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New polaritonic materials in the THz range made of directionally solidified halide eutectics

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Abstract

Directionally solidified alkali halide binary eutectics have been recently proposed as THz polaritonic metamaterials based on their ordered microstructure and the suitable phonon–polariton resonances in the THz range of the spectrum. In the present work we focus on the search of new available eutectic systems both binary and ternary eutectics with well-ordered fibrous or lamellar microstructures and interparticle distances from 1 to several tens of microns. Simple effective homogenization models have been used to calculate effective permittivity and transmittance in the THz range of eutectic slices. This lets us identify the electromagnetic spectral ranges where hyperbolic dispersion is expected together with a significant transmittance value. The hyperbolic dispersion range shifts with microstructure size, that is, with growth parameters, showing that the materials response can be finely tuned by the manufacture conditions. Applications with these materials cover the electromagnetic range from 5 to 20 THz.

Keywords: THz; Metamaterials; Eutectics; Alkali halides; Polaritonics

1. Introduction

THz waves are used in communications, imaging or sensing technologies. Nowadays also, there are new laser sources that give THz technology increased importance. According to Tonouchi,[1] higher power THz sources, more sensitive THz sensors and more functional materials are still required to realize all kinds of imagined applications.

In particular, there is a need for passive elements that would serve to handle (focussing, shaping and guiding) the THz beams. Suitable materials for these devices include materials with very large, near zero or negative dielectric constant in the appropriate wavelength range. Small losses are also required so that subwavelength guiding or focusing can be made possible. Existing metamaterials in the THz range would fulfil these requirements but the fabrication methods based on micro/nano machining of 2D or 3D architectures are yet expensive and time consuming.[2] Large 2D metal–dielectric metamaterials have been produced by drawing techniques, using technologies similar to those developed for photonic crystal optical fibres fabrication.[3,4] Recently, a bottom-up technique to fabricate composite meta-atoms for photonic wavelengths by self-assembling of metallic particles has also been implemented.[5] Negative effective permeability or permittivity has also been obtained in composite materials consisting of aligned metallic or polaritonic wires embedded in a dielectric matrix.[6–8] The reason is that frequency ranges of negative permittivity (with hyperbolic dispersion relations) or negative permeability occur in some uniaxially anisotropic materials. These anisotropic media may present lower losses than resonance based negative permeability, negative permittivity materials.

Directionally solidified eutectics (DSEs) are in situ self-organized composites of two or more crystalline phases. The use of this kind of composite to manufacture metamaterials has been proposed previously.[9,10] The microstructure of DSEs may consist of rods of one phase embedded into the matrix of the other phase or of alternate lamellae with a dominant alignment direction (the pulling direction or the growth direction).[11] DSEs mimic in bulk form anisotropic phase orderings that are otherwise achieved by costly top-down or nano-fabrication approaches.[12] The characteristic length of the transverse microstructure of DSEs for well ordered, coupled microstructures spans from tens of nanometers to tens of microns. These are subwavelength dimensions for THz radiation, and thus, appropriate homogenization theories can be applied to approximately describe the propagation of THz waves

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in these materials. Required low losses and large dielectric contrast are achieved by alkali halides in the THz range (or FIR). They show wide ranges of transparency in this region and the negative or very large dielectric constant is provided by the phonon–polariton resonance which, moreover, in these compounds, consists of a single mode. In addition, having small values of the entropy of melting, coupled, halide eutectic composites generate well-ordered microstructures presenting anisotropic dielectric behaviour.[13]

Recently, polaritonic metamaterial behaviour has been proved in NaCl–LiF and KCl–LiF rod-like directionally solidified eutectics.[14] They were solidified by the Bridgman method so that 14 mm diameter ingots were prepared and characterized by FTIR reflectance spectroscopy. The IR reflectance of KCl–LiF was reasonably well reproduced by electromagnetic calculations assuming a perfectly hexagonal arrangement of LiF rods inside the chloride matrix. The response contained the Mie-resonance of the LiF polaritonic rods at large rod diameters and converged to a rod-size independent LiF polaritonic resonance at small rod-size diameters. In the latter case, a simple Maxwell–Garnett effective medium model can describe the reflectance spectra. This description, shown by Foteinopoulou et al.[15] to be suitable whenever the ratio or periodicity (a) to wavelength in vacuum (λ) satisfies the relationship $a/\lambda < 0.1$, generates a material with hyperbolic dielectric permittivity in certain wavelength ranges that would allow the subwavelegth guiding and large light transmittance in Fabry–Perot cut slices.[16–18] The potentiality of those self-organized easy-to-grow materials has been, consequently, put forward, and the search for new eutectic systems working at different wavelengths as well as the investigation of real materials with its intrinsic variability in size of the dispersoids and experimental demonstration of the predicted properties requires more work.

In the present manuscript we report the microstructure and THz dielectric permittivity in the quasistatic approximation (sufficiently long wavelength limit) of some selected alkali halide eutectics. We aim at showing the potentiality of these materials as a source for metamaterials or polaritonic photonic crystals in the THz, and at encouraging theoretical as well as experimental work in understanding and identifying properties and applications hidden in those easy-to-manufacture self-assembling composites.

2. Background

As we have said in the Introduction, the materials chosen for this study are the simplest halide salts. The THz properties of alkali halides are determined by the phonon–polariton interaction. In the simple rock-salt structure the simplest description contains one single phonon polariton with transverse (ω_T) and longitudinal (ω_L) frequencies so that the dielectric constant (real part) is negative in the interval $\omega_T < \omega < \omega_L$ (Reststrahlen region), and positive outside this interval. Damping of the phonon polariton broadens the Im(ε) curve, and ε does not diverge at $\omega = \omega_T$. In Fig. 1 we sketch the frequency range of negative permittivity, Re(ε) < 0 (ω_T and ω_L values are the extreme points of the segments on the plot) for several

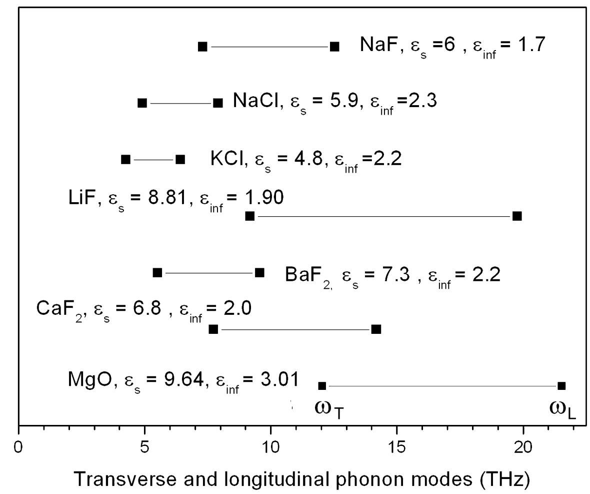

Fig. 1. Reststrahlen region and permittivity of some halides and MgO below (ε_s, static permittivity) and above (ε_{inf}, high frequency permittivity) the phonon–polariton dispersion region.

materials (alkali halides, fluorite and MgO). The static ($\omega \ll \omega_T$) and high frequency ($\omega \gg \omega_L$) approximate values of Re(ε) are also given in the diagram. For the chosen materials it can be seen that ω_T ranges between 142 cm^{-1} (4.26 THz) for KCl and 306 cm^{-1} (9.17 THz) for LiF or 401 cm^{-1} (12.0 THz) for MgO; while ω_L ranges from 214 cm^{-1} (6.41 THz) for KCl to 659 cm^{-1} (19.8 THz) for LiF and 718 cm^{-1} (21.5 THz) for MgO.[19]

The materials used in this study have been prepared by solidification from the melt of eutectic mixtures.[11] Directional solidification of eutectic composites consisting of phases with low melting entropy produces a solid with a microstructure of separated phases, lamellae, fibres or more complex morphologies, well aligned along the solidification direction. Unidirectional alignment along the solidification direction induces anisotropic properties in otherwise isotropic composites. The size and morphology of the eutectic structure can be modified by simply changing the growth rate according to the following relationship between interphase spacing a and the solidification rate v:

$$a_2 \cdot v = K_1 \quad (1)$$

K_1 is a constant which depends on the eutectic system under study. Hence, finer microstructures would be obtained at higher growth rates. The eutectics utilized in this study are composed of low melting entropy single phases and consequently, solidify on a coupled growth regime with well aligned, highly homogeneous microstructures. For volume fractions of the minority phase $f < 0.3$ we obtain fibrous microstructures. Otherwise the expected microstructure is lamellar.

With respect to the electromagnetic properties, the permittivity of an anisotropic composite formed by phase f embedded in phase m (at volumetric fraction $1-f$), assuming that the microstructure consists of long fibres or platelets of phase f aligned in the Z direction and with deep subwavelength size in the XY transverse plane, can be calculated using an arithmetic average for parallel polarization (Eq. (2a)) or the Maxwell