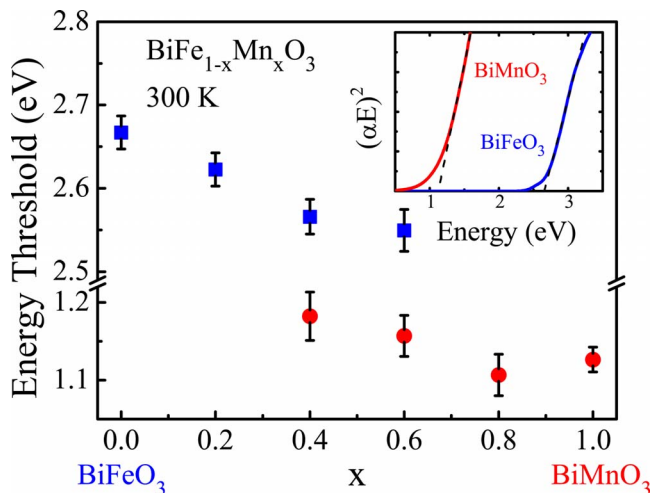


FIG. 3. (Color online) Main panel: energy threshold extracted from absorption data at 300 K using the direct gap method illustrated in the inset (solid lines: measured; dotted lines: linear fit) where examples of BiMnO_3 and BiFeO_3 are shown.

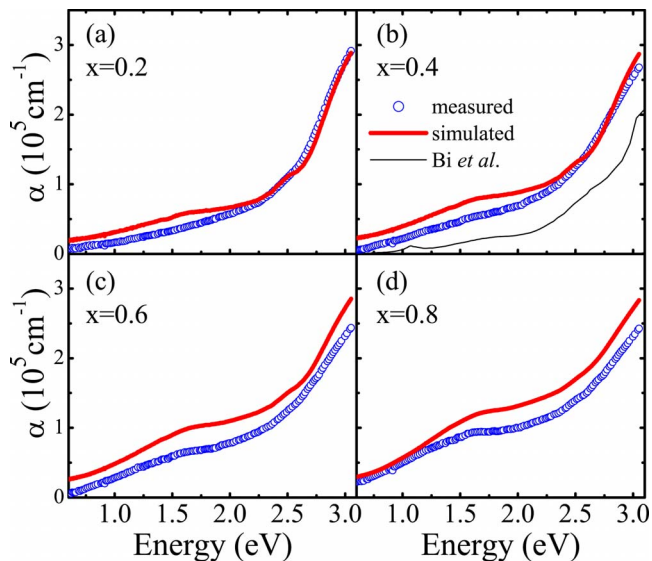


FIG. 4. (Color online) Comparison between measured (open circles) and simulated (thick lines) absorption spectra for $\text{Bi}(\text{Fe}_{1-x}\text{Mn}_x)\text{O}_3$ thin films. The simulation assumes a linear combination of BiMO_3 and BiFeO_3 end members spectra according to atomic ratio. The thin line in (b) is calculated using the $x=0.5$ data from Ref. 23.

ter of this excitation.²⁵ Second, the measured near infrared intensity is overall lower than that of the simulation, consistent with the phase-diagram in which a strong distortion of the oxygen octahedra (in monoclinic phase) only exists at high Mn concentration.¹⁴

In conclusion, we measured the optical properties of $\text{Bi}(\text{Fe}_{1-x}\text{Mn}_x)\text{O}_3$ solid solution films and show that thin film polar oxides like the mixed metal system studied here have the potential to collect light in the near infrared range of the solar spectrum, separate charge by virtue of the intrinsic ferroelectricity (assuming these substituted systems retain ferroelectric character), and, by charge transfer processes, connect efficiently with other important energy levels in a working solar device. This band gap tuning may be present in other mixed metal polar oxides.

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