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Continuously controllable optical band gap in orthorhombic ferroelectric KNbO$_3$-BiFeO$_3$ ceramics

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The optical bandgap of orthorhombic ferroelectric KNbO$_3$ is shown to be continuously controllable via Bi and Fe co-substitution according to a K$_{1-x}$Bi$_x$Nb$_{1-x}$Fe$_x$O$_3$ doping mechanism. The room temperature X-ray diffraction data combined with Raman spectroscopy analysis show the polar orthorhombic crystal structure to persist up to $x = 0.25$, while the bandgap narrows monotonically by 1 eV (−33%). In-situ Raman spectroscopy corroborates the polar nature of all compositions in the temperature range of −100 to 200 °C. The ability to control the bandgap while maintaining the spontaneous polarisation makes the K$_{1-x}$Bi$_x$Nb$_{1-x}$Fe$_x$O$_3$ system interesting for photoinduced processes in a wide temperature range. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4982600]

Coupling of light absorption in ferroelectrics (FEs) with properties such as photovoltage, photostriction, photoelasticity and photocatalysis can be exploited to create novel photoactive devices. Interestingly, the photoresponse of FEs is characterised by photovoltages that exceed several times their bandgap values. Moreover, the internal electrical field arising from the spontaneous polarization exhibited by FEs may be employed to separate photogenerated charge carriers, enabling them to reach the surface and subsequently to interact and react with molecules in the surrounding media. In principle, photo-induced currents can also be established, provided that bandgaps of FEs are able to capture a vast range of the solar spectrum. BiFeO$_3$ with a band gap of ~2.67 eV has long been recognized to have the narrowest band gap of robust ferroelectric perovskite oxides, while most ferroelectrics have bandgaps wider than 3 eV. These wide bandgaps limit light absorption primarily to the ultraviolet region; therefore, these materials are only able to capture ~8–20% of the solar spectrum. Recently, Agarwal et al. fabricated Si-integrated Pt/(Bi$_{0.9}$Sm$_{0.1}$)(Fe$_{0.97}$Hf$_{0.03}$)O$_3$/LaNiO$_3$ heterostructures. This doped BiFeO$_3$ thin film was reported to exhibit a band gap of 2.63 eV. Other reports on double doped BiFeO$_3$ thin films exhibit similar bandgap values.

Bandgap engineering of FEs into the visible is emerging as an active research area. It has been shown that chemical doping can be strategically employed to successfully narrow the bandgap of KNbO$_3$ (KN), a well-known ferroelectric. In the classic work by Shirane et al., the room-temperature spontaneous polarisation of single-domain KN was reported as 41 ± 2 μC/cm$^2$. This large spontaneous polarisation was rationalised on the basis of the non-centrosymmetric position of Nb$^{5+}$ cations within the NbO$_6$ octahedra. This distortion is driven by the hybridisation of the empty d-orbitals of Nb$^{5+}$ with the O$^{2-}$ p-orbitals. The relative wide optical bandgap of pure KN is also linked to the nature of the bonding between O anions and Nb cations. The large differences in electronegativity between the O and the Nb ions leads to the valence band to be formed by the 2p O states and the conduction band by the d states of the Nb transition metals sitting within the O octahedra. Hence, the excitation across the band gap in KN is essentially a charge transfer from the O 2p states at the valence band maximum (VBM) to the Nb d states at the conduction band minimum (CBM). One of the strategies to narrow the band gap is by shifting up the VBM. In terms of doping, this may be achieved through substitution of Nb$^{5+}$ in KN by lower valence Me$^{3+}$ dopants. The expulsion of non-bonding 3d$^0$ orbitals of Me$^{3+}$ and 2p$^6$ orbitals of O$^{2-}$ may lead to a higher VBM.

Grinberg et al. showed the bandgap of ferroelectric (1-x)KNbO$_3$-xBaNi$_{0.5}$Nb$_{0.5}$O$_{3.3}$ (KBNNO) ceramics to be tailored to values as low as 1.39 eV for $x = 0.10$. Nevertheless, in this system, the presence of oxygen vacancies may contribute to ~0.5 eV of the total band gap narrowing. Moreover, oxygen vacancies are detrimental to polarization switching and may also trap photogenerated charge carriers. Yu et al. investigated (1-x)KNbO$_3$-xBaCo$_{0.1}$Nb$_{0.5}$O$_{3.3}$ and reported the narrowest band gap of ~2.4 eV for $x = 0.5$, but again this system contains oxygen vacancies. Recently, Pascual-Gonzalez et al. studied bandgap engineering of KNbO$_3$ via chemical doping with a fixed 5% Bi(Me,Yb)O$_3$ (where Me = Fe or Mn) content and observed a reduction in the direct bandgap down to 2.2 eV, without having to rely on oxygen vacancies to such narrowing of the bandgap.

In this letter, the crystal structure and band structure of (1-x)KNbO$_3$-xBiFeO$_3$ (KNBF) (0 ≤ $x$ ≤ 0.25) were investigated by X-ray powder diffraction combined with Raman spectroscopy and diffuse reflectance ultraviolet and visible spectroscopy (DRUV-vis). Previously, it was shown that the bandgap of KN can be modified by dopants other than...
transition metals, here the ability to systematically control the bandgap of KNbO₃ by varying the content of BiFeO₃ is shown. The simultaneous replacement of K⁺ and Nb⁵⁺ by Bi³⁺ and Fe³⁺, respectively, is expected to prevent the formation of lattice defects, such as oxygen vacancies. Nevertheless, this premise is still to be experimentally proved in future investigations, because the photovoltaic effect induced by the electromigration of oxygen vacancies is unstable.¹³ The Fe³⁺ substitution for higher-valence Nb⁵⁺ may give rise to increased repulsion between the O 2p and Fe 3d states and thereby to a higher VBM.

KNBF ceramics were fabricated as described elsewhere using the following precursor powders, K₂CO₃ (>99.0% Sigma-Aldrich), Nb₂O₅ (>99.9%, Sigma-Aldrich), Bi₂O₃ (>99.9%, Sigma-Aldrich), and Fe₂O₃ (>99.9%, Sigma-Aldrich). XRD patterns were acquired using a PANalytical diffractometer (model Empyrean) in the 2θ range 20–80, with a step size of 0.02°, and with a scan length of 600 s per step. Raman spectra were obtained with a Renishaw Raman microscope (model InVia) using a 532 nm solid state (100 mW) laser, in back-scattering geometry. Temperature-dependent Raman measurements were carried out using a Linkam stage (model THMS600). Capacitance measurements were carried out with an Agilent LCR meter (model e4980A). Finally, DRUV-vis spectra were acquired in the range 200–1600 nm using a Shimadzu UV-VIS-NIR Spectrophotometer (model UV-3600 Plus). Fine BaSO₄ powder was used as a non-absorbing standard. To estimate the band gaps, first the Kubelka-Munk (K-M) function given below was calculated

\[ F(R) = \frac{(1 - R)^2}{2R}, \]

where R is the experimental reflectance referred to the BaSO₄ standard. Hereafter, the K-M function (or F(R) curves) is considered to be proportional to the optical absorption. Hence, the absorption coefficient, \( \alpha \), can be substituted by \( F(R) \) in the Tauc equation

\[ (h\nu\alpha)^n = A(h\nu - E_g) = [h\nu F(R)]^n, \]

where \( h \) is the Planck’s constant, \( \nu \) is the frequency of vibration, \( \alpha \) is the absorption coefficient, \( E_g \) is the bandgap, and \( A \) is the proportional constant; for direct allowed transition, \( n = 2 \) and for indirect allowed transition, \( n = 1/2 \).

Fig. 1 shows the room-temperature XRD data for KNBF ceramics. Within the detection limits of the technique, all ceramics appear to be single-phase, as shown in Fig. 1(a). All reflections in the XRD data for undoped KN can be assigned to an orthorhombic perovskite described by the Amm2 space group. The typical peak splitting expected for a perovskite with orthorhombic crystal symmetry is clearly evident in undoped KN, but within the resolution of our measurements, only single peaks are visible for doped ceramics, as shown in Fig. 1(b); however, Raman spectroscopy provides a strong evidence that these materials are isorstructural. Reflections shift slightly but systematically towards higher 2θ angles with increasing x, indicating that the co-solvability of BiFeO₃ and KNbO₃ is accompanied by a decreasing unit cell volume. The average orthorhombic crystal symmetry for the doped compositions is also corroborated by the Raman spectroscopy data shown in Fig. 2. The typical spectral features exhibited by the ferroelectric KNbO₃ orthorhombic polymorph are also visible in the Raman spectra of all doped ceramics. This spectral similarity is sufficient to simultaneously ascertain the orthorhombic crystal symmetry and the occurrence of long-range polar order in the doped materials as explained below.

From the group theory analysis, orthorhombic KN (\( x = 0 \)) should exhibit 12 Raman active optical modes of 4A₁⁺ + 4B₁⁻ + 3B₂⁻ + 2A₂ symmetries, which can be separated into translational modes of isolated K⁺ and internal modes of the NbO₆ octahedra. Modes in the KN Raman spectrum are labelled according to the single-crystal assignment by Quittet et al.¹⁴ Hence, in the low- to mid-wavenumber region, the Raman spectrum of KN is characterised by (i) a mixed sharp mode at 192 cm⁻¹, (ii) a Fano-type interference dip at 197 cm⁻¹, (iii) a broad B₁ (TO) mode centered at 250 cm⁻¹, (iv) a B₂ (TO) at 272 cm⁻¹, (v) a sharp mode at 278 cm⁻¹, (vi) and another mode at 294 cm⁻¹. Spectral features (i), (ii), and (vi) are believed to be a fingerprint for the occurrence of long-range polar order in KNbO₃. The sharp mode at 192 cm⁻¹ is actually a mixed mode due to B₁(TO), A₁(TO), A₁(LO), and B₂(TO) modes, while the mode at 294 cm⁻¹ is due to A₁(LO) and A₁(TO), but because of the resolution limit.
of the instrument, they appeared merged as a single peak. The high wavenumber region (>500 cm⁻¹) of the Raman spectrum of KNbO₃ is characterized by a (vii) a B₁(TO) mode at ~532 cm⁻¹, (viii) a A₁(TO) mode at ~600 cm⁻¹, (ix) a low intensity A₁(LO) mode at 831 cm⁻¹. 

Upon doping, new modes emerge in the low frequency regime; however, since at this stage, information on their origin is merely speculative, they are merely labelled as 1 and 2. The new mode 1 is relatively broad and appears ~110 cm⁻¹, whereas mode 2 appears as a shoulder to the sharp mixed mode at 192 cm⁻¹. The relative intensity of mode 2 appears to increase with increasing x. In the past, these modes have been associated with A-O vibrations, in particular, to nm-sized clusters rich in either Bi³⁺ or K⁺ cations. Finally, the A₁(LO) mode at 831 cm⁻¹ appears to become broader with increasing x. This broadening may be associated with the emergence of new modes too, as previously observed, due to breathing of the octahedra, when occupied by different B cations. The general broadening of the Raman modes from the doped ceramics, Fig. 2, results from increased lattice disorder, which manifests itself by the emergence of Urbach tails in the Tauc plots (Fig. 5).

In-situ Raman spectroscopy analyses were carried out in the –100 to 200°C temperature range in order to assert the presence of long-range polar order over a wide temperature range. For the sake of simplicity, data are only presented for KN, x = 0.05 and 0.20 at three different temperatures (–100°C, 25°C, and 200°C). In Fig. 4(a), the spectra collected at –100°C show, in the 150–300 cm⁻¹ region, the spectral signature typical for the ferroelectric rhombohedral polymorph. On heating to 25°C, the low frequency region becomes consistent with the ferroelectric orthorhombic polymorph, as shown in Fig. 4(b). Finally, at 200°C, close to the dielectric anomalies in Fig. 3, splitting between B₁(TO) and A₁(TO) modes in the medium frequency range becomes less evident as x increases, all compositions, however, still show the features of long-range polar order. It is also worth noting that the aforementioned modes 1 and 2 are present at all temperatures. Hence, based on both permittivity measurements and Raman spectroscopy analysis, all ceramics studied exhibit dielectric anomalies associated with structural phase transitions, and their ferroelectric nature is corroborated by the presence of a Fano-type resonant dip in their Raman

![FIG. 3. Temperature dependence of εᵣ for KN, x = 0.05 and x = 0.25 ceramics measured at 100 kHz.](image)

![FIG. 4. In-situ Raman KN, x = 0.05 and x = 0.20 ceramics at (a) –100°C, (b) 25°C and (c) 200°C. Bose-Einstein factor applied to data.](image)
rowing of the bandgaps, Fig. 5. A correlation between the relative permittivity, Fig. 3, appears to follow the narrow bandgaps for KN and x/C24 increases with increasing x. The optical absorption spectra of other than the direct charge transfer between O and Nb atoms, i.e., across the bandgap. Around 2.5 eV, there is a clear shoulder, present in all doped materials, whose magnitude increases with increasing x. The optical absorption spectra of Fe3+ containing substances are known to exhibit three types of electronic transitions, namely, Fe3+ ligand field transitions or d-d transitions, ligand to metal charge transfer transitions, and pair excitations resulting from the simultaneous excitation of two neighbouring Fe3+ that are magnetically coupled. Bukert et al.18 carried out an optical spectroscopy study in BiFeO3 and observed three well-defined absorption features at 1.22 eV, 1.66 eV, and 2.14 eV, which were assigned to charge-transfer excitons and in-gap defect states probably related to oxygen vacancies. More experiments are underway to gather a further insight into the phenomena observed in Fig. 5(b). All KNBF show Urbach tails; however, their appearance in optical absorption near band edges are expected in any material with disorder having a correlation length of order of the interatomic spacing, as this causes fluctuations in the electron energies ∼(eV)2.

Crystal chemistry arguments can be recalled to partially explain bandgap narrowing in KNBF as follows: (i) the replacement of Nb5+ by Fe3+ creates underbonded O2− adjacent to the Fe3+, which form FeO6 octahedra, (ii) Bi3+ which tend to be off-center, create short, strong Bi-O (covalent) bonds that partially compensate for the loss of B-O bonding, (iii) K+ do not off-center and are less prone to compensate the decrease B-O bonding. As a result, the repulsion between the non-bonding O charge densities and Fe 3d states is relatively weak, leading to an upshift of the VBM, which is composed of O 2p and Fe 3d states. The lattice distortion decreases markedly with x increasing from 0 to 0.05 and remains small (i.e., below the resolution limit of X-ray diffraction) above this concentration, as shown in Fig. 1. Coincidentally, the bandgap narrowing is the greatest in this compositional range as shown in Fig. 5, and the A1 (LO) and A1 (TO) modes exhibit the largest shift, as shown by the dashed lines in Fig. 2. Hence, the magnitude of distortion is expected to have a major effect on the bandgap, modifying both CBM and VBM. The exact effect will depend on the coupling between the lattice strain and atomic displacements, understanding of which obviously requires further studies.

In summary, it was demonstrated that the band gap of orthorhombic ferroelectric KNBO3 can be systematically narrowed by 1 eV (i.e., a ∼33% reduction) via co-substitution of K and Nb by Bi and Fe, respectively. Remarkably, this bandgap narrowing is achieved while maintaining long-range polar order over a wide temperature range.

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