Low-Loss Tunable Infrared Plasmons in the High-Mobility Perovskite (Ba,La)SnO₃

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1. Introduction

Noble metals are the go-to choices for applications in plasmonics because of their relatively low optical losses and robustness,[1–5] with intrinsic bulk plasmons emerging in the visible regime. Although surface plasmons in these materials can be pushed down to the near infrared (IR) by shaping the materials into structures of high aspect ratio, this solution is not ideal, and alternative materials with their bulk plasmon frequency already in that spectral range would be useful. Additionally, traditional plasmonic metals do not allow for active tuning or ultrafast optical switching because of their high electron density, to which added doping charges can only contribute negligibly. Alkali metals present lower electron densities that place their plasmons in the near-IR-visible region with extremely low losses,[6] but these materials are unstable under ambient conditions and thus challenging to integrate in actual devices with long-term stability. The appeal of tunable carrier density, high carrier mobility, and good chemical stability has motivated the search for alternative plasmonic materials,[7] including transparent conducting oxides (TCO),[8,9] transition metal nitrides,[8,10] chalcogenides,[11] and alloys,[12] as well as two-dimensional materials,[13] especially graphene[14–16] and black phosphorus.[17,18] Among these, doped binary oxides, such as In₂O₃, SnO₂, ZnO, and CdO, have been intensively studied in various geometries for their IR plasmonic properties.[19–22] More recently, semi-metallic perovskite oxides SrBO₃ (with B = Ge, V, or Nb)[23–26] have also been identified as alternative IR plasmonic materials.

BaSnO₃ exhibits the highest carrier mobility among perovskite oxides, making it ideal for oxide electronics. Collective charge carrier oscillations known as plasmons are expected to arise in this material, thus providing a tool to control the nanoscale optical field for optoelectronics applications. Here, the existence of relatively long-lived plasmons supported by high-mobility charge carriers in La-doped BaSnO₃ (BLSO) is demonstrated. By exploiting the high spatial and energy resolution of electron energy-loss spectroscopy with a focused beam in a scanning transmission electron microscope, the dispersion, confinement ratio, and damping of infrared localized surface plasmons (LSPs) in BLSO nanoparticles are systematically investigated. It is found that LSPs in BLSO exhibit a high degree of spatial confinement compared to those sustained by noble metals and have relatively low losses and high quality factors with respect to other doped oxides. Further analysis clarifies the relation between plasmon damping and carrier mobility in BLSO. The results support the use of nanostructured degenerate semiconductors for plasmonic applications in the infrared region and establish a solid alternative to more traditional plasmonic materials.
The combination of appealing plasmonic and electronic properties in a single material adds extra versatility in the design of actual devices. In search of such materials, we consider BaSnO$_3$ (BSO), which is a wide band gap (2.9 to 3.2 eV) perovskite oxide that holds great promises for applications in oxide electronics.

This material has a room-temperature carrier mobility >300 cm$^2$ V$^{-1}$ s$^{-1}$ in single crystals, which is the highest among all transparent conductors and perovskite oxides, exceeding III–V semiconductors at high carrier densities.

This indium-free TCO also has exceptional stability of oxygen vacancies even under extreme biasing conditions or at elevated temperatures. Although several experimental works have studied the IR optical properties of bulk crystals, thin films, and ensembles of nanocrystals, individual La-doped BSO (BLSO) nanoparticles with well-defined doping and shape have not been characterized yet. To that end, we exploit electron energy-loss spectroscopy (EELS) in a monochromated scanning transmission electron microscope (STEM), which allows for the spatial and spectral characterization of low-energy excitations at the single-particle level.

In this work, we systematically study plasmons emerging in BLSO nanocrystals with well-defined shapes by measuring their spectral and spatial characteristics using state-of-the-art STEM-EELS. We observe IR plasmons in the 50–800 meV energy range, and image their spatial distribution and localization in BLSO nanorods. We further explore the doping limit of La in BSO and the associated plasmon energies, which allow covering a wide range of IR frequencies reaching up to the telecom wavelength at 1.55 μm. In addition, we characterize the surface plasmon dispersion, confinement ratio, lifetime, and quality factor in individual nanoparticles with varying sizes. By comparing our results with recent studies of plasmons in conventional plasmonic metals (Au, Ag, Cu), we establish BLSO as an appealing plasmonic material more suitable to the infrared range, with some degree of tunability, and a low level of losses that correlates well with the carrier mobility.

2. Results and Discussion

We synthesized nanocrystals of BLSO with varying sizes and geometries by a sol–gel method modified from ref. [35] (Experimental Section). Through atomic resolution high-angle annular dark-field (HAADF) imaging in Figure 1a,b, and X-ray diffraction (Figure S1, Supporting Information), we confirmed the expected cubic perovskite structure. For the BLSO rods and cubes, we also observed that the BLSO particles have (100) terminated surfaces. Core-loss EELS in Figure 1b shows the presence of Ba, Sn, O, and La in the doped samples. Here, La acts as n-type dopant that replaces a portion of the A-site Ba, which introduces free electrons that occupy the bottom of the conduction band. With sufficient La doping, the Fermi level is located above the conduction band minimum (by typically less than 1 eV), making BLSO a degenerate semiconductor. The collective oscillations of these conduction band electrons form IR plasmons that we study in this paper. We also investigate the doping limit of La in BSO and the maximum plasmon energy in this material with STEM-EELS. The bulk plasmon energy and the corresponding La percentage are extracted from low-loss and core-loss EELS, respectively. As shown in Figure 1c,d, both the bulk carrier plasmon energy and La M$_{4,5}$ edge intensity increase with nominal doping level. The low-loss and core-loss EELS signals are obtained from the same region, which allows correlating composition and plasmonic properties at the nanoscale. We find that highly doped BLSO can support plasmons up to an energy of 0.8 eV (corresponding to a wavelength of 1.55 μm), supporting BLSO as a promising candidate for plasmonics applications (such as epsilon-near-zero-based devices) at the telecom wavelength with better optical properties than traditional TCOs because of the high carrier mobility of BLSO.

However, we find that doping inhomogeneity can play a role at high doping...
levels. Therefore, we limit our investigation to moderately (5%) La-doped BSO in the rest of this paper.

Besides the peaks assigned to bulk plasmon excitations denoted by red markers in Figure 1c, additional peaks appear at lower energies. These can also be observed in the aloof EELS spectra shown in Figure 2b, where surface plasmon resonances of free charge carriers in BLSO are probed when the electron beam is placed just outside a BLSO nanorod displayed in Figure 2a. We attribute these resonances to different localized surface plasmon (LSP) modes, which are spatially imaged in the energy-filtered maps shown in Figure 2c. Regions of high intensity in the maps are associated with an accumulation of induced electric field that is characteristic of LSP excitations, as inferred from theoretical simulations (Figure S2, Supporting Information). The distribution of these hotspots strongly depends on geometry. In particular, in the rectangular BLSO nanorod shown in Figure 2a [length $L = 427 \text{ nm}$, aspect ratio (AR) $\approx 7$], we observe multiple LSPs oscillating along the long axis, starting with a dipolar mode of wavelength $\lambda_{n=1} = 2L$, and two higher-order modes ($\lambda_{n=2} = L$ and $\lambda_{n=3} = 2L/3$). A transverse LSP mode is also observed at energies above 400 meV. In the BLSO cube shown in Figure 2d ($L = 50 \text{ nm}$, AR $\approx 1$), we observe plasmon resonances of shorter wavelengths characterized by field and charge accumulation at the corners, edges, and faces of the cube (Figure 2e).[41–44]

One distinct difference between degenerate semiconductors and metals refers to the spatial confinement of LSPs with sub-eV energies. Noble metals present large ratios of the real and imaginary parts of the dielectric function in the IR, which guarantees high quality factors of their LSP resonances. However, the corresponding plasmon wavelengths are very close to those of free-space photons in the IR because they host large densities of conduction electrons, so their bulk plasmons appear in the visible part of the spectrum, therefore demanding high ARs to move surface plasmons to the IR, where the dielectric function takes larger absolute values. In contrast to noble metals, LSPs in degenerate semiconductors can produce a large confinement ratio in IR plasmons because of their lower carrier densities, which lead to bulk plasmon energies already placed in the IR, so smaller ARs and lower values of the dielectric function already provide strongly confined plasmons in that region. With the plasmon energy and wavelength from the measured EELS energy-filtered maps in Figure 2c, we can readily obtain the plasmon confinement ratio in BLSO nanoparticles, as shown in Figure 2d, which turns out to be about one order of magnitude larger than for noble metals. In Figure 2f, we demonstrate that LSPs in BLSO nanoparticles have wavelengths $\approx 6$ to 12 times shorter than the photon wavelength at the same energy (but we note that a factor of 20 can be reached with the corner modes in nanocubes). The large spatial confinement is equally evident from the plasmon dispersions of BLSO...
calculated for an infinite waveguide with a square cross section (see also Figure S3, Supporting Information for calculations with different cross sections), which deviates away from the light line much more than the dispersion calculated for Ag waveguides of similar characteristics.

Next, we study plasmon spectra for the series of BLSO nanorods shown in Figure 3a, which have a similar cross section but varying length and aspect ratio. These rod-like particles have rectangular cross sections and lengths of \( \approx 200-1200 \) nm, with AR ranging from 4 to 12. They are supported in part by lacy carbon TEM grids, while mostly suspended in vacuum. The EEL spectra shown in Figure 3b were acquired with the beam placed just outside the nanorod tip or cube corner, as indicated by the colored markers in Figure 3a. With the help of the spatial mapping demonstrated in Figure 2, we attribute the sharpest and most intense resonance peaks present in all spectra to the dipolar modes \((n = 1)\). While the dipolar LSPs decrease in energy with increasing AR, their spectral width also decreases substantially. For a quantitative assessment of this trend, we performed Lorentzian fitting to extract the full width at half maximum (FWHM) of all peaks corresponding to the observed LSPs, including the higher-order LSPs. As shown in Figure 3c, the FWHM can be as small as 35 meV for the nanorod with the largest AR and increases to about 120 meV for higher-energy LSPs. The quality factors Q (defined as the ratio of the plasmon energy to the FWHM) obtained for these plasmons are shown in Figure 3d. The dipolar modes are found to have Q factors in the 2–5 range, while higher-energy LSPs show Q up to 8. Compared with other doped semiconductor nanocrystals,[45–47] the LSPs observed in this study exhibit the largest Q factors in the mid-IR.

While plasmon damping is often associated with carrier mobility of the material, such correlation is generally not direct, as several factors other than carrier mobility (i.e., nonlocal effects, surface quality, and radiative coupling) can play an essential role in determining the plasmon lifetime. We notice such variation of LSP FWHM with particle size and geometry in Figure 3c and further study the plasmon FWHM as a function of nanoparticle AR and particle length \( L \) in Figure 4 and Figure S6 (Supporting Information), respectively. We notice a substantial increase of LSP damping for BLSO particles with decreasing AR. To understand the possible origin of this trend, we calculate aloof EEL spectra for varying nanoparticle dimensions and extract the FWHM of the theoretically predicted peaks. We model the optical properties of BLSO using a Drude dielectric function, which we find is sufficient for describing the charge carriers in doped BSO (Figure S4, Supporting Information), and perform numerical modeling as described in Methods. Also shown in Figure 4, we find that the calculated FWHM of the dipolar plasmons increases only slightly above the bulk damping value \( h/\gamma_{\text{bulk}} = 35 \) meV here considered for the model, and in particular, the increase is only about 5 meV.

Figure 3. a) HAADF-STEM images of BLSO rod-like particles with varying length and aspect ratio (AR, see labels). b) Aloof EELS spectra acquired for beam positions as indicated by the color-matching crosses in (a), near the tip of the BLSO nanorods. c) LSP FWHM and d) quality factor as a function of LSP energy.
for small AR or L. In the opposite limit, for very large AR or L, the FWHM of the dipolar plasmons only moves by 2–3 meV below the bulk Drude damping. However, we stress that the calculated results deviate substantially from the experimental observations, especially when the particle sizes (and so the AR too) are small.

To further understand this discrepancy in the spectral widths, we calculate the optical scattering and absorption spectra near BLSO nanorods (SI) to analyze the origin of the plasmon damping. These quantities are roughly proportional to the cathodoluminescence (CL) and EELS probabilities, respectively, so we show in Figure S7a,b (Supporting Information) the intensity ratio between these two probabilities (EELS/CL), which takes large values for the range of AR and L studied here, suggesting a dominantly nonradiative character of the plasmonic excitations. We therefore conclude that damping in these excitations is mainly contributed by material properties (i.e., intrinsic effects of the material and its modification due to the specific geometry of the particles), while radiative damping plays a negligible role.

To compare plasmon damping in BLSO with other plasmonic materials, it is also illuminating to look at their respective normalized plasmon dispersions (Figure 5). The surface plasmon dispersion relations are evaluated for infinite slabs with thickness of 50 nm.[50] We adopt the Drude model permittivity $\varepsilon(\omega) = \varepsilon_e - \omega_p^2/\omega(\omega + i\gamma)$ with parameters $\varepsilon_e = 4.0$ and $E_{bulk} = \hbar v_F/\sqrt{\varepsilon_e} = 4.6$ eV for silver, and $\varepsilon_e = 4.5$ and $\omega_p^2 = e^2 N/e_0 m^*$ for BLSO, where $N$ is the carrier density (see legend in Figure 5) and $m^*/m_c = 0.2$ is the carrier effective mass.[51]

We plot the plasmon energy as a function of wave vector $q$, normalized to $E_{bulk}$ and the Fermi wave vector $q_F$, respectively. For the same ratio $E/E_{bulk}$ of the plasmon energy $E$ to the bulk plasmon energy $E_{bulk}$, plasmons sustained by free carriers with lower density possess a higher ratio of the wave vector $q = 2\pi/\lambda$ to the Fermi wave vector $q_F$ compared to Ag, and this behavior extends up to the large-wave-vector limit, where the plasmon frequency converges to the non-retarded limit $q_F/\sqrt{\varepsilon_e} + 1$. In addition to their high spatial confinement, this indicates that BLSO plasmons are closer to the single-particle excitation (SPE) regime. It has been observed that surface plasmons exhibit a damping that increases with $q$, even before reaching the onset of SPEs at $q = q_F$. This might happen because for increasing wave vectors, shorter-wavelength plasmons are more likely to be scattered by doping inhomogeneities, neighboring nanoparticles, and shape irregularities. The differences in LSP energy between our simulations and experiments (Figure S5, Supporting Information) are likely related to these extra scattering mechanisms, which are not contemplated in the theory. Furthermore, we investigate LSPs up to the high $E/E_{bulk}$ regime, where size effects are known to affect both the energy and width of LSPs.[53] A phenomenological model has often been used to take into account the size effects via the expression:

$$\gamma = \gamma_{bulk} + \frac{q_F}{L} \left(\frac{1}{2} + \frac{\gamma}{2\pi q_F}\right)$$ (1)

where $v_F$ is the carrier Fermi velocity, $A$ is a phenomenological parameter that depends on particle morphology, surface details, and the surrounding medium, and $L$ is the particle size. We find that $\gamma_{bulk} = 30$ meV and $A$ in the range of 2 to 3 provides a reasonable agreement of $\gamma$ as a function of $L$ in comparison with experiment, as shown in Figure 4. Although such size dependence has been observed for small metal particles,[55] the physical explanation of the phenomenon is somewhat controversial,[56] with two possible explanations for the increase in damping with decreasing particle size associated with either additional surface scattering determined by a size-independent electron mean free path[54] or the increasing role of the inhomogeneous electron density profile at the surface.[57] The range of particle size in which we observe an increase in plasmon FWHM is relatively large compared to that of metal particles ($\sim 10$ nm or less), an effect that can be possibly related to the lower density of free carriers in BLSO.
It is also worth noting that the Debye temperature for BaSnO$_3$ is around 500 K,[60] above the temperature at which we perform our experiments. High-frequency phonons could contribute to carrier scattering[61] when higher-energy mid-IR LSPs are excited. However, electron–phonon interaction was only found to limit the plasmon lifetime within a small energy region around the optical phonon frequency.[60,61] Thus, the contribution from this scattering mechanism to the damping of high-energy plasmons may require further investigation.

Nevertheless, the dipolar plasmons in BLSO discussed in Figures 3 and 4 are systematically displaying smaller values of the FWHM than those in noble metals of the same size.[68,69] The reported BLSO plasmons reach their FWHM limit at an AR between 10 and 20, which is 2 to 3 times smaller than that for Ag, Au, or Cu. The BLSO particles required to support IR LSPs are much smaller than those made of noble metals, which makes radiative damping negligible in the former. In addition, both the intrinsic carrier mobility and the particle size affect the damping of plasmons in degenerate semiconductors, including BLSO. At large sizes, the FWHM of LSPs are primarily limited by the carrier mobility. In contrast, in smaller particles, additional contributions to plasmon damping are observed. The narrowest LSP that we found in BLSO has a FWHM of 35 meV (i.e., a dephasing time of 38 fs). This amounts to a lower limit of carrier mobility $\mu = 160 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which falls within the range of carrier mobilities previously determined for this material.[52,68] Given that the carrier mobility in BaSnO$_3$ can be as high as 300 cm$^2$ V$^{-1}$ s$^{-1}$, it is likely that better synthetic approaches and fabrication processes will lead to even better IR plasmons in doped BSO with more compact dimensions compared to noble metals.

3. Conclusions
In summary, we systematically identified and characterized infrared localized surface plasmons in individual nanocrystals of La-doped BaSnO$_3$ by STEM-EELS. Our results show that infrared plasmons sustained by BLSO are superior in spatial confinement ratio compared to those in noble metals. We also demonstrate that, with high enough La doping, BLSO can have a sufficiently large density of free carriers for its bulk plasma frequency to reach the telecommunication wavelength at 1.55 $\mu$m/0.8 eV. Our analysis of LSPs in BLSO nanorods with varying length and aspect ratio shows that the low-loss IR plasmons are primarily limited by non-radiative damping, which is closely related to the carrier mobility. Our results emphasize the strong potential of this high-mobility perovskite oxide for application in infrared plasmonic devices.

4. Experimental Section

BLSO Synthesis: A recipe for BaSnO$_3$ nanoparticle synthesis via a sol–gel approach modified from ref. [35] was followed. Chloride salts of Ba, La, and Sn were weighed in desired molar ratio and added in a mixture of deionized water and ethanol. Citric acid was then added into the solution. The solution was then kept at 80°C under stirring for 30 min to aid complete dissolution. Overdosed ethylene glycol was then added, and the solution was heated to 100°C for 2 h until the gel was formed.

Annealing at 600°C followed by annealing at 1000°C in atmosphere resulted in phase pure cubic BLSO. Nanorod-like and cubic-shaped BLSO particles can often be found in the product. When doping was successful and relatively uniform, the powder had a greenish and blue appearance, for small and large particle size, respectively.

Another synthetic route involved the formation of BaSn(OH)$_3$ as the middle product[64,65] via participation at room temperature, followed by high-temperature annealing to form perovskite BaSnO$_3$. For this route, the solution containing salts of Ba, La, and Sn was kept at 80°C under vigorous stirring, while a NaOH solution was added dropwise until reaching a pH > 7. During this process, Argon purging was also required to prevent the formation of oxides. At this point, white participation should already form, which is BaSn(OH)$_3$. Subsequent annealing above 600°C in Argon allowed BSO nanorods to be formed with large length and aspect ratio. However, we find that it is difficult to incorporate La dopant into the A-site via this approach. Thus, this method is not suitable for producing plasmonic BLSO.

STEM-EELS: A Nion UltraSTEM 100 scanning transmission electron microscope was used in this work. The microscope features a HERMES electron monochromator to improve the energy resolution. Energy loss spectra and energy-filtered maps were taken with energy resolution in the 10–12 meV range. The EELS detector dispersions were 0.9 and 1.3 meV pixel$^{-1}$ for point of EELS spectra acquisition and EELS mapping, respectively. Alloof energy loss spectra were recorded with a detector dwell time of 256 ms. EELS spectra taken in vacuum far away from any specimen or grid were used to obtain the elastic background, which was then removed from the spectra containing the inelastic signal.[66,67]

Numerical Simulations: The theoretical calculations were performed using the software Comsol Multiphysics (RF module)[68,69] where a line current representing the electron beam was implemented as a field source. The induced electric field $\mathbf{E}^\text{ind}$ was then used to evaluate the frequency and spatially dependent loss probability $\Gamma(\omega)$ as[70]

$$
\Gamma(\omega, \mathbf{R}) = \frac{\pi\hbar}{\omega_{\text{ind}}} \int dz \operatorname{Re}\left\{\mathbf{E}^\text{ind}(\mathbf{R}, z, \mathbf{a})e^{-\imath\mathbf{a}\cdot\mathbf{z}}\right\}
$$

Here, electrons moving with constant velocity $\mathbf{v}$ parallel to the $z$ axis and intersecting the $xy$ plane at $\mathbf{R}$ were assumed.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.
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