Negative-epsilon conditions in the dispersive $LiNbO_3$-Ag nanoparticles composites

Negative – epsilon conditions in the dispersive $LiNbO_3 - Ag$ nanoparticles composites

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Abstract. The silver (Ag)–embedded lithium niobate ($LiNbO_3$) composites are theoretically analyzed under the effective medium Maxwell–Garnett approximation to account on the optimal conditions through which such composites present negative epsilon conditions. The dielectric function of Ag nanoparticles (NPs) is described by Drude theory with an additional Lorentz oscillator term to take into account the interband electronic transitions which typically occur in noble metals. The $LiNbO_3$ dielectric function is evaluated through the Sellmeier equations. Once the effective dielectric function (ϵ_{eff}) is evaluated, we investigate the negative epsilon condition ($\epsilon'_{eff} < 0$) as a function of the frequency. The results showed that, for given volumen fraction values, the negative epsilon (NE) condition is satisfied for critical sizes of Ag NPs. This condition defines an interval of energies, called NE range. That NE range enlarges for increasing radius and becames narrower for decreasing volume fractions. Furthermore, the calculated Fröhlich frequency is nearly close to the lower-energy limit of NE range. In addition, the calculated extinction spectra of the composite are analyzed in terms of the radius of Ag NPs.

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1. Introduction

An extremely large variety of metal/dielectric combinations (types of materials and configuration) called *metamaterials* are currently the subject of intense studies, revealing new fundamental properties leading to novel devices with improved performances [1, 2]. Indeed, metamaterials are synthetic structures with electromagnetic properties not readily available in the nature, such as artificial magnetism and negative index. The latter characteristic may lead to interesting scientific developments and serve as platform for a variety of applications in different areas such as photonics [3], optical cloaking and multiscale light coupling (see [4] and refs. therein).

Actually, the possibility of creating optical negative index metamaterials (NIM) and espilon-near-zero (ENZ) materials using nanostructured metal-dielectric composites has triggered intense basic and applied researches over the past several years [5, 6]. Much efforts are dedicated to the engineering and extension of the functionalities of materials at optical frequencies, specially to design NIM or ENZ in the visible range of electromagnetic spectrum (see for example refs. [2, 5, 7]). Most of these attempts take advantage of plasmonic behaviour of noble metals such as silver and gold in addition to dielectric bulk materials to design arrays of NIM thin films composite materials. In this context, a suitable design of metal-based composite requires both positive and negative permitivities to compensate the lossy behaviours of many systems [8, 9]. With the emergence of quantum dots (QDs), silver coated core-shell nanocrystals (NCs) have been also employed to compensate the gain emission of QDs [10] and to obtain a negative-refractive index material. Webb et al. [3] and Fu et al. [11] later on, have proposed semiconductor QDs mixture as a lossless negative dielectric constant optical material. Recently, we theoretically investigated optical properties of II-VI core-shells distribution mixtures made of two type-I sized nanoshells as a plausible negative dielectric function material [12].

In addition to metal–dielectric composites and QDs-based negative materials, well established active ferroelectric materials; such as lithium tantalate ($LiTaO_3$) or lithium niobate ($LiNbO_3$) have recovered a great interest in plasmonic nanostructures, and are subject of a considerable amount of study due to its important role in several fields such as integrated optical technologies or non–linear optics. Indeed, Yannopapas and Paspalakis [13] have designed a multilayered metamaterial consisting of alternating planes of the ferroelectric $LiTaO_3$ and n–type germanium (Ge) spheres in air. This metamaterial has a negative refractive index and, at the same time, the electromagnetic radiation propagates with a group velocity that is of the order of 10^5 slower than the vacuum one. Furthermore, Yraola et al. [14, 15] have proved that Nd^{3+}–doped periodically poled $LiNbO_3$ shows a spontaneous emission and nonlinear response enhancement by Ag nanoparticles inclusion. The above authors claim that this composite could be a plausible metameterial with a plenty of applications in non–linear optics among others.

In the search of NIM's having both negative ϵ and μ values, specific physical and geometrical conditions play a key–role in controlling the values of permittivity and permeability [8]. In this paper, we focus in materials whose dielectric constant may reach negative values for specific conditions. We show that a $LiNbO_3 - Ag$ composite can exhibit NE characteristics in the visible range of electromagnetic spectrum, after a good control of both the Ag-metallic nanoparticles densities and sizes. This could open a new route to finding and designing negative dielectric materials out of the

commonly used periodic systems.

In the present study, the effective dielectric function of the composite is evaluated by using the Maxwell–Garnett effective theory. Such model is appropriate when the NPs concentration is small enough, so that the composite may be considered as a dilute environment. From the composite´s effective dielectric function, we study the compositional and geometrical parameters which could satisfy the negative epsilon condition.

The rest of paper is organized as follows. In section 2, the Drude–Lorentz theory for the Ag NPs and the Maxwell-Garnett theory for the composite are described. The implementation of the model in the composite $LiNbO_3$ with Ag NPs along with a discussion of the results are given in section 3. The main remarks and conclusion of this work will be given in section 4.

2. Theoretical model

The system under investigation is a composite constituted by the $LiNbO_3$ material, considered as an embedding medium, with inclusions of Ag NPs of nanometric size randomly distributed in the matrix. To evaluate its effective dielectric function (ϵ_{eff}), we proceed first by defining the dielectric functions of each composite´s component. For $LiNbO_3$, as a first approach, we use for the average dielectric function the relationship $\epsilon_e = n_{av}^2$, where

$$n_{av} = \frac{2n_o + n_e}{3} \tag{1}$$

being n_o and n_e the ordinary and extraordinary refractive indexes, respectively, which are defined by means of the well known Sellmeier equations as functions of the wavelength of the incident light [16]. In the range of 400 nm-700 nm, outside the absorption-edge of $LiNbO_3$, the difference between the ordinary and extraordinary indexes is so small (i.e., less than 4 per cent) that the above average refractive index could be considered as a good approximation. In this study, we choose a wavelength value of 450 nm yielding an ϵ_e around 5.5.

For the Ag NPs, we use the Drude theory of free electrons with the addition of one Lorentz oscillator term in order to take into account the interband electronic transitions which typically occur in noble metals. Also, we consider the NP size effect in the plasmonic damping term; then the Ag NPs permittivity is written as [17]

$$\epsilon_{Ag} = 1 - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma} + \frac{g\omega_L^2}{\omega_L^2 - \omega^2 - i\Gamma_L\omega}. \tag{2}$$

In the above eq., ω_p and Γ are, respectively, the Ag plasma frequency ($\omega_p = 9.17\ eV$) and its size-dependent damping term defined by $\Gamma = \gamma + Av_F/R$, being γ the bulk damping term ($\gamma = 0.021\ eV$), $A = 1$, v_F, the Ag Fermi velocity ($v_F = 1.39 \times 10^8 cm/s$) and R the radius of the Ag NPs; while the values of the parameters related to the Lorentz oscillator term are $g = 2.2$, $\omega_L = 5.27\ eV$ and $\Gamma_L = 1.14\ eV$, respectively [17]. Therefore, with the definition of the size-dependent term in the damping parameter one includes details of the scattering process of the electrons with the particle surface. We assume a value of $A = 1$ which is similar to the case of Ag particles in a matrix Al_2O_3 [17, 18].

Once the dielectric functions of the matrix and the Ag NPs are defined, we apply the

Maxwell-Garnett effective theory to describe the (ϵ_{eff}) of the composite, assuming two hypothesis: i) the radiation wavelength is much greater than the nanoparticle radius and ii) the volume fraction of Ag NPs, f, is very small [19]; then we have,

$$\frac{\epsilon_{eff}-\epsilon_e}{\epsilon_{eff}+2\epsilon_e}=f\frac{\epsilon_{Ag}-\epsilon_e}{\epsilon_{Ag}+2\epsilon_e}=fQ. \tag{3}$$

By solving the above equation, we obtain the following composite´s dielectric function, that is

$$\epsilon_{eff}=\frac{\epsilon_e(1+2fQ)}{1-fQ}. \tag{4}$$

It follows from eq. 4 that Q is also a complex frequency-dependent parameter with its corresponding real and imaginary parts. In general, low loss and negative epsilon conditions in the investigated composites are met when $\epsilon''_{eff}\approx 0$ and $\epsilon'_{eff}<0$ at given frequencies. From mathematical standpoint, imposing low loss or negative epsilon conditions is equivalent to finding structural parameters for which the Q-parameter fulfills the above criteria.

From eq. 4, we find that such conditions for negative epsilon material can be reached for two specific cases: i) $Q'>1/f$ or ii) $Q'<-1/2f$, in an extremely low limit when Q'' becomes vanishingly small (i.e. $Q''\to 0$). Indeed, for a given value of the volume fraction, the above conditions over Q' are satisfied for some critical sizes of Ag NPs in a specific range of ω. As the second condition (i.e. $Q'<-1/2f$) represents the lower limit for Ag NPs radius in order to achieve the NE condition, hereafter, we will consider such condition as that of physical meaning over all the work. These features will be discussed in section 3 with more details. Once again, according to the definition of Q in eq. (3), the negative epsilon condition can be explicitly expressed as a function of volume fraction, embedding medium dielectric constant and frequency-dependent dielectric functions of Ag NPs. That is;

$$\epsilon_e(f+2)/(f-1)<\epsilon'_{Ag}<\epsilon_e(2f-2)/(2f+1). \tag{5}$$

With the above considerations, we obtain a range of frequencies where the negative epsilon condition is satisfied for specific values of f and R. This interval is similar to that previously reported in the literature for a distribution of nanoshells embedded in an homogeneous medium [20]. On the other hand, we investigate the Fröhlich condition for spherical NPs; i.e., the solution of equation $\epsilon'_{Ag}=-2\epsilon_e$.

Finally, in order to investigate the optical properties of the composite as a function of their structural parameters, the extinction coefficient is calculated following the ref. [21] from the real and imaginary parts of ϵ_{eff}; i.e.,

$$\alpha(cm^{-1})=\frac{8.88\times 10^7}{\lambda(nm)}\sqrt{-\epsilon'_{eff}+\sqrt{(\epsilon'_{eff})^2+(\epsilon''_{eff})^2}} \tag{6}$$

where λ, the wavelength of the incident light, is given in nanometers.

3. Results and discussion

Within the Drude–Lorentz model, we will seek at the solutions which satisfy the negative epsilon condition using Maxwell-Garnett theory in dilute environment. In eq. 4 we show that for a given volume fraction, $Q'<-1/2f$ defines a critical–sizes

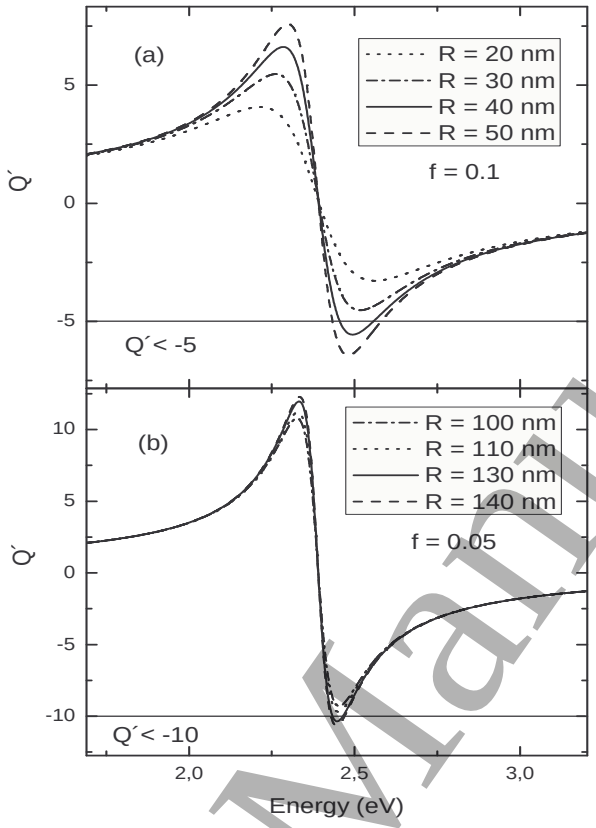

Figure 1. *Real part of the term Q as a function of energy for f = 0.1 (a) and f = 0.05 (b) with different radii. The reference lines at Q'=-5 (a) and Q'=-10 (b) define the critical region where the negative epsilon condition is satisfied. That limits are related to critical sizes of Ag NPs in the composite for any given volume fraction.*

region of Ag NPs that satisfies NE conditions. To illustrate this feature, we show in figure 1, Q' as a function of energy for $f = 0.1$ and $f = 0.05$ with different values of radii. In fact, from figure 1 (a) we find that the condition $Q' < -1/2f$; i.e., $Q' < -5$ for $f = 0.1$, is satisfied when $R \geq 40\ nm$ (see the reference line in the figure); while for $f = 0.05$, that condition (with $Q' < -10$), is satisfied when $R \geq 130\ nm$ (see figure 1 (b) with the base line). Then, we can conclude that the increase of the volume fraction entails a reduction of the critical size of Ag NPs in order to get the negative epsilon condition.

The expansion of ϵ'_{Ag} in terms of ω yields a six-order polynomial for specific values of f and R. By imposing $\epsilon'_{Ag} < \epsilon_e(2f-2)/(2f+1)$, we obtain only one solution with physical meaning; i.e., an unique real positive value of energy. The condition $\epsilon'_{Ag} > \epsilon_e(f+2)/(f-1)$ yields also to an unique real solution. Thus, the imposed restrictions lead to both lower- and upper-energy limits where the negative epsilon condition is satisfied for specific structural parameters of the composite; i.e., volume fraction and Ag NPs size. Hereafter, this energy range will be called NE range. To illustrate the above discussion, we plot in figure 2 the composite dielectric response

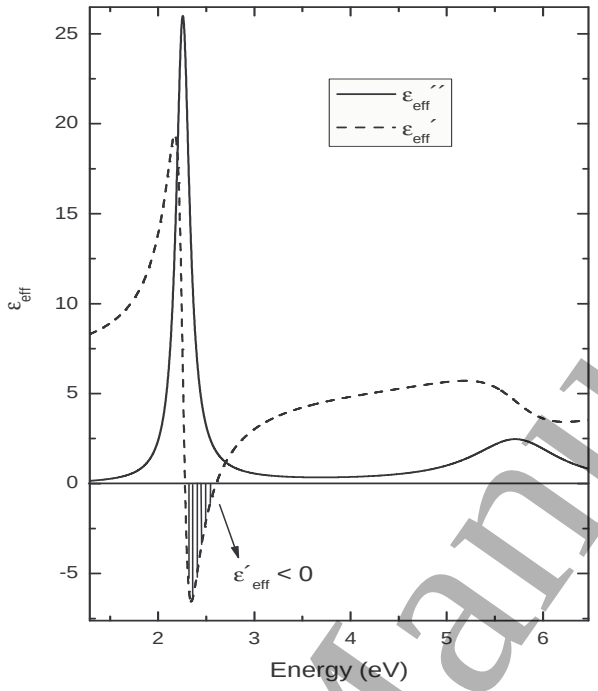

Figure 2. *Effective dielectric function of the composite $LiNbO_3$ with Ag NPs as a function of energy. The volume fraction is $f = 0.1$ and the radius of Ag NPs is $R = 50$ nm. The zero-reference line and the shaded area mark out the NE range.*

for $f = 0.1$ and $R = 50\ nm$. We obtain that the NE range is between 2.30 eV and 2.59 eV, values which are the solutions of the above six-order polynomials. The reference line at zero along with the shaded area is to mark out the NE condition (see figure 2). Besides, in the interval 3.3 eV - 4.5 eV, the loss is very low, where $\epsilon''_{eff} \approx 0$.

In order to investigate the NE range dependence with the structural parameters, we show in figure 3 the real part of the composite dielectric response for $f = 0.1$ and $R = 40\ nm$, 50 nm and 60 nm. We obtain that the NE range is slightly enlarged for increasing sizes (see inset of figure 3). However, for decreasing values of f, the NE range becomes narrower. To evidence this fact, figure 4 shows the composite dielectric response for $f = 0.05$ and $R = 130\ nm$, where the NE range is between 2.34 eV and 2.50 eV. The base line at zero and the shaded area mark out the NE condition (see details in figure 4). Besides, the interval 3.1 eV - 4.8 eV defines a very low loss regime. To summarize, at given values of volume fraction correspond critical NP–sizes at which the NE conditions take place. The higher the volume fraction (e.g. f = 0.1), the smaller the NPs critical sizes to produce negative epsilon conditions in $LiNbO_3 - Ag$ composite. At the same time, the peak-intensity increases with NP–radius for each investigated volume fraction.

On the other hand, single noble metal NPs strongly interact with visible light when is resonantly excited at their surface plasmon frequency. Such resonant behavior is due to the confinement of the conduction electrons inside the particle which set up an

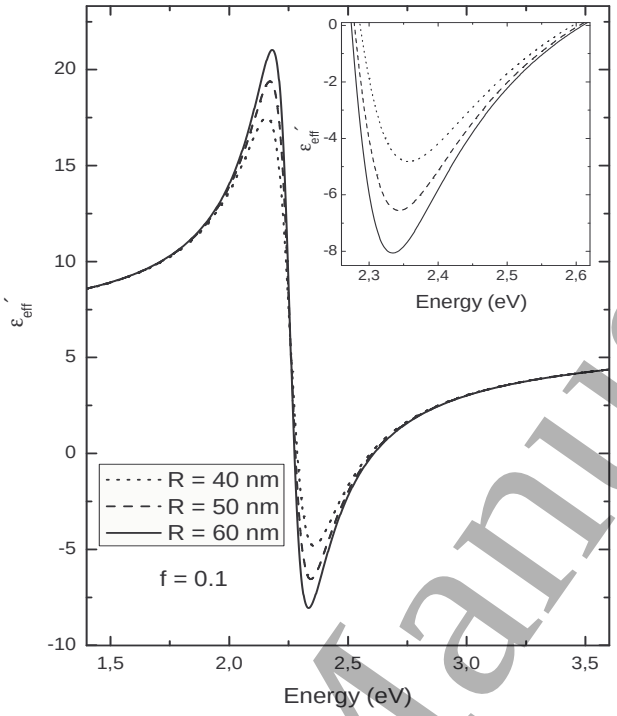

Figure 3. *Real part of the composite effective dielectric function for $f = 0.1$ and $R = 40\ nm$, $50\ nm$ and $60\ nm$, where the NE range is shown with details in the inset.*

effective restoring force due to surface polarization upon a light–induced displacement of the conduction electrons. For spherical NPs, the resonance occurs when the Fröhlich condition $\epsilon'_{Ag} = -2\epsilon_e$ is met, where the polarizability of the NP shows a resonant enhancement. The expansion of this condition yields a six–order polynomial in frequency with an only one solution with physical meaning. The Fröhlich frequency depends on the Ag NPs size and the permittivity of the embedding medium. Besides, this value is nearly close to the lower limit of the NE range. Figure 5 shows the Fröhlich frequency as a function of the Ag NPs size, where a slight dependence on the radius is obtained. Indeed, the Fröhlich energy is 2.38 eV for a composite with $R = 50\ nm$ and 2.39 eV for $R = 130\ nm$.

Finally, we will analyze the extinction dependence on the size of Ag NPs when the NE condition is fulfilled. We define extinction as the extinction coefficient multiplied by the NP size as in ref. [22]. Figure 6 shows the composite extinction for three radii of Ag NPs with equal value of $f = 0.1$. We obtain two symmetric bands peaked around 2.3 eV and 5.8 eV, respectively. The first band can be ascribed to the surface plasmon resonance of Ag NPs, while the second can be attributed to the interband electronic transitions. The extinction intensity increase with the radius, while the Full Width at Half Maximum (FWHM) seem to be size-independent. Then, we can conclude that the extinction of the composite is dependent on the radius of the Ag NPs embedded in lithium niobate.

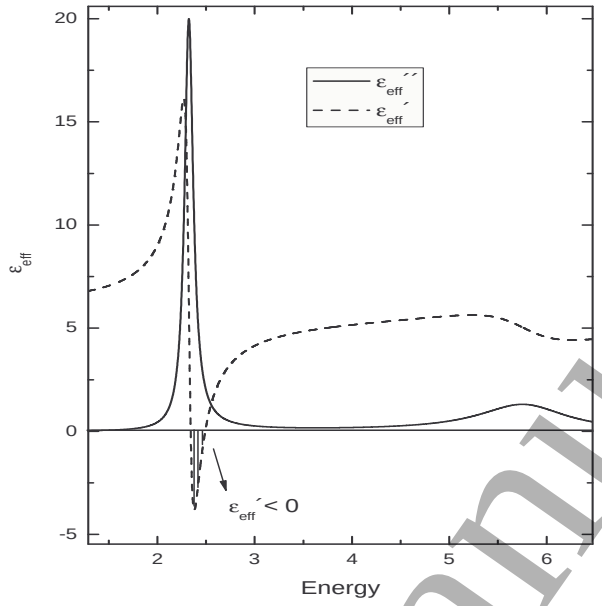

Figure 4. *Effective dielectric function of the composite $LiNbO_3$ with Ag NPs as a function of energy. The volume fraction is $f = 0.05$ and the radius of Ag NPs is $R = 130$ nm. The reference line at zero and the shaded area is to mark out the NE range.*

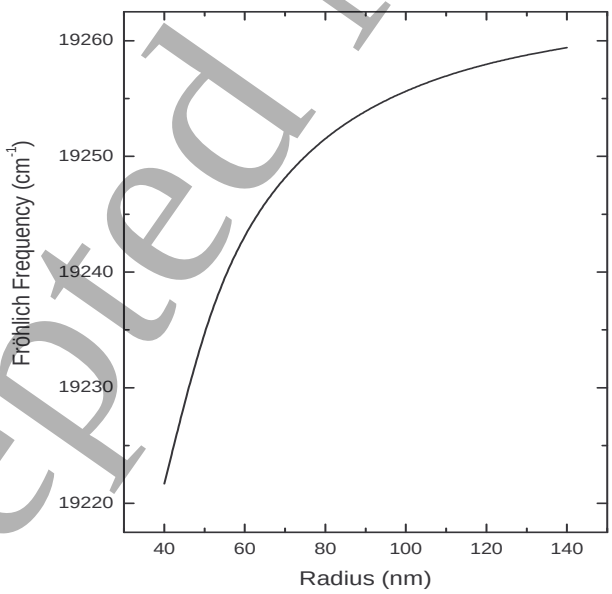

Figure 5. *Fröhlich frequency of the $LiNbO_3$ composite as a function of Ag NPs radius.*

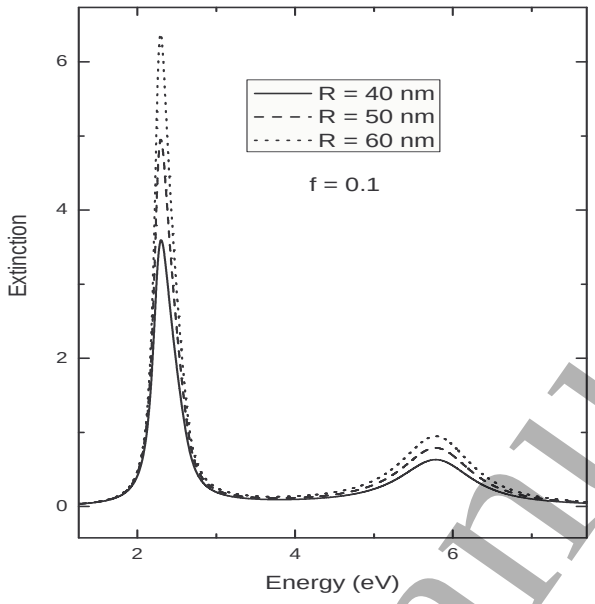

Figure 6. *Extinction of the composite $LiNbO_3$ with Ag NPs versus energy for different radii R = 40 nm, 50 nm, 60 nm and equal volume fraction f = 0.1. For these values, the NE condition is fulfilled.*

4. Conclusions

We theoretically proposed a plausible negative epsilon composite by including Ag NPs in the lithium niobate as an embedding material. We evaluated the effective dielectric function of this composite by the Maxwell-Garnett effective theory. To describe the Ag NPs dielectric function, we use the Drude–Lorentz model to take into account the interband electronic transitions, typical in noble metals. For the description of $LiNbO_3$ dielectric function, we use the Sellmeier equations. We showed that the negative epsilon condition is satisfied from a critical size of Ag NPs when the volumen fraction is given. This condition defines an interval of energies, called NE range, characterized for specific structural parameters; i.e., f and R. In fact, the NE range enlarges for increasing radius and becames narrower for decreasing volume fractions. Furthermore, the Fröhlich frequency is nearly close to the lower–energy limit of the NE range. Finally, the extinction of the composite depends on the radius of Ag NPs embedded in lithium nobiate.

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References

[1] S. Xiao, V.P. Drachev, A.V. Kildishev, X. Ni U.K. Chettiar, H.K. Yuan and V.M. Shalaev, Nature **466** (2010) 9278.

[2] M.I. Stockman, Optics Express **19** (2011) 22029.
[3] K.J. Webb and A. Ludwig, Phys. Rev. B **78** (2008) 153303.
[4] R. J. Pollard, A. Murphy, W.R. Hendren, P.R. Evans, R. Atkinson, G.A. Wurtz, A.V. Zayats and V.A. Podolskiy, Phys. Rev. Lett. **102** (2009) 127405.
[5] C.M. Soukoulis, S. Linden and M. Wegener, Science **315** (2007) 47.
[6] V.M. Shalaev and F. Traeger, Appl. Phys. B **84** (2006) 1.
[7] G. Dolling, M. Wegener, C.M. Soukoulis and S. Linden, Opt. Lett. **32** (2007) 53.
[8] A. Boardman, V.V. Grimalsky, Y.S. Kivshar, S.V. Koshevaya, M. lapine, N.M.Litchinitser, V.N. Malnev, M. Noginov, Y.G. Rapoport and V.M. Shalaev, Laser Photonics Rev. (2010) 1.
[9] X. Ni, S. Ishii, M.D. Thoreson, V.M. Shalaev, S. Han, S. lee and A.V. Kildishev, Optics Express **19** (2011) 25242.
[10] X. Meng, A.V. Kildishev, K. Fujita, K. Tanaka and V.M. Shalaev, Nano Lett. **13** (2013) 4106.
[11] Y. Fu, L. Thylén and H. Agren, Nano Lett. **8** (2008) 1551.
[12] R.M. de la Cruz and C. Kanyinda-Malu, Physica E **63** (2014) 229.
[13] V. Yannopapas and E. Paspalakis, J. Opt. **12** (2010) 104017.
[14] E. Yraola, P. Molina, J.L. Plaza, M.O. Ramírez and L.E. Bausá, Adv. Materials, doi:10.1002/adma.201203176 (2012).
[15] P. Molina, E. Yraola, M.O. Ramírez, J.L. Plaza, C. Heras and L.E. Bausá, Nano Lett. **13** (2013) 4931.
[16] C.A. Morrison and R.P. Leavitt in *Handbook of the Physics and Chemistry of Rare Earths*, ed. by K.A. Geschneider Jr. and L. Eying, North Holland, New York 1982, Vol. 5, Cap. 46, p. 461.
[17] V.P. Drachev, U.K. Chettiar, A.V. Lidishev, H.K. Yuan, W. Cai and V.M. Shalaev, Optics Express **16** (2008) 1186.
[18] A. Hilger, M. Tenfelde and U. Kreibig, Appl. Phys. B **73** (2001) 361.
[19] U. Woggon in *Optical properties of semiconductor quantum dots* (Springer, Berlin, 1996).
[20] Y. Zeng, Q. Wu and D.H. Werner, arXiv:1002.3382v1 [physics.optics] (2010).
[21] M.A. Garcia, J. Phys. D: Appl. Phys. **44** (2011) 28301.
[22] R.M. de la Cruz, C. Kanyinda-Malu and P. Rodríguez, Physica E **44** (2012) 1868.