DIELECTRIC RESPONSE IN AN ORDERED RECTANGULAR ARRAY OF Ag NANOPARTICLES ON $LiNbO_3$

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Abstract

An ordered array of silver (Ag) nanoparticles (NPs) on the uniaxial $LiNbO_3$ material is theoretically analyzed under an extended Maxwell-Garnett (M-G) effective approximation to account on the anisotropic effects. Structural parameters such as NPs radius and interparticle distances in the array play a key-role in the evaluation of the dielectric response in both parallel and perpendicular directions. In fact, the negative epsilon (NE) condition is satisfied for specific values of the above parameters. This condition defines an interval of energies, called NE range. We compare these results to that obtained for a random distribution of Ag NPs embedded in $LiNbO_3$ matrix.

Keywords: Ferroelectric materials, metallic nanoparticles, extended Maxwell-Garnett theory

1. INTRODUCTION

Recently, some authors have shown the interest in combining the optical response of metallic nanostructures with the optically active ferroelectric materials. Indeed, Yraola et al. [1] and Molina et al. [2] have demonstrated that Nd^{3+}-doped periodically poled $LiNbO_3$ shows a spontaneous emission and nonlinear response enhancement by Ag nanoparticles inclusion. Also, these authors claim that this composite could be a plausible metamaterial with a plenty of applications in non-linear optics among others. In the search of negative index metamaterials (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. In our previous work, we show that a random distribution of Ag NPs embedded in $LiNbO_3$ matrix can exhibit negative epsilon condition in the visible range of electromagnetic spectrum, after a good control of both the Ag-metallic nanoparticles densities and sizes [3].

In this work, we generalize the research in the $LiNbO_3$-Ag composite to an ordered rectangular array of Ag NPs on $LiNbO_3$ matrix, system which is quite similar to the experimentally-grown periodical poled $LiNbO_3$ with Ag NPs inclusions [1]. We show that the array of Ag NPs on $LiNbO_3$ matrix can exhibit NE characteristics in the visible-ultraviolet range of electromagnetic spectrum, when a good control of the Ag-metallic nanoparticles densities and sizes along with the appropriate interparticle distances in the rectangular array is done.

2. THEORETICAL MODEL

We investigate an ordered system of identical spherical Ag NPs that occupy all lattice sites of a two-dimensional (2D) rectangular array. This rectangular array has characteristic interparticle distances *a* and *b* for the longitudinal and transversal directions, respectively. The scheme of the system is depicted in **Figure 1**, where the NPs have radius *R* and they are on the uniaxial $LiNbO_3$ material. Besides, the $LiNbO_3$ extraordinary axis coincides with the longitudinal direction, while its ordinary axis coincides with the transversal direction of this lattice.

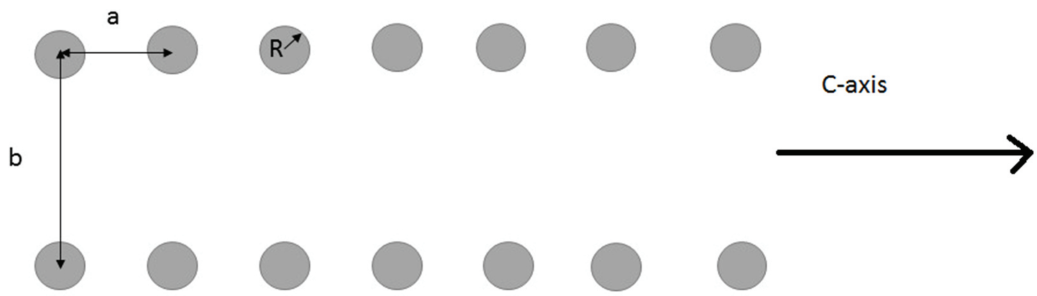

Figure 1 Scheme of the ordered rectangular array of Ag NPs on an uniaxial $LiNbO_3$ matrix

As it is well known, the Maxwell-Garnett (M-G) model can be used to describe the effective dielectric function of a medium composed of metallic nanoparticles embedded in a dielectric medium. In fact, when the particles are randomly distributed in a three-dimensional (3D) system, the sum of dipoles contributing to the local field cancels out on average. The Drude model is used to describe the dielectric function of the metallic particles. For small filling factor, *f*, the surface plasmon resonance (SPR) condition is fulfilled at

$$\omega_{SPR} = \frac{\omega_p}{\sqrt{1+2\varepsilon_e}} \tag{1}$$

where ω_p is the plasma frequency of free electrons in the bulk metal. In our case, ε_e will be evaluated by means of the Selmeiller equations.

For particles distributed in a two-dimensional (2D) array, such as in thin films containing a layer with NPs, as our investigated system, the sum of dipolar electric fields does not cancel out anymore. Accordingly, one may expect dissimilar contributions to the local electric field in case the applied electric field is parallel or perpendicular to the longitudinal axis of the lattice, and this will result in anisotropic effective dielectric functions. Consequently, there will be two SPR conditions; i.e.,

$$\omega_{SPR,\parallel}^2 = \omega_{SPR}^2 \left(1 - \frac{9.03}{2}\left(\frac{R}{a}\right)^3\right); \tag{2}$$

$$\omega_{SPR,\perp}^2 = \omega_{SPR}^2 \left(1 + 9.03\left(\frac{R}{a}\right)^3\right) \tag{3}$$

where the factor 9.03 comes from the convergence of the series that parametrizes the lattice for the inverse cube sum [4]. Eqs. (2) and (3) are a generalization to take into account that our array is rectangular. On the other hand, this structure might not be expected to follow the dielectric function predicted by the M-G model due to the previously described anisotropy of the dipolar interaction with the electric field. Then, an extended M-G model, which accounts for both the plasmon resonance in each particle and the interaction of charges in close particles, should be considered [5]; i.e., the effective dielectric function of the rectangular lattice is given as

$$\varepsilon_{eff,j} = \varepsilon_e \left[1 + \frac{3f\left(\varepsilon_{i,j} - \varepsilon_e\right)}{\left(\varepsilon_{i,j} + 2\varepsilon_e\right) - f\left(\varepsilon_{i,j} - \varepsilon_e\right)}\right] \tag{4}$$

with

$$\varepsilon_{i,j}(\omega) = 1 + \frac{f_c\,\omega_p^2}{\left(j(-1)^j\omega_{c,j}^2 - \omega^2\right) - i\Gamma(R)\omega}, \quad j = 1,2. \tag{5}$$

In eqs. (4) and (5), *i* refers to the inclusion, *j* = 1 is for the electric field along the C-axis of the crystal, while *j* = 2 is for the perpendicular direction; f_c accounts for the oscillator strength, $\omega_{c,j}$ are the coupling frequencies as defined in ref. [6] in which the rest of constants are also described.

Finally, low loss and negative epsilon (NE) conditions in the investigated arrays are met when $\varepsilon''_{eff} \approx 0$ and $\varepsilon'_{eff} < 0$ at given frequencies. From mathematical standpoint, imposing low loss or negative epsilon conditions is equivalent to finding structural parameters for which the above criteria are fulfilled. Indeed, we obtain a range of frequencies where the NE condition is satisfied for specific values of *f, R*, *a* and *b*.

3. RESULTS AND DISCUSSION

We will obtain the effective dielectric function when the electric field is parallel or perpendicular to the longitudinal axis of our 2D array; i.e., along the extraordinary or ordinary axis of $LiNbO_3$, respectively. Hereafter, we will denote them $\varepsilon_{eff,||}$ and $\varepsilon_{eff,\perp}$, respectively. In order to clarify the presentation of our results, we show in separate subsections the dependences of $\varepsilon_{eff,||}$ and $\varepsilon_{eff,\perp}$, with the i) NPs radius and ii) the interparticle distances *a* and *b* of the rectangular array.

3.1. NPs radius effects on $\varepsilon_{eff,||}$ and $\varepsilon_{eff,\perp}$

Figure 2 depicts the real part of $\varepsilon_{eff,||}$ and $\varepsilon_{eff,\perp}$ for Ag NPs rectangular array with radii ranging between 5 nm and 40 nm, being R/a = 0.5, R/b = 0.25 and f = 0.1 for all investigated cases. We can observe the anisotropy effects on $\varepsilon_{eff,||}$ and $\varepsilon_{eff,\perp}$. Firstly, for the parallel direction, the resonances in both the real and the imaginary parts of ε_{eff} belong mainly to the near VIS spectrum range, while for perpendicular direction, the resonances in ε'_{eff} and ε''_{eff} belong mainly to the VIS-UV spectrum range. For the real part, we obtained the negative epsilon (NE) condition, $\varepsilon'_{eff,||} < 0$, from a critical value of 10 nm, while the condition, $\varepsilon'_{eff,\perp} < 0$, is obtained from a critical size of 15 nm.

If we compare these results with those previously reported in reference [3] for 3D randomly distributed Ag NPs in $LiNbO_3$, the NE condition is fulfilled for a radius smaller; i.e., for the 3D random distribution with the same f = 0.1, $\varepsilon'_{eff} < 0$ is satisfied from a critical value of 40 nm. This reduction of critical size for the rectangular array can be due to the interaction of charges in close particles, which entails a different behavior of the effective dielectric function. Besides, the array of Ag NPs is on an uniaxial $LiNbO_3$ surface and some volume of the Ag NPs are in contact with air. This feature is different from the case of a 3D random distribution where all NPs are embedded in $LiNbO_3$ matrix. On the other hand, the NE range (energy interval where NE condition is accomplished) is approximately between 0.74 eV and 1.80 eV for $\varepsilon'_{eff,||}$, while for $\varepsilon'_{eff,\perp}$ is approximately between 3.0 eV and 3.38 eV. Therefore, the NE range for $\varepsilon'_{eff,||}$, is broader than the relative to 3D random distribution with the same f = 0.1. For $\varepsilon'_{eff,\perp}$, this range has approximately equal width to that of 3D random distribution (compare **Figure 2** with results of reference [3]). Besides, we obtain that $\omega_{SPR,||}$ = 1.79 eV, value which is close to the upper-energy limit of the NE range of $\varepsilon'_{eff,||}$, while $\omega_{SPR,\perp}$ = 2.79 eV is out of the NE range of $\varepsilon'_{eff,\perp}$. Therefore, the above features characterize the anisotropy between $\varepsilon'_{eff,||}$ and $\varepsilon'_{eff,\perp}$. Conversely, the NE range is slightly enlarged for increasing radii in both $\varepsilon'_{eff,||}$ and $\varepsilon'_{eff,\perp}$, characteristic which is similar to that obtained for 3D random distribution of Ag NPs [3].

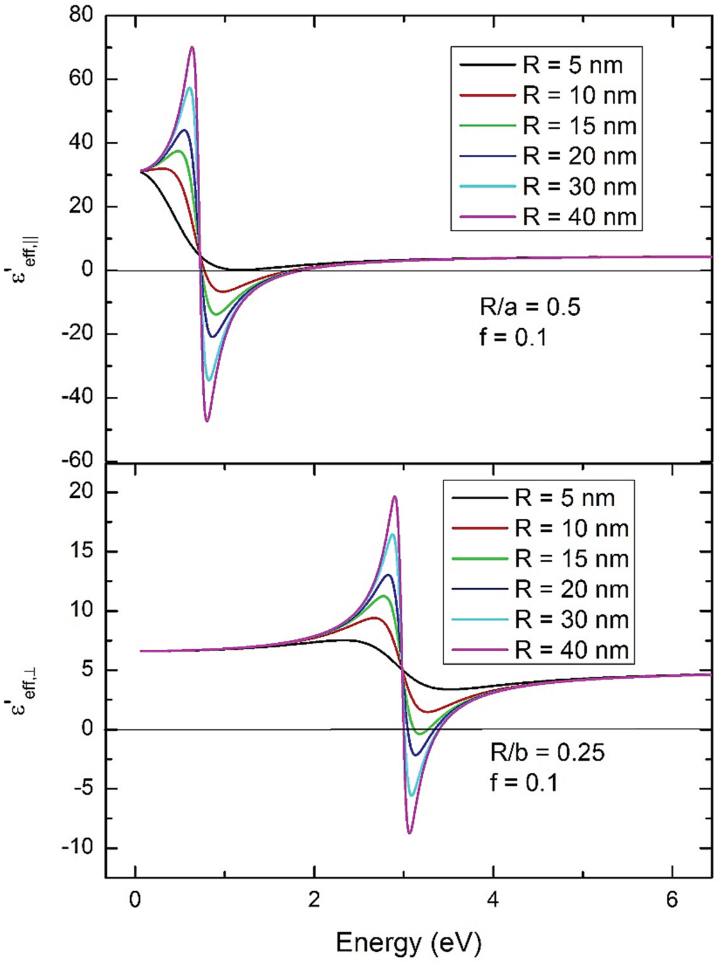

Figure 2 Real parts of $\varepsilon_{ff,||}$ and $\varepsilon_{eff,\perp}$ of the array. The filling factor is f = 0.1 and R/a = 0.5, while R/b = 0.25 for all investigated cases. The zero-reference line mark out the NE range

Although it is not shown here, for the imaginary part, the resonance of $\varepsilon''_{eff,||}$ peaks between 0.51 eV to 0.72 eV for increasing radii, while the resonance of $\varepsilon''_{eff,\perp}$ peaks between 2.93 eV to 2.98 eV. For both peaks, their FWHM are narrower with increasing radii, where the energy range characterized by $\varepsilon''_{eff} \approx 0$ is greater. On the other hand, the dependence of $\varepsilon''_{eff,||}$ and $\varepsilon''_{eff,\perp}$ with the energy is similar to that reported in reference [3] for 3D random distribution of Ag NPs in $LiNbO_3$ matrix.

3.2. Effects of the rectangular array interparticle distances on $\varepsilon_{eff,||}$ and $\varepsilon_{eff,\perp}$

We show in **Figure 3** the real part of $\varepsilon_{eff,||}$ and $\varepsilon_{eff,\perp}$ for Ag NPs rectangular arrays with R = 15 nm, f = 0.1, where the parallel interparticle distance *a* ranges between 30 nm to 90 nm and the perpendicular distance *b* ranges between 45 nm to 90 nm. We choose this radius and filling factor values in order to be sure that the NE condition is satisfied in both directions. For the parallel direction, the resonances belong mainly to the near-VIS spectrum of the system ranging between 1 eV to 2.3 eV; while for perpendicular direction, the resonances belong mainly to the VIS-UV spectrum ranging between 2 eV to 4 eV. We have for $\varepsilon'_{eff,||}$, that the NE condition is fulfilled for all *a* values investigated and it is characterized by the following features: i) The NE range is narrower for increasing *a* distances, where its width seems to have a limit value when the interparticle distance *a* is great enough; i.e., *a* = 90 nm; ii) The NE range is blue-shifted for increasing *a* values, where the shift seems reach a limit for great enough *a* values; iii) The $\omega_{SPR,||}$ value is out of the NE range for *a* values lower than 45 nm, while for higher values, the $\omega_{SPR,||}$ belongs to the NE range. Attending to $\varepsilon'_{eff,\perp}$ we obtain that the NE condition is fulfilled for interparticle distances higher than *b* = 60 nm that can be considered as a critical distance. We also notice that the NE range become broader until to get a saturation value for *b* = 90 nm. Besides, for greater *b* values, the NE condition is red-shifted, conversely to the already commented parallel case.

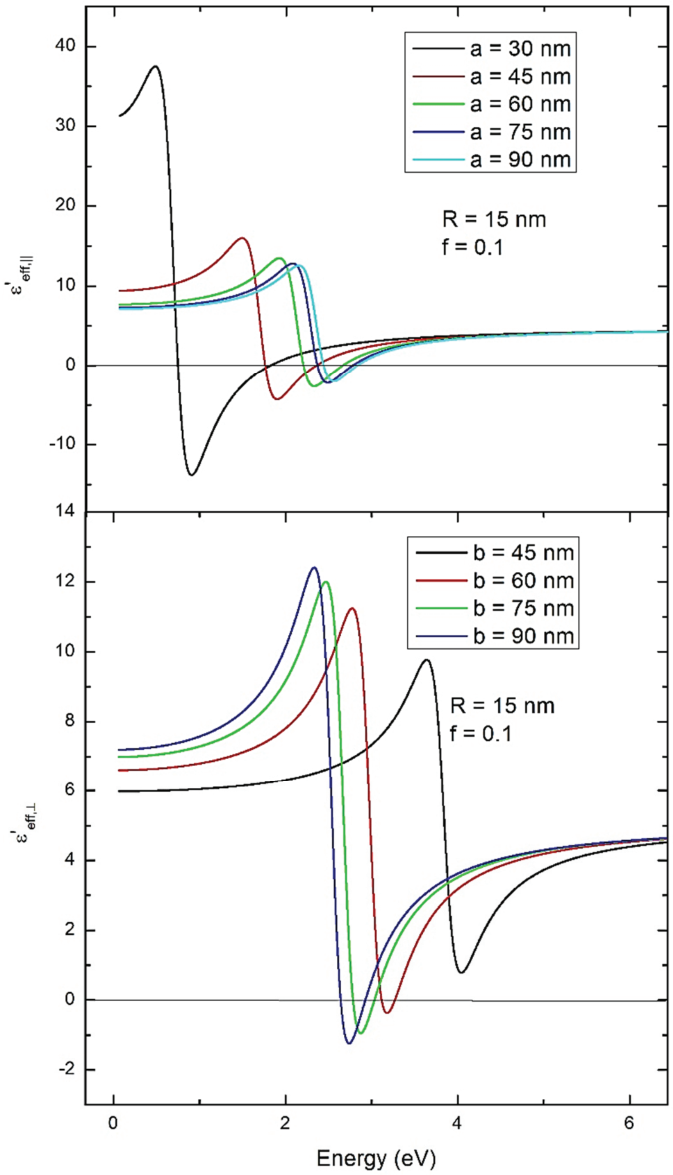

Figure 3 Real parts of $\varepsilon_{eff,||}$ and $\varepsilon_{eff,\perp}$ of the array. The filling factor is f = 0.1 and R=15 nm for different interparticle distances *a* and *b* for all investigated cases. The zero-reference line mark out the NE range

Although it is not shown here, for the imaginary part, the resonance of $\varepsilon''_{eff,||}$ peaks between 0.5 eV to 2.3 eV for increasing interparticle distances, while the resonance of $\varepsilon''_{eff,\perp}$ peaks between 2.2 eV to 4.0 eV. In both cases, their FWHM are mainly independent of *a* or *b* distances. The range where the lossless condition is fulfilled is wide. This characteristic could improve the performance of photoelectronic devices. Finally, the dependence of $\varepsilon''_{eff,||}$ and $\varepsilon''_{eff,\perp}$ with the energy is similar to that reported in reference [3] for 3D random distribution of Ag NPs in uniaxial $LiNbO_3$ matrix.

4. CONCLUSION

We have evaluated the effective dielectric function of an ordered rectangular array of Ag NPs on $LiNbO_3$ matrix along the parallel and perpendicular directions to the crystal's C-axis. For this purpose, we used an extended Maxwell-Garnett effective theory to take into account the anisotropy of the dipolar interaction with the electric field. The effects of NPs radius and rectangular array interparticles distances on the dielectric response were analyzed. Our results show that the negative epsilon condition is satisfied from a critical size of Ag NPs when the filling factor and the interparticles distances (*a* and *b*) have particular values. This condition defines an interval of energies, called NE range, characterized for specific structural parameters. In fact, the NE range enlarges for increasing radius, characteristic which is similar to that obtained for 3D random distribution of Ag NPs embedded in $LiNbO_3$. On the other hand, the NE range width seems to have a limit value when the interparticle distances, *a* and *b*, are great enough. Besides, for greater *b* values, the NE range is red-shifted, conversely to the parallel case, where for greater *a* values the NE range is blue-shifted. Finally, we obtain that the surface plasmon resonance frequencies along the C-axis and perpendicular directions belong to the NE range for particular values of the structural parameters.

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