Novel optically active lead-free relaxor ferroelectric (Ba$_{0.6}$Bi$_{0.2}$Li$_{0.2}$)TiO$_3$

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Received 31 January 2016, revised 10 April 2016
Accepted for publication 12 April 2016
Published 11 May 2016

Abstract

We discovered a near-room-temperature lead-free relaxor-ferroelectric (Ba$_{0.6}$Bi$_{0.2}$Li$_{0.2}$)TiO$_3$ (BBLT) having A-site compositionally disordered ABO$_3$ perovskite structure. Microstructure-property relations revealed that the chemical inhomogeneities and development of local polar nano-regions (PNRs) are responsible for dielectric dispersion as a function of probe frequencies and temperatures. Rietveld analysis indicates mixed crystal structure with 80% tetragonal structure (space group $P4mm$) and 20% orthorhombic structure (space group $Amn2$), which is confirmed by the high resolution transmission electron diffraction (HRTEM). Dielectric constant and tangent loss dispersion with and without illumination of light obey nonlinear Vogel–Fulcher (VF) relations. The material shows slim polarization–hysteresis ($P-E$) loops and excellent displacement coefficients ($d_{33} \sim 233$ pm V$^{-1}$) near room temperature, which gradually diminish near the maximum dielectric dispersion temperature ($T_m$). The underlying physics for light-sensitive dielectric dispersion was probed by x-ray photon spectroscopy (XPS), which strongly suggests that mixed valence of bismuth ions, especially Bi$^{5+}$ ions, comprise most of the optically active centers. Ultraviolet photoemission measurements showed most of the Ti ions are in $4+$ states and sit at the centers of the TiO$_6$ octahedra; along with asymmetric hybridization between O $2p$ and Bi $6s$ orbitals, this appears to be the main driving force for net polarization. This BBLT material may open a new path for environmental friendly lead-free relaxor-ferroelectric research.

Keywords: relaxor, dielectric spectroscopy, polar nano regions, ferroelectric

(Some figures may appear in colour only in the online journal)

1. Introduction

Relaxor ferroelectrics (RFE) are one of the major subjects in solid state physics that deal with the physics of dynamic relaxation processes. During the past six decades scientists have been working to develop novel lead-free RFE with high electromechanical coefficients and high dielectric constants. Several physical models have been proposed, such as the random-field model, random-bond model, cationic order-disorder model, mean field model (spin glass and dipolar glass), polar nano-region model (PNRs), etc [1–11]. Relaxors are widely useful for technological applications such as transducers and actuators due to their exceptionally high dielectric constant, piezoelectric constant
and electromechanical coefficients; however, optically active RFE may provide an extra degree of freedom for the development of power and energy efficient devices, such as modulators, tuning elements, optically active bistable switches, and memory elements. In the past several lead-based relaxors and lead-free relaxors have been invented; among them PbMg1/3Nb2/3O3 (PMN) is a well known classical relaxor; and PbSc1/2Nb1/2O3 (PSN) is a classical example of cation order-disorder at the B-site [12–16]. The (1 − x)(Na0.5Bi0.5)TiO3−xBaTiO3 (NBT-BT) compound near its morphotropic phase boundary (MPB) is one of the most highly investigated lead-free RFE with A-site cationic disorder [17]. Ba(Zr,Ti)O3, (Ba,Sr)TiO3 and Ba(Sn,Ti)O3 are other popular lead-free materials with isovalent A/B-site cation substitution and have been explained on the basis of a soft pseudo-spin glass model [18–20]. The tetragonal tungsten bronze (TTB) complex oxide structures include many RFE; however, the complex nature of their microstructure and microstructure-property relations restricts investigation of the basic mechanisms responsible for their relaxor behavior [21]. Li-doped KTaO3 is also one of the most fascinating relaxors, showing dielectric dispersion due to dipolar interaction between randomly distributed off-center cations and a polarizable lattice [22].

LiNbO3 and KNbO3 are well known electro-optic (EO) polar materials in which EO effects arise due to displacement of central cations with respect to oxygen anions in NbO6 (B-site) octahedra and their interaction with incident light. In this situation an external light source falls on the crystal surface, which modifies the electronic band structure of the crystal and significantly changes the electrical response of the lattice [23, 24]. BaTiO3 has shown strong nonlinear EO properties among the lead-free perovskites. In the present investigation modification of BaTiO3 by non-isovalent cations Li and Bi at the Ba-site leads to large changes in dielectric constant and dispersion under moderate laser light illumination. Abel et al showed that Si/SrTiO3(4 nm)/BaTiO3 (130 nm) heterostructures display the electrical properties of at least five times larger Pockels coefficients of effc bandgap semiconducting ferroelectric SbSI (Tc = 292 K, Es = 1.83 eV, and Ps = 30 μC cm−2); in the first system UV light changes Ti1+ valence state, whereas in SbSI illumination of light pumps electrons into the conduction band. The illumination of light also changes the phase transition temperature (Tc) of BaTiO3 (∆Tc = −2.6 K with 470 nm illumination) and affects the electronic structure of SbSI [26–28].

The discovery of relaxor behavior in ABO3 structures with B-site non-isovalent (PMN) and isovalent cations Ba(Zr,Ti) O3, and Ba(Sn,Ti)O3 led to the random field model and pseudo-spin-glass model, respectively; however, it is still unclear as to what leads to relaxor behavior of non-isovalent substitution at A-sites of the ABO3 structure. In this letter we have tried to understand these problems in addition to reporting the discovery of a novel optically active RFE.

We found that chemically unstable valence states of Bi ions may create an unstable chemical potential which is responsible for optically active centers, particularly involving Bi5+ ions. The symmetric lineshape of O1s suggests high sample quality with stable ABO3 structure. The photo-sensitivity of this compound is attributed to Bi valence fluctuations. This is a new and rather specific example of optically active ferroelectricity [29, 30].

2. Sample preparation and experimental methods

Polycrystalline BBLT ceramics were prepared by a conventional ceramic processing technique. Sigma-Aldrich high purity (~99.9%) precursor oxides and carbonates of Li2CO3, BaCO 3, Bi2O3, and TiO2 were used to synthesize BBLT polycrystalline ceramics. Precursors for the desired stoichiometry were mechanically milled in wet conditions in IPA (isopropyl alcohol) for 2 h for homogeneous mixing. This mixed powder was calcined at 850 °C for 10 h. The granulated powder was shaped into circular discs of diameter 13 mm and thickness 1–2 mm under uniaxial pressure of 5–6 tons per square inch and later sintered in air at 1200 °C for 4 h to achieve 96% of theoretical density. X-ray diffraction (XRD) patterns were obtained using a Bruker AXS D8 Advance x-ray diffractometer having the Cu-kα (λ = 1.5405 Å) monochromatic radiation, in the 2θ range between 20° to 60°, and analyzed by Rietveld analysis. The temperature-dependent dielectric and polarization properties were measured by Hioki LCR Meter model 3532–50 and Radiant Precision Multiferroic Tester, using a homemade probe station on as-grown samples. The opto-electric measurement was carried out with a homemade sample holder with quartz windows to transmit the laser light. A weak monochromatic laser source with wavelength 405 nm and energy-density 25 mW cm−2 was used for this opto-dielectric study. The top surfaces of the pellets were coated with conducting indium tin oxide (ITO) with 50–100 Ωmm resistance to illuminate the light. X-ray photoemission spectroscopy (XPS) measurements were performed by using an Omicron μ-metal ultra-high vacuum (UHV) system equipped with a monochromatic Al Kα x-ray source (hv = 1486.7 eV) and a multi-channeltron hemispherical electron energy analyzer (EA 125). The ultraviolet photoemission spectroscopy (UPS) measurements were performed with a high-intensity vacuum ultraviolet source (HIS 13) at the He I (hv = 21.2 eV) line, having a beam spot of 2.5 mm diameter. The total energy resolution was about 400 and 100 meV for monochromatic Al Kα and He I excitation, respectively. The voltage-displacement vector D(E) characteristic was obtained with an aixACCT single beam laser interferometer (aixSBLI). A scanning electron microscopy-energy dispersive x-ray (SEM-EDX) technique was used to ascertain the chemical compositions and grain distribution in the matrix using a Zeiss EVO MA-10. The determination of PNRs, crystal structures, and lattice planes was via a Technai G20, 300 kV; high resolution transmission electron microscope (HRTEM) on mechanically and ion-milled thin slabs.
### 3. Results and discussion

#### 3.1. X-ray diffraction and transmission electron microscopy

Figure 1(a) shows the Rietveld analysis of experimental data, which indicates the presence of both tetragonal phase (space group P4mm) and orthorhombic phase (space group Amm2) with volume ratio of 4:1, which is further confirmed by the HRTEM diffraction pattern (figure 1(b)). The fitting parameters $\chi^2 = 1.72$, $R_p = 7.26$, $R_w = 9.88$, and $R_{exp} = 7.53$ for both systems suggest the accuracy of our assumptions for the crystal structures were well obtained within the fitting errors. SEM-EDX data revealed that the stoichiometry of the final composition matched with the initial assumption within ±10% error limit of the EDX. A SEM image in the inset of figure 1(a) indicates superior compactions of fine spherical grains with an average grain size less than a few microns. Chemically inhomogeneous dark patches with dimension less than 1 mm were seen throughout the matrix (marked in figure 1(c)). Lattice planes observed by HRTEM matched with the data obtained from the (1 1 0) plane of XRD; however, it would be disingenuous to distinguish the lattice planes of both phases with low magnification HRTEM images, figure 1(d).

Interestingly, we were able to see the tiny PNRs with coexistence of both the phases; however, the tetragonal phase was the dominant phase in the matrix. It would also be difficult to distinguish the PNRs and chemically inhomogeneous regions. Chemical inhomogeneity, grain size, impurities, and crystal structures decide the sizes of PNRs and ferroelectric domains.

#### 3.2. Dielectric spectroscopy

The dielectric constant and tangent loss of BBLT ceramics as a function of temperatures and frequencies under various conditions are shown in figures 2(a)–(f). We have probed the dielectric response under three different warming conditions, depending on the experimental limitations: (i) cooling the system until 80 K and collecting the dielectric data on heating from 223 K to 673 K; (ii) dielectric data without cooling, i.e. from room temperature and above; and (iii) dielectric data from room temperature and above under illumination of weak 405 nm laser light with energy density 25 mW cm$^{-2}$. The important findings from the dielectric data are as follows: (i) significant relaxor shift in dielectric maximum temperature (from $T_m = 353$ K at 1 kHz to 393 K at 1 MHz); (ii) maximum tangent loss temperature shifts from 275 K at 1 kHz to 302 K at 1 MHz and tangent loss values generally increases with increase in probe frequency—a kind of fingerprint for REF; (iii) the magnitude of $T_m$ values increases after cooling and illumination of external light, and magnitudes of $T_m$ depend on probe frequencies; (iv) suppression of another kink near 523 K–563 K, similar to the NBT-BT ferroelectric-to-paraelectric phase transition under illumination of light; and finally, (v) significant increase in magnitude of dielectric constant ($\varepsilon$) at higher probe frequency under illumination of weak laser light (however the magnitude of $\tan \delta$ remains nearly unchanged under illumination). The first phase transition fits a well-behaved relaxor system, i.e. dielectric loss increases with increase in frequency but a second anomaly near 523–563 K does not obey the nonlinear $V$–$F$ relation. This second anomaly may be either due to another phase transition (as observed in NBT-BT system) or a non-structural transition (e.g. semiconductor-insulating) or a symmetry-preserving structural transition (e.g. one in which disorder increases but long-range symmetry is unchanged; or a glassy transition from ergodic to non-ergodic). Note that to confirm the idea that this is second structural phase transition (symmetry-breaking), one should do a detailed structural study, but this is beyond the scope of the present investigation [31].

The increase in the dielectric constant and its dispersion can be explained on the basis of change in charge carrier concentrations ($n$), since this material is semiconducting. In general, for an n-type ferroelectric semiconductor, electrons are responsible for change in dielectric constant behavior under illumination of light. This nonequilibrium charge carrier photoresponse increases the concentration in the recharged levels (traps ~ $N$) and adds an addition free energy term ($F_2$) to the total free energy of system. The net free energy of the crystal with an additional factor for the electron subsystem can be written as:

$$F = F_1 + F_2 + F_3,$$

where $F_0(T)$ is free energy for paraelectric regions, $F_0(T) = f(P = 0, \sigma_f = 0, N_f = 0, F_1)$ is ferroelectric regions,

$$F_1 = F_0 + \frac{1}{2} \alpha P^2 + \frac{1}{4} \beta P^4,$$

and the electron subsystem (photo-induced)

$$F_2 = \sum_i N_i E_i(T, P, \sigma_k) = \sum_i (E_i - u_1 - u_2) = NE_i,$$

where $E_i = \text{bandgap}$; $u_1$, energy level of electron traps; $u_2$, energy level of hole traps; a free-electron concentration $n$ at energy level $N_i$ and $\dot{E}$ corresponding to $E_i - u_1 - u_2$. In the present case, the contribution of recombination levels has been ignored assuming a high resistivity semiconductor (for charge neutrality, $p = n + N$, where $p$ and $n$ represent free hole and electron concentrations).

The energy term $\dot{E}$ can be expanded in a series in $P, T$, and conductivity ($\sigma_k$) as follows:

$$\dot{E}(P, T, \sigma_k) = \dot{E}_0(P, T) + \frac{1}{2} \dot{E}_{0P} P^2 + \frac{1}{4} \dot{E}_{0P^2} P^4 + \sum_k \dot{E}_{0k} \sigma_k + \frac{1}{2} \sum_{k} \sum_{l} \dot{E}_{kl} \sigma_k \sigma_l + P^2 \sum_k \dot{E}_{k} \sigma_k$$

$$+ \frac{1}{2} \sum_{k} \sum_{l} \dot{E}_{kl} \sigma_k \sigma_l + P^2 \sum_k \dot{E}_{k} \sigma_k$$

Using the equations (1)–(4), we obtain the free energy equation for the highly populated semiconductor ferroelectric under illumination of light:

$$F(T, P, N, \sigma_k) = F_0 + \frac{1}{2} \alpha N P^2 + \frac{1}{4} \beta N P^4$$

$$+ N \sum_k \dot{E}_{0k} \sigma_k - \frac{1}{2} \sum_{k} \sum_{l} \dot{E}_{kl} \sigma_k \sigma_l - P^2 \sum_k \dot{E}_{k} \sigma_k$$

$$+ \frac{1}{2} \sum_{k} \sum_{l} \dot{E}_{kl} \sigma_k \sigma_l + P^2 \sum_k \dot{E}_{k} \sigma_k$$

$$+ \frac{1}{2} \sum_{k} \sum_{l} \dot{E}_{kl} \sigma_k \sigma_l + P^2 \sum_k \dot{E}_{k} \sigma_k$$

$$+ \frac{1}{2} \sum_{k} \sum_{l} \dot{E}_{kl} \sigma_k \sigma_l + P^2 \sum_k \dot{E}_{k} \sigma_k$$
where the coefficients are defined as $F_{0N} = F_0 + NE_0 \alpha N = \alpha + aN, \beta N = \beta + bN, \nu N = \nu k + \beta \nu k N$, and $sN = s k + \beta s k N$

The change in free energy and wave function under illumination dictates the moderate change in dielectric constant, spontaneous polarization, piezoelectricity and shift in Curie temperature ($T_c$) or $T_m$. All these parameters can be deduced from the free energy for ferroelectric semiconductor, equation (5).

After solving the free energy equation for a second order ferroelectric phase transition, we found the change in the $T_c$ or $T_m$ under illumination of light is as follows:

$$T_{0N} - T_0 = \Delta T_N = -(C/2\pi) aN = -(\varepsilon_0 C) aN$$

Where $C$ is the Curie–Weiss constant; $T_{0N}$ and $T_0$ are the Curie points with and without illumination of light. The condition for the free energy minimum is $\left(\frac{\partial^2 F}{\partial \varepsilon^2}\right) = N\alpha > 0$. It follows that $a > 0$ and hence extra electrons lower the Curie point. $N$ represents the electron concentration in traps near the conduction band. The relation between $\varepsilon$ and $C$ are for ferroelectric regions ($T < T_0$): $\varepsilon = -C/[2(T - T_0)]$. Experimentally a small change in $\Delta T_N \sim 7$ K at 10kHz was observed which supports the theoretical prediction of small change in $\Delta T_N$ under illumination.

The dielectric constant and temperature hysteresis ($\Delta T_h$) are related using the equation $\varepsilon(T_c)\Delta T_h \cong C$; if we assume that electrons do not change the Curie-Weiss constant $C$, then they significantly reduce the temperature hysteresis $\Delta T_h \cong T_m - T_0 = \frac{1}{8\pi} C^\frac{\beta}{\gamma}$ where $T_m$ is the dielectric maximum temperature; $T_c$ the Curie–Weiss temperature; ($\alpha, \beta, \gamma$) are constants; $P$, polarization. Hence carrier injection increases the dielectric constant: $\varepsilon_{N}(T) > \varepsilon(T)$ [26–28]. Experimentally a significant change in $\Delta \varepsilon \sim 30$ at 10kHz was observed, which supports the theoretical prediction in $\Delta \varepsilon$ under illumination.

3.3. VF relation

The dielectric constant and loss maxima temperatures for various conditions were fitted with a nonlinear VF relation (equation (7)), as shown in figure 3 [32–34].

Figure 1. (a) Shows XRD patterns and its Rietveld analysis fitting using mixed phase process i.e. tetragonal and orthorhombic crystal structures. SEM image for surface morphology is shown in inset. Figures (b)–(d) illustrate mixed phase diffraction patterns, existence of nanoscale chemical inhomogeneous regions, and lattice resolved (1 1 0) crystal planes, respectively. Nanoscale dark patches are marked in the figure (c).
\begin{equation}
    f = f_0 \exp \left( -\frac{E_a}{k_B(T_m - T_f)} \right)
\end{equation}

where \( f \) is the experimental frequency; \( f_0 \), a pre-exponential factor corresponding to asymptotically high temperatures; \( E_a \) the activation energy; \( k_B \) Boltzmann’s constant; and \( T_f \) the static freezing temperature. The fitted parameters \( E_a = 0.14 \) eV, 0.09 eV, 0.05 eV, and 0.07 eV \((\pm 0.02 \) eV) and \( f_0 = 2.5 \times 10^{11} \) Hz, \( 3.5 \times 10^{12} \) Hz, \( 3.2 \times 10^9 \) Hz, and \( 3.0 \times 10^{10} \) Hz and \( T_f = 277 \) K, 242 K, 311 K, and 302 K \((\pm 5 \) K) were obtained for the experimental data on \( T_m \) with V–F fitting under three different conditions: (i) measurement of dielectric constant and tangent loss data on cooled system, (ii) dielectric constant \( T_m \) from 300 K (RT) without cooling, and (iii) dielectric constant \( T_m \) from 300 K without cooling and under illumination of light. These values match numerical values for other relaxor systems within the limit of their uncertainties [28]. For example, \( f_0 \) is typically of order 3–100 GHz.
3.4. Polarization and piezoelectric properties

Figures 4(a) and (b) show the polarization loops as a function of applied E-fields and temperatures without and with illumination. In both cases a slim P–E hysteresis loop was observed near room temperature that drastically gets slimmer in the window regions of dielectric dispersion (300 K–450 K) and above which is nearly constant. Similar trends were observed for the saturation polarization ($P_s$) and coercive field ($E_c$), as shown in figure 4(c). This slim hysteresis near $T_m$ is classic relaxor systems. The monotonically large decrease in $P_s$ above $T_m$ suggests a possible strong candidate for electrocaloric effects [35]. The merger of $P_s$ near the $T_m$ supports the theoretical prediction of negligible effect of illumination on polarization magnitude near or above $T_m$. It can be clearly seen from figures 4(a)–(c) that a significant change in magnitude of polarization was observed under light. The displacement–voltage ($D–V$) butterfly-like characteristic loops provide a low coercive field (~0.5 kV cm$^{-1}$) with saturation at 2 kV cm$^{-1}$. As shown in the figure 4(d), they prove that piezoelectric samples can be displaced mechanically with a coefficient of displacement ($d_{33}$) of about 233 pm V$^{-1}$. Note that our samples are thin ceramic slabs; in view of this, the $d_{33}$ values are quite comparable with lead- and lead-free ferroelectric thin films [36]. The low coercive field in displacement butterfly loops may be due to the experimental conditions: On a thin slab (~300 μm) at 10 Hz frequency compared to the 1.5 mm thick slab used for temperature dependent $P–E$ measurements. The characteristic butterfly shape of the $D–V$ plot due to a large bipolar signal is determined by the polarity reversal process in ferroelectrics when the coercive field strength is reached in the reversed field ($-E_c$). At the polarity reversal, the contraction of the sample reverses into expansion again, since the polarization and the field are again parallel.

3.5. Diffuse absorption and reflectance spectroscopy

Figure 5 illustrates the reflectance spectra and Kebulka–Munk (KM) function $F(\lambda)$ (inset) of BBLT fine polycrystalline ceramic powder in the UV–visible range. It shows a diffuse dip in reflectance spectra and a diffuse peak in absorption spectra (not shown here), which is the signature of bandgap regions. To estimate the exact bandgap of the system, the KM function was derived using the equation, $F(\lambda) = (1 - R^2/2R$, where $R$ is % of reflectance. This equation is widely used for precise bandgap calculations [37]. The inset shows a diffuse kink near 450 nm wavelength in d$F(\lambda)/d\lambda$ versus wavelength spectra which provides 2.76 eV bandgap. The obtained bandgap is comparable to the well known ferroelectric semiconductors [25–27]. The low bandgap of BBLT compared to other ferroelectric perovskites makes it an optically active RFE for modest wavelengths. The unsaturated reflectance tail above the bandgap suggests the presence of defects (optically active trap centers), especially oxygen vacancies.

3.6. X-ray photon spectroscopy

Room-temperature photoemission measurements were performed on in situ heat treated samples at 623 K under a base vacuum of ~5.0 × 10$^{-11}$ mbar. The heat treatment was performed in situ for desorbing surface adsorbates. The binding energy of all the spectra was calibrated by measuring C 1s (285.0 eV) core levels which were monitoring throughout the experiment particularly before and after each core level spectra collected. Note that the bulk polycrystalline sample has many different terminations at the surface and plausible surface origin of Bi 4f [285.0 eV] high binding energy peak, we recorded all the XPS spectra at room temperature and at a take-off angle of 60° to achieve the maximum bulk sensitivity. The Bi 4f core-level XPS spectrum of BBLT is shown in figure 6(a). The spectra exhibit 4f$_{5/2}$ and 4f$_{7/2}$ spin-orbit doublet peaks located at ~157.8 (159.9) and ~163.2 (165.2) eV, respectively. The binding energy difference between the two pairs of spin-orbit peaks is about 5.4 (5.3) eV. A large separation of 2.1 eV between the two contributions of each spin-orbit photoemission signal was observed, suggesting that Bi is in a mixed valence state with Bi$^{3+}$ and Bi$^{5+}$ ion valency [38, 39]. We performed double-peak fitting for 4f$_{7/2}$ and 4f$_{5/2}$ spectra, using a $\chi^2$ iterative program, and the concentration of Bi$^{3+}$ and Bi$^{5+}$ valence states is obtained about 55% and 45%, respectively. The Ba 3d symmetric spectra are shown in figure 6(b) with two pairs of spin–orbit split components at 778.4 (Ba 3d$_{3/2}$) and 793.6 (Ba 3d$_{5/2}$) eV, which indicates Ba (Ba$^{2+}$) present in +2 valence states. Figure 6(c) shows the highly symmetric (529.85 eV) O 1s spectrum which is free from hydroxyl-like species bound to different sites, normally observed at 532 eV [40]. It indicates a high-quality polycrystalline samples with minimal effect of grain boundaries in their functional properties. Figure 6(d) shows the Ti 2p and Bi 4d core-level spectrum. The Ti 2p spectrum shows 2p$_{3/2}$ and 2p$_{1/2}$ spin-orbit doublet peaks located at ~458.6 and 464.0 eV, respectively. We have fitted the 2p$_{3/2}$ spectrum by two distinct features: a small signal at 456.5 eV attributed to the Ti$^{3+}$ (15%) component, and the Ti$^{4+}$ main signal (85%) appearing at higher binding energy at 458.5 eV. The small Ti$^{3+}$ signal lies nearly within the experimental fitting errors (±5%) [41]. The Bi 4d spectrum shows 4d$_{3/2}$ and 4d$_{5/2}$ spin-orbit doublet peaks located at ~440.0 and 463.5 eV, respectively. Figure 6(e) shows the core level spectra of Ti 3s and Li 1s. The sharp peak of Ti 3s...
shadowed the lattice site of Li cations generally mentioned at 55.6 eV; however, strong evidence of interstitial Li cations at 51.8 eV obtained, compared to the lattice occupancy of Li ions, from 53 to 55 eV, depending on the chemical potential of substitution site [42, 43]. It was more difficult to attribute unambiguously the peak at 52 eV as the substitution site of Li cations.

The angle-integrated valence band photoemission spectrum of the sample is shown in figure 6(f). A major sharp feature at ~2.4 eV of Ti^{4+} states of the TiO_{6} octahedra was obtained;
however, a very small feature at 1.5 eV was also seen due to the Ti 3d states from Ti$^{3+}$ valence state (~5%). The features in the binding energy region of 2–3 eV are mainly from the hybridized Ti 3d (Ti$^{4+}$)–O 2p states, while the features between 3–7 eV are strongly mixed character of O 2p and Bi 6s states with a small Ti 3d contribution. All together, XPS and UPS results confirm the presence of mixed valence states of Bi with polarization due to displacement of Ti$^{4+}$ cations from the center of octahedra and hybridization of Bi cations with neighboring oxygen 2p orbitals. The structural refinements, ABO$_3$ perovskite structure and XPS data suggest the highest probability for the presence of mixed valance Bi$^{3+}$/Bi$^{5+}$ cations at A-site and Ti$^{4+}$ at B-site. The system maintains the charge neutrality during growth process and electrical neutrality under external ambience conditions such as electric-field, temperature, humidity, light illumination and pressure by a reduction of the Ti$^{4+}$ at B-site. Similar effects were observed in several ferroelectrics that contain titanium and bismuth cations [38, 39, 44].

4. Conclusions

We have successfully developed a stable novel lead-free RFE after partial (40%) substitution of Ba-site of BaTiO$_3$ with optically active Bi and Li cations. Bismuth exists in mixed valence states along with freely available Li cations at the interstitial sites, which make the BBLT more optically active. This Bi$^{5+}$ cation acts as an optically active center, which significantly enhances the dielectric constant under moderate illumination. The mixed crystal phases, chemically inhomogeneous nanoscale regions, PNRs, and mixed valence states provide a favorable condition for the dielectric dispersion, high
piezoelectric coefficients, and development of optically active nano-domains. A thermally activated phase transition (onset of a paraelectric phase) near 523 K–563 K is significantly suppressed under illumination of weak light which might be a topic of further research. The frequency dependent phase transition temperatures follow a nonlinear dependence of probe frequencies and a VF relation. The presence of external light source drastically changes the dielectric dispersion. One can easily see that light does not allow the merger the dielectric spectra with the underlying conduction background which generally occurs after $T_m$ (under normal dark conditions). The dielectric dispersion persists well above the $(T_m)$, and it suggests the presence of PNRs—chemically and optically active regions for $T \gg T_m$; however, at elevated temperatures thermally activated charge carriers may also be responsible for large dielectric dispersion. As expected from RFE, we have obtained a high value of displacement coefficient of 233 pm V$^{-1}$, which makes BBLT more attractive for optically active actuators, sensors and bistable switches.

Acknowledgment

AK acknowledges the CSIR-MIST (PSC-0111) project for their financial assistance. PP thanks CSIR network projects NWP55, PSC0109 and OLP120132 for financial support. Hitesh Borkar would like to acknowledge the UGC (SRF) to provide fellowship to carry out PhD program. AB thanks UGC (JRF), India for fellowship towards his PhD program. Authors would like to thank Dr V N Ojha (Head ALSIM) and Dr Sanjay Yadav, for their constant encouragement and Dr S P Singh for UV-Visible measurement.

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