Effective Dielectric Constant of Metal Chalcogenides Ag-PbSe Nanocomposite

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Abstract

We have discussed the effective optical properties of Ag-PbSe plasmonic nanocomposites with different filling fraction in a broad frequency range at terahertz frequencies. The structures are composites of two different kinds of nanospheres, one made from chalcogenide dielectric materials PbSe and the other from a of Ag metal. In this paper, a theoretical approach is proposed to calculate an effective dielectric peroperties of Ag metallic nanospheres, randomly distributed and embedded in a uniform PbSe chalcogenide medium. The effective optical properties of the embedded particles is considered as well as surface plasmon resonance (SPR) of the Ag metal nanoparticles. It is found that the value of the effective dielectric properties decreases as a result the resonance wavelength shifts to shorter wavelengths.

keywords: Nanostructured Materials; Plasmonics; Effective Permittivity; Refractive Index
I. INTRODUCTION

Strong resonances which appear at optical frequencies for metal nanoparticles result from the resonant oscillation of free electrons on the surface of the particles and are referred to as localized surface plasmon resonances (LSPRs). By altering the shape of the metallic particles, one can sensitively manipulate the observed resonant frequencies throughout the UV and visible and even into the NIR [1–3]. Highly anisotropic shapes, such as rods or plates, may display multiple modes, while sharply faceted shapes are desirable due to the large electric field enhancements observed at tips and edges [3, 4]. The focusing properties of plasmonic particles have been harnessed to enable a number of new technologies and sensitive measurement tools, such as surface-enhanced Raman spectroscopy (SERS) [5], LSPR/SPR sensing [6, 7], photothermal therapy [8], and plasmon-enhanced fluorescence [9–11].

The mixing of Clausius-Mossotti relation (CMR), the Kramers-Kronig Relations and the theory of linear response [12], are applied for formulation of metal-dielectric effective permittivity \( \varepsilon(q, \omega) \) of a homogeneous system near Mie resonance modes. The structure is assumed to be non-magnetic metallic and dielectric spheres. Relative to the incident light wavelength, scattering by small spherical particles is based upon the exact Mie solution of the diffraction [13]. All scattering objects can be represented by effective electric polarizability densities. The experimental composites will be made using a variety of fabrication methods, including thin-film deposition, focused-ion-beam milling, and self-assembly [14]. Both the past theoretical and experimental studies revealed that the properties of surface plasmons depend on multiple parameters, including shape, size, and composition of metal nanostructures, and dielectric constant of the media surrounding metal nanostructures.

Recently, Yannopapas et al. have been presented a new set of artificial structures which can exhibit a negative refractive index in a broad frequency range from the deep infrared to the terahertz region [15]. Their structures were composites of two different kinds of non-overlapping spheres, one made from inherently non-magnetic polaritonic and the other from a Drude-like material. Their results are explained in the context of the extended Maxwell-Garnett theory and are reproduced by calculations based on the layer KorringaKohnRostoker method, an ab initio multiple scattering theory.

More recently, we obtain plasma frequency and linear relation of frequencies with the effective permittivity. We have proposed an improved method to retrieve the effective parameters (index of refraction, impedance, permittivity, and permeability) of metamaterials from transmission and reflection data. Extents far above the calculated relations are very good match with effective permittivityrelated environment, including nanospheres of some metals and a samples of the high refractive index dielectric material. [16]. In the other work, we present a new set of nanostructured composites which can exhibit a phenomenon known as surface plasmon resonance in a broad frequency range from the deep infrared to the terahertz region. The effective permittivity and refractive index of zinc sulfide/Ge and zinc oxide/Ge composites have been calculated over terahertz frequencies [17].
In this paper, an effective dielectric constant of metallic nanospheres, randomly distributed and embedded in a uniform chalcogenide dielectric medium, has been calculated. The paper is organized as follows. Section II illustrates how an effective dielectric constant of composites of inherently non-magnetic spherical particles arises within the context of an extended Maxwell–Garnett theory. The effective medium properties are studied using the extended Maxwell–Garnett theory method, which is based on rigorous multiple-scattering theory, using a well documented computer code in this section. We present results of the effective permittivity and refractive index of simulated composites in Section III. Finally, summary and conclusions follow Section IV.

II. THEORETICAL FRAMEWORK

Consider a system of \( N \) non-overlapping spherical metallic particles randomly distributed in the background media and interacting with each other and with an incident plane monochromatic wave, whose wavelength \( \lambda \) is assumed to be much larger than the average size of the particles in the cluster (i.e., electrostatic approximation). The particles have approximately the same radius \( R \) and embedded in a dielectric continuous matrix with dielectric constant \( \epsilon \). Due to the influence of the external field as well as the interaction between particles in the solution, all particles in the system will obtain some polarization. The total effective dipole moment of particle \( i \), accounting mutual neighboring many-particle interactions

For two-component composite materials, when the volume fraction of the inclusions is smaller than that of host and the interaction of the two kinds of particles can be neglected, the total electric and magnetic polarizations can be assumed to be proportional to \( \sum_{i=a,b} N_i \alpha_i^{e,m} \), where \( N_i \) and \( \alpha_i^{e,m} \), \( i = a, b \), represent the number densities and the electric and magnetic polarizabilities of the particles of type \( a \) or \( b \). Under these assumptions, the quasi-static extension of the Maxwell–Garnett formula, also known as extended Maxwell–Garnett formula, can be obtained by Mie theory

\[
\epsilon_{\text{eff}} = \frac{\epsilon_h}{k^3 + 3i \left( \frac{f_a d_a^e}{r_a^3} + \frac{f_b d_b^e}{r_b^3} \right)}
\]

where \( k \) is the wavenumber in the host medium. \( f_i = 4\pi N_i r_i^3 / 3 \), \( i = a, b \) represent their respective filling fractions. \( d_a^e \) and \( d_b^e \) are the Mie electric dipole scattering coefficients of the two type of constituent particles and are given by

\[
d_i^e(\omega) = \left[ \frac{j_1(\omega r_i^3)[krj_1(\omega)][krj_1(\omega)]^\prime \epsilon_i - j_1(\omega)[krj_1(\omega)][krj_1(\omega)]^\prime \epsilon_h}{h_1^+(\omega)[krj_1(\omega)][krj_1(\omega)]^\prime \epsilon_h - j_1(\omega)[krh_1^+(\omega)][krj_1(\omega)]^\prime \epsilon_i} \right]
\]

where \( j_1(h_1^+) \) is the spherical Bessel (Hankel) function for \( l = 1 \) and \( [xj_1(x)]^\prime = d[zj_1(z)] / dz \big|_{z=x} \), etc.
The effective medium parameters of composite comprising different spheres embedded in a matrix, can be obtained from polarizability $\alpha_i$ corresponding to the electric polarizability with $r = r_i$. The coefficients for the spherical harmonics in the resonance modes are given by [13, 16]

$$a_1 = j\frac{2}{3} (k_0^2 \mu_b \epsilon_b)^{3/2} \frac{\mu - \mu_e F(\theta)}{2 \mu_b + \mu_e F(\theta)} r^3,$$

$$b_1 = j\frac{2}{3} (k_0^2 \mu_b \epsilon_b)^{3/2} \frac{\epsilon - \epsilon_e F(\theta)}{2 \epsilon_b + \epsilon_e F(\theta)} r^3,$$

where

$$F(\theta) = \frac{2(\sin \theta - \theta \cos \theta)}{(\theta^2 - 1) \sin \frac{\theta}{2} \cos \theta},$$

$$\theta = k_0 r \sqrt{\epsilon_i \mu_i}.$$

The polarizabilities of electric and magnetic dipoles can be written as [13]

$$\alpha = 4\pi r^3 \frac{\epsilon_b - \epsilon_e F(\theta)}{2 \epsilon_b + \epsilon_e F(\theta)} = \frac{3 f_b \left[ \frac{\epsilon_b - \epsilon_e F(\theta)}{n \frac{2 \epsilon_b + \epsilon_e F(\theta)}{n \frac{2 \epsilon_b + \epsilon_e F(\theta)}}} \right]}{f \frac{1 - \mu_e F(\theta)}{n \frac{2 + \mu_e F(\theta)}}},$$

$$\beta = 4\pi r^3 \frac{1 - \mu_e F(\theta)}{2 + \mu_e F(\theta)} = \frac{3 f \left[ \frac{1 - \mu_e F(\theta)}{n \frac{2 \epsilon_b + \epsilon_e F(\theta)}} \right]}{f \frac{1 - \mu_e F(\theta)}{n \frac{2 + \mu_e F(\theta)}}},$$

where $r = r_e$ and $r = r_m$ are defined for spheres in the electric and magnetic resonance, respectively.

The uniformity of the material in the directions perpendicular to the $THz$ propagation wave vector is also of key importance. When the diffraction limited spot size of terahertz radiation is far larger than the material’s dimension an effective medium theory should be employed to model the composite material’s dielectric function (see Refs. [16, 17], for more details). The nanostructured materials satisfy this restriction. When attempting to model a composite conductive material a suitable model for the optical properties of each constituent should therefore be chosen, and then combined using an effective medium theory. For a composite consisting of two sets of resonating spheres effective medium models can obtain to read

$$\frac{\epsilon_{eff} - \epsilon_b}{\epsilon_{eff} + 2\epsilon_b} = f_e \left( \frac{2 \epsilon_b + \epsilon_e F(\theta_e)}{\epsilon_b - \epsilon_e F(\theta_e)} \right) + f_m \left( \frac{2 \epsilon_b + \epsilon_m F(\theta_m)}{\epsilon_b - \epsilon_m F(\theta_m)} \right),$$

$$\frac{\mu_{eff} - 1}{\mu_{eff} + 2} = f_m \left( \frac{2 + F(\theta_m)}{1 - F(\theta_m)} \right),$$

where $\theta_m = k_0 r_m \sqrt{\epsilon_i \mu_i}$ and $\theta_e = k_0 r_e \sqrt{\epsilon_i \mu_i}$.

The similar equation for $K$ spheres in electric resonance and $N$ spheres are given by

$$\frac{\epsilon_{eff} - \epsilon_b}{\epsilon_{eff} + 2\epsilon_b} = \frac{1}{3 \epsilon_b} \left( \sum_{k=1}^{K} n_{ak} \alpha_{ak} + \sum_{n=1}^{N} n_{bn} \alpha_{bn} \right).$$
By substituting polarizabilities, Eq. (4) into Eq. (7), with \( r = r_i \) for the spheres in the electric resonance, we obtain

\[
\frac{\varepsilon_{\text{eff}} - \varepsilon_h}{\varepsilon_{\text{eff}} + 2\varepsilon_h} = \sum_{k=1}^{K} \frac{f_{ak}}{G(\Theta_{ak})} + \sum_{n=1}^{N} \frac{f_{bn}}{G(\Theta_{bn})}.
\]  

(8)

There are the effective permittivity with two sets of spheres. The effective permeability can also be calculated in a similar way.

When Eq. (7) is a discrete summation, samples can be taken with the Dirac delta function from continuous probability density functions \( g_1(r_a) \) and \( g_2(r_b) \), which describe the particle size distributions of spheres in the electric and magnetic resonances under the normalization conditions \( \int_0^{\infty} g_1(r_a) \, dr_a = \int_0^{\infty} g_2(r_b) \, dr_b = 1 \). The effective permittivity for the continuous size distributions is given by

\[
\frac{\varepsilon_{\text{eff}} - \varepsilon_h}{\varepsilon_{\text{eff}} + 2\varepsilon_h} = f_a \int_0^{\infty} \frac{g_1(r_a)}{C(r_a)} \, dr_a + f_b \int_0^{\infty} \frac{g_2(r_b)}{C(r_b)} \, dr_b,
\]

(9)

where \( 1/G(\Theta_a) \) and \( 1/G(\Theta_b) \) are integrable functions, \( f_a \) and \( f_b \) are the volume fraction of spheres in the electric resonance and the volume fraction of spheres in the magnetic resonance mode, respectively.

The base part in the calculation of the proposed nanocomposite material is the effective approach which will provide us with the effective parameters. To describe the optical properties, two sets of quantities are used: the real and imaginary parts of the complex refractive index \( n = \Re [n] + i \Im [n] \) and the real and imaginary parts of the complex dielectric function (or relative permittivity) \( \varepsilon(\omega) = \Re [\varepsilon(\omega)] + i \Im [\varepsilon(\omega)] \). These two sets of quantities are not independent; either may be thought of as describing the intrinsic optical properties of nanocomposite. In this work, we will be primarily concerned with nonmagnetic materials for which \( \mu = 1 \). The dielectric function is in general complex, with a significant imaginary part \( \varepsilon_2 \) in spectral regions with absorption. It is often convenient to disentangle the contribution to \( \varepsilon \) from bound modes (lattice vibrations and core electrons) and the component arising from free charges. In the THz and mid-IR frequency ranges, lattice vibrations contribute via transverse optical phonon absorption (in polar materials), while at optical frequencies interband transitions alter \( \varepsilon \). More specifically, we consider the case of a three-dimensional crystal consisting of dielectric spheres in air, i.e., spheres whose relative dielectric permittivity is described by [17]

\[
\varepsilon(\omega) = \varepsilon_\infty \left( 1 + \frac{\omega_T^2 - \omega_L^2}{\omega_T^2 - \omega^2 - i\omega\gamma} \right),
\]

(10)

where \( \varepsilon_\infty \) is the asymptotic value of the dielectric permittivity at high frequencies, \( \omega_T \) is the transverse optical phonon frequency, and \( \omega_L \) is longitudinal optical phonon frequency. Its dispersion could be calculated using the Kramers-Kröning relation from the interband
FIG. 1: The real part of effective permittivity of a Ag-PbSe plasmonic nanostructured composite with two types of nanospheres as a function of the wavelength.

absorption spectrum. \( \gamma = \gamma_1 + \beta \omega^2 \), where \( \gamma \) is a damping constant, which can be separated into a frequency-independent term \( \gamma_1 \) and a frequency-dependent term \( \beta \). For the sake of clarity, the damping constant will be neglected for the time being, i.e., we set \( \gamma = 0 \) dielectric function \( \epsilon(\omega) \) is that of a single-resonance DrudeLorentz model and it satisfies the KramersKronig relations.

III. RESULTS AND DISCUSSION

Let us begin by presenting the dielectric function \( \epsilon(\omega) \) of the nanocomposite under consideration. The parameters such as: size of the nanospheres, the asymptotic value of the dielectric permittivity \( \epsilon_\infty \), plasmonic frequency \( \omega_p \), \( \omega_L \) and \( \omega_T \) the longitudinal and transverse optical phonon frequencies and \( \gamma \) the damping constant for phonons \( \gamma \), for PbSe and Ag are shown in Table I. It is noted that in absence of absorption the dielectric constant diverges at \( \omega = \omega_T \) and becomes zero at \( \omega = \omega_L = \omega_T = \sqrt{\epsilon_0/\epsilon_\infty} \) where \( \epsilon_0 \) and \( \epsilon_\infty \) are the
static and optical dielectric constants, respectively. For frequencies at the far infrared region mobile charge carriers can also contribute to the optical response of a nanocomposite.

TABLE I: The parameters of the transverse (\(\omega_T\)) and longitudinal (\(\omega_L\)) optical phonon frequencies, the asymptotic value of the dielectric permittivity, plasmonic frequency (\(\omega_p\)) and the sphere radius of PbSe and Ag nanospheres.

<table>
<thead>
<tr>
<th>Material</th>
<th>(\omega_T/2\pi) (THz)</th>
<th>(\omega_L/2\pi) (THz)</th>
<th>(\epsilon_\infty)</th>
<th>(\omega_p)</th>
<th>(\gamma)</th>
<th>Radius of spheres (nm)</th>
<th>Spheres filling fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbSe</td>
<td>1.17</td>
<td>3.32</td>
<td>26</td>
<td>–</td>
<td>–</td>
<td>445</td>
<td>0.37</td>
</tr>
<tr>
<td>Ag</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>9.00</td>
<td>0.021</td>
<td>335</td>
<td>0.19</td>
</tr>
</tbody>
</table>

In order to calculate the effective medium parameters of the mentioned nanostructured discussed in the section 2, we have used the modified version of the EFFE2P code [15].

The effective dielectric functions are complex and the imaginary part is associated with the extinction of the propagating beam due to scattering. The results of the effective properties as a function of the wavelength for a plasmonic nanocomposite made from Ag-PbSe nanoparticles are shown in Figs. 1-5. The real and imaginary parts of effective relative dielectric permittivity and permeability of the Ag-PbSe nanocomposites as a function of the frequency are shown in Figs. 1, 2 and 3.

In Fig. 1 it is obvious that there are regions where \(\epsilon_{eff}\) has negative real part as a result of the Mie resonances occurring in these regions. The electric activity is attributed to the large polarization induced to each sphere due to their enormous dielectric permittivity. The real part of the effective relative dielectric permittivity of the nanocomposite assumes negative values in different frequency resulting in frequency gaps.

To illustrate the optical transition mechanism in detail, the imaginary part of effective dielectric function has also been given in Fig. 2 and 3. It is well known that the imaginary part of the permittivity and permeability, which is related to the dissipation (or loss) of energy within the medium can describe the optical transition well. We distinguish between the real part and the imaginary part in Fig. 3.

TABLE II: The minimum and maximum value of effective permittivity and effective refractive index for Ag-PbSe at their corresponding wavelengths.

<table>
<thead>
<tr>
<th>Effective parameter</th>
<th>(\lambda(\mu\text{m}))</th>
<th>Minimum value</th>
<th>Maximum value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\epsilon_{eff})</td>
<td>98.5</td>
<td>-4101</td>
<td>4013</td>
</tr>
<tr>
<td>(n_{eff})</td>
<td>98.5</td>
<td>-0.23</td>
<td>107</td>
</tr>
</tbody>
</table>
FIG. 2: The imaginary part of effective permittivity of a Ag-PbSe plasmonic nanostructured composite with two types of nanospheres as a function of the wavelength.

The real and imaginary parts of effective relative index of the above composites are also shown in Figs. 4 and 5. Before each plasmonic peak, in the real effective refractive index, the transmittance is suppressed. Because Re(ε_eff) becomes negative in these frequency ranges giving rise to a practically imaginary refractive index. After making of the nano-structure, the intrinsic optical transition has a shift to the low-energy range, which means that the band gaps are narrowed by Ag layered. This show evident that the interaction of terahertz radiation with matter provides a vital low-energy probe of the electronic nature of a nanostructured system close to its equilibrium state. It is also evident that there is also a wider transmittance peak from ω/ω_0, corresponds to a region of refractive index with positive real part (the matching of the frequency regions is not perfect as Fig. 4 is based on an effective medium approximation). In between these peaks, the transmittance is suppressed as only Re(ε) becomes negative giving rise to a practically imaginary refractive index (see Fig. 5).

The minimum and maximum values of effective permittivity and refractive index of Ag-PbSe nanocomposite at its plasmonic resonance frequency are represented in Table II. We
FIG. 3: The real and imaginary parts of effective permeability of a Ag-PbSe plasmonic nanostructured composite with two types of nanospheres as a function of the wavelength, for different volume fractions of the embedded particles.

clearly see that the value of the maximum values of effective dielectric permittivity decrease with an increasing filling fraction and the minimum increase. The induced dispersion is so strong that the nanocomposite will effectively have metallic properties in a finite spectral domain. The first is of obvious nature and concerns the shift of the resonance towards shorter wavelengths. A trace from the intrinsic metallic Ag follows a Drude type dependency at different wavelengths.

Signs of real values of effective permittivity, in terms of frequency changes, is given in table III, indicate the real values of effective permittivity for a frequencies band, for each composites. It is also evident for finding of SPPs in these nano-structures.
FIG. 4: The real part of effective refractive index of a Ag-PbSe plasmonic nanostructured composite with two types of nanospheres as a function of the wavelength.

TABLE III: Sign of the Real values of effective permittivity of Ag-PbSe nanocomposite in terms of wavelength changes in µm.

<table>
<thead>
<tr>
<th>Composite</th>
<th>(90.0–94.8)</th>
<th>(94.8–98.3)</th>
<th>(98.3–98.5)</th>
<th>(98.5–100.0)</th>
<th>(100.0–105.0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-PbSe</td>
<td>Re($\epsilon_{eff}$) &gt; 0</td>
<td>Re($\epsilon_{eff}$) &lt; 0</td>
<td>Re($\epsilon_{eff}$) &lt; 0</td>
<td>Re($\epsilon_{eff}$) &gt; 0</td>
<td>Re($\epsilon_{eff}$) &gt; 0</td>
</tr>
</tbody>
</table>

IV. SUMMARY AND CONCLUSION

We have discussed the effective optical properties of Ag-PbSe plasmonic nanocomposites at terahertz frequencies. The effective properties of this nanocomposite have been shown to be useful for predicting the response of functional devices and sensors at this range of frequencies. We discussed the dependency of effective properties on the material from which
FIG. 5: The imaginary part of refractive index of a Ag-PbSe plasmonic nanostructured composite with two types of nanospheres as a function of the wavelength.

the nanocomposites are made. In general, with this analysis we have shown that plasmonic nanocomposites can be used in the design of terahertz elements. However, these effective properties are only useful if they can predict the properties of functional devices.

This result is useful to assess the conditions under which a nanoparticle-based nanocomposite metamaterial can be assimilated to an effective medium. Our results may be very helpful to better understand the dielectric properties of nanocomposites in terahertz region and optimize device parameters in the future. The stronger intrinsic absorption of good metals such as Au and Ag eventually turns out to be something useful, since it suppresses the interaction between neighboring nanoparticles in the nanocomposite. This ability opens the door for considering plasmonic nanocomposites comparably to ordinary metamaterials in a future instrument design process. This will have implications for many applications in terahertz.
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References