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Absorption in Metamaterials: Turning Loss into Gain

INTRODUCTION

Nature has often served as inspiration for engineers. The setae of gecko feet are mimicked for climbing robots, the vivid coats of butterflies and peacocks motivate research in structural colors, and the streamline shapes of certain species of fish are imitated in automobile design to reduce drag. Sometimes, however, nature specifies rules of design that beg to be superseded in order to realize new technologies. In all known naturally occurring media, for example, light propagates according to the right-hand rule and obeys Snell's Law, given by:

$$\theta_t = \sin^{-1} \left(\frac{n_i}{n_t} * \sin \theta_i \right) \tag{1}$$

where

$$n_i = \sqrt{\varepsilon_i \mu_i} \tag{2}$$

and n_i is the index of refraction, θ_i and θ_t are the angles with respect to the surface normal of incidence and transmission, respectively, at the interface of two materials, and ε and μ are the electrical permittivity and magnetic permeability of a material, respectively. That natural materials follow the right-hand rule implies a positive index of refraction, which means that either or both ε and μ are positive. Although negative values of permittivity occur in nature (particularly in metals at frequencies below the plasma frequency), negative permeability has not been observed.

What if it were possible for a material to possess simultaneously negative values for permittivity and permeability? Russian physicist Victor Veselago was one of the first to study this question in detail, and he arrived at some mind-bending conclusions: simultaneously negative permeability and permittivity would entail a negative index of refraction, and a negative index would flip the angle of refraction to the opposite side of the normal (and yield a reverse of the Doppler shift, among other odd effects) (1). Materials with negative indices of refraction came to be included under the broader category of "metamaterials." Metamaterials define man-made structures fabricated with artificial periodicity designed to respond to and manipulate incident electromagnetic radiation.

Perhaps the most common and sought-after application of metamaterials is the ability to focus electromagnetic waves with better resolution than conventional optics (2). This application requires metamaterials that have a negative index of refraction. Metamaterials may also be used to enhance absorption, and that subject will also be covered in this article with the motivation of exploring the potential application of metamaterials to solar photovoltaics. First, we begin with a review of the recent developments in metamaterials and the basics of their design and operation.

PENDRY AND NEGATIVE REFRACTION

After Veselago made his predictions in 1968 about the physical ramifications of systems with simultaneously negative permittivity and permeability, the problem of producing such a material would not be solved for more than thirty years. In the intervening period, important discoveries were made in research into plasmonics and photonic crystals that preceded the advent of metamaterials. Both of these phenomena involve the coupling between light and matter, typically matter that has a structure that is on the order of the wavelength or smaller than the incident radiation. For example, nanoscopic metal particles were found to support surface plasmons – collective oscillations of electrons – when excited by radiation of a certain frequency (*3*). These surface plasmons were associated with a negative dielectric constant and the ability to localize light and helped guide researchers seeking to better manipulate light at short wavelengths. Another important step in the development was the fabrication of organized periodic structures that act as an effective medium but with a much larger period than the atomic lengths of bulk material. In 1999, Smith et. al introduced such an artificial periodic structure that yielded surface plasmon-like effects but consisted of square

loops of wire with dimensions and spacing that were on the scale of millimeters. Even though the components of this array consisted of materials with bulk values of permittivity that were positive, the loop geometry arranged periodically resulted in an effective dielectric constant that was negative for the whole structure at microwave frequencies (~10 GHz) (4). Yet even in these periodic macro- or nanostructured materials, electromagnetic radiation was still understood to obey the right-hand rule.

It was in 1999 that J. B. Pendry from Imperial College made the leap that jumpstarted the field of metamaterials with an article describing how materials that exhibit a negative magnetic permeability can be constructed from non-magnetic materials (5). For the first time, a tractable approach to the design of a material with simultaneously negative permittivity and permeability existed. Pendry's great insight was that permittivity and permeability are just averaged representations of the electromagnetic response of a medium, even though the medium is composed of discrete atoms that each has an individual response to incident light. His concept was to fabricate a periodic structure that would act as an artificial crystal lattice and thereby produce an effective electromagnetic response different from that of the bulk material.

Not just any ordered, sub-wavelength structure yields a negative effective permeability and permittivity. The critical properties of the constituent units in a metamaterial lattice are capacitive and/or inductive elements. When electromagnetic radiation of the proper frequency excites this capacitive or inductive response, a magnetic field develops that counters the magnetic field of the incident radiation and yields an effective negative permeability for the entire medium. For example, two thin metal sheets can be wound and nested inside one another to form a split ring configuration, one of the most elementary metamaterial structures. When the fluctuating magnetic field of an electromagnetic wave is oriented parallel to the cylinder length, current is induced in each split ring element and capacitance develops in the gap between the outer sheet and inner sheet. This capacitance leads to an effective permeability (μ_{eff}) that is given by (5):

$$\mu_{eff} = 1 - \frac{\frac{\pi r^2}{a^2}}{1 + \frac{i2\sigma}{\omega r \mu_0} - \frac{3}{\pi^2 \mu_0 \omega^2 C r^3}} = 1 - \frac{\frac{\pi r^2}{a^2}}{1 + \frac{i2\sigma}{\omega r \mu_0} - \frac{3dc_0^2}{\pi^2 \omega^2 r^3}}$$
(3)

where r is the radius of the outer cylinder, a is the spacing between cylinders, σ is the bulk resistivity of the cylinder material, d is the spacing between the thin sheets, and C is the capacitance of the structure given by $C=\epsilon_0/d=1/dc_0^2\mu_0$. From this equation, it can be seen that a larger value of capacitance leads to a smaller denominator in the fraction and thus a decreasing effective permeability. With the ability to produce a material with an effective negative magnetic permeability, the next step to producing a negative index of refraction material is to design one that has negative permeability and permittivity in the same frequency range.

Early efforts to produce a material with an effective negative index of refraction succeeded by using two distinctly different structures arranged periodically to simultaneously yield a negative permittivity and permeability. In 2001, Shelby et. al reported the first observation of a negative index metamaterial. The material consisted of a two-dimensional matrix of mm-scale split rings and copper strips which were designed to elicit negative magnetic permeability and a negative permittivity, respectively, over a similar frequency region *(6)*. The scale of the components yielded a negative index of refraction over a portion of the microwave spectrum.

Since Shelby et. al proved that an artificially periodic structure could allow a negative index of refraction, the drive has been to do so at ever higher frequencies. The frequency band over which a metamaterial has a negative index is in large part determined by the feature sizes and lattice constant of the metamaterial structure. As an illustration, in Figure 1 the effective magnetic permeability is plotted as a function of frequency for the nested split ring configuration described by Equation 3 for a range of ring sizes. As is evident even in this crude calculation, very small feature sizes (less than 1µm in the calculation, and in reality on the order of 100-300nm) are required to make a metamaterial that is active in the visible range.



Figure 1: Effective magnetic permeability for an array of nested split rings, where r is the outer radius of the rings. Using σ =1.55E-8 Ω -m for silver and lattice constant a=2.5*r

It would seem that producing metamaterials that are active at shorter wavelengths would just be a matter of scaling. Following this approach, researchers in 2005 demonstrated a negative index material consisting of a two-layer metal film stack with etched holes separated by a dielectric that, with feature sizes of 360µm and a lattice constant of 860µm, was active in the near-infrared at a frequency of 150GHz (7). Pushing the active frequency region into the visible regime is more challenging, however, because of the requirement that the feature sizes of the metamaterial be significantly shorter than the wavelength of incident light. Given that visible light ranges in wavelength from about 390-750nm, feature size requirements push the limit of modern fabrication technology. Additionally, and very importantly, metals tend to experience much greater losses at visible frequencies, which not only makes it more difficult to design effective visible-frequency metamaterials, but also reduces the ratio between transmitted and absorbed radiation (8). Still, in 2007 a negative-index metamaterial was reported at 780nm using a grid similar to that of Zhang et. al but with a lattice constant of 300nm and square holes100nm on a side (9), and in 2009 a similar structure was fabricated with a peak wavelength of 580nm (10). Finally, in 2010 a metamaterial structure consisting of a matrix of gallium phosphide-wrapped silver cylinders (75nm diameter) in a silver carrier yielded a negative index of refraction with a strong transmission/absorption ratio in the blue visible region at a frequency of 480nm (11). Although the fabrication is challenging, metamaterials have now been demonstrated that cover a significant stretch of the visible spectrum.

ABSORPTION IN METAMATERIALS

The preceding section showcased the dramatic results of metamaterial structures that successfully manipulated the *real* part of the permittivity and permeability to produce a negative index of refraction. What is the potential of metamaterials to manipulate the *imaginary* part of the permittivity and permeability? In the remainder of this article, we explore work on absorption in metamaterials with an eye to how metamaterials might be used to construct a better solar photovoltaic cell.

The coupling between metamaterial structures and electromagnetic radiation via capacitance and inductance suggests that, instead of merely reacting to incident radiation to change the index of refraction, electromagnetic energy may also be stored and subsequently dissipated by similar structures to yield a large absorption. Since permeability and permittivity are characterized by a real part (which describes propagation in a medium) and an imaginary part (which describes absorption and loss in a medium), perhaps it is possible to manipulate the imaginary component of ε and μ to be simultaneously large over a given frequency range and thus absorb radiation well. The approach is similar to the one used for negative index metamaterials, except that the structures are designed to optimize the imaginary portion of the permittivity and permeability.

In 2008, Landy et. al introduced a metamaterial structure with high effective absorption over a narrow band in the microwave range (10-12.5 GHz) and near unity absorption at 11.5 GHz (12). This

feat was accomplished with a metamaterial structure consisting of a silver double split ring resonator (similar to the electrically resonant structures described in (13)) separated in the direction of radiation propagation from a cut wire strip by a dielectric layer. The electrically resonant split rings couple to the electric field without any magnetic interaction, while the magnetic response was a product of the induction current driven between the cut wire and the center conductor of the split ring resonator. The resonance that is established between the inductive and capacitive portions of the "circuit" allows energy to be stored and subsequently dissipated via ohmic and dielectric loss. In reality, absorption in the dielectric is much larger than ohmic losses in the metal conductors.

For solar energy conversion applications, it is desirable to be able to absorb energy over a broad band of frequencies centered at the solar maximum. The challenge here is two-fold: not only is it relatively difficult to engineer metamaterials that are active in the UV/visible/near-infrared range in which most solar energy arrives at the earth's surface, but most metamaterials are active over a narrow band. Padilla presented a hopeful roadmap to achieving broader band absorption in metamaterials by using a unit cell that consists of a variety of different size metamaterial "atoms" (14). That is, instead of a periodic system consisting of a single type of active structure, a periodic system with a repeating unit cell that is itself composed of many unique active structures can leverage the combined interaction between the structures of various size with different frequencies to produce an effective response over a much broader frequency band than is possible with the single active structure approach. Absorption over a relatively wide portion of the solar spectrum may now be within reach; the challenge then becomes how to convert that absorbed electromagnetic radiation into useful energy.

METAMATERIALS AS PHOTOVOLTAIC CONVERTERS

The absorption capability of metamaterials has been proposed as a way to make superior thermoelectric or thermo-photovoltaic converters. For example, a metamerial absorber could be used to effectively capture radiation from a broad frequency range and then re-emit it in a narrow band to a photovoltaic cell with a bandgap that is precisely tuned to the wavelength of the re-emitted radiation. Such an approach holds promise, but might there be a more efficient approach to converting the energy absorbed by the metamaterial into a useful output? What follows are questions rather than conclusions (as well as some speculation), but a topic that I would be interested to pursue if the ideas have merit.

Metamaterials function by coupling capacitively and inductively to electromagnetic fields. It follows then that at resonant frequencies, the tiny structures that compose a metamaterial contain stored electrical energy. The question that I am interested is then: "Can this stored electrical energy be retrieved from these individual structures before it is dissipated to phonon modes?" Perhaps this goal could be realized by producing a sort of active solar cell in which each capacitive structure is connected to a transistor/diode that allows the capacitor to discharge every time a critical voltage threshold is reached. Such a new incarnation of the photovoltaic cell could be imagined to absorb radiation more efficiently than silicon owing to the metamaterial design and avoid the recombination losses associated with conventional solar cells with a semiconductor absorber.

A second question that struck me is whether it would be possible to tap the currents that are established in metamaterial structures for direct radiation-to-electrical energy conversion. As an analogy, imagine two reservoirs of water, one located a few feet higher in elevation than the other. Now picture waves generated in the lower elevation reservoir that are sufficient in size to surmount the dam dividing the two, thus increasing the volume of the elevated reservoir. Were one to then craft a channel connecting the higher reservoir to the lower one and insert a turbine in between, energy could be recovered in returning the water levels of the two reservoirs to their original state. Likewise, could the oscillating surface plasmons (waves) excited in metamaterial structures be similarly harvested? Would it be possible, for example, to adjoin two metals of different work function separated by a thin dielectric and a diode connected to the outside world to siphon electrons from the surface wave of the lower-potential metal every time a surface wave exceeds a threshold value? It would be interesting to

further explore these concepts to determine whether they might form the foundation for a new genre of

photovoltaic devices.

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2.57 / 2.570 Nano-to-Macro Transport Processes Spring 2012

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