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Micropillar Templates for Dielectric Filled Metal Arrays and Flexible Metamaterials

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Photonic structures in two dimensions with building units in the micron and nanometer range are being researched and fabricated for their potential applications in many different areas. Micropatterned metal-dielectric structures have been proposed for sensors from the visible (VIS) to the THz range [¹, ²]; complex patterned photonic structures are used and further studied as electromagnetic (EM) wave absorbers for light harvesting in photovoltaics [³, ⁴], or selective thermal emitters [⁵]. Metamaterials in the near infrared (NIR) and THz range are needed to enhance light-matter interaction for the manipulation of THz waves or in sensing devices. [⁶] The availability of compact, subwavelength THz band-pass filters would boost new technological developments in the THz sensing or imaging devices. In many of these applications the structures comprise metal and dielectric features, as they exploit the light confinement in deep subwavelength regions near the edges of metallic particles.

A number of techniques exist to fabricate them. For metamaterials and subwavelength transmission, the pitch size has to be much smaller than the light wavelength while for properties relying on dielectric resonances, feature size and wavelength are of the same order or magnitude. In general the feature dimensions and the inter-feature distances have to be precise. Consequently, to span the electromagnetic range from THz to the visible (VIS), the microstructures need to have sizes from several microns down to several nanometers. Photolithography is the most effective way of fabrication for the larger sized ones. As the

wavelength decreases, many available techniques require point-by-point scanning, and as a result are slow and appropriate only for small area samples [5]. Of particular interest is the fabrication of metamaterials on flexible substrates, on which some progress has already been made [7]. A handful of procedures also exist to infill previously patterned templates to reach 3D functional photonic structures [8].

Self-assembling procedures to fabricate photonic structures and metamaterials stand out as inexpensive, scalable procedures [9, 10]. Directional solidification of eutectics belongs to this class of procedures. Aligned microstructures, with transverse dimensions in the micron range, self-assemble spontaneously during the controlled solidification process [11, 12]. Phonon-polariton metamaterials [13, 14, 15, 16] or nanoplasmonic structures [17] based on eutectics start to be studied, and more recently also template-directed directional solidification of salt eutectics have resulted in promising 3D mesostructured materials [18]. The achievement of metal-dielectric (or polaritonic) structures based on this self-assembling approach would constitute a real breakthrough, as large scale photonic structures would become cheap and easy to manufacture. But eutectic compositions are fixed by thermodynamics, even if kinetics can help to deviate somewhat off the equilibrium composition. One consequence is that eutectic systems that combine metal-dielectric compounds are rare [17]. Binary or multinary eutectics where all final compounds are of similar chemical nature is the common case, and there are many of them among halides [16, 19] or oxides [20]. Therefore to get advantage of eutectics to get microstructured metal surfaces, metallization after growth is required [12]. In the literature many eutectic microstructures have been reported: rod, lamellae and interpenetrated among regular eutectics; cellular, broken-lamellae, globular, spiral or even SRR like geometries, etc. among irregular eutectics, with different degree of homogeneity of interspacing and size of the component phases. The size of the building units is controlled by the solidification rate, so that, it covers the range from tenths of microns to tens of microns [12, 20]. Note that large surfaces are easily achieved (few cm² size) [16, 21, 22]. Still, the choice of the eutectic system is a compromise between optical properties of the components, microstructure (shape size and homogeneity) that is feasible and application wavelength.

In the present communication we report on the fabrication of diverse metal-dielectric microstructures by means of simple procedures and based on a directionally solidified regular eutectic substrate as template. The uniqueness of this approach lies in the achievement of a holey metal film with the holes filled by a polaritonic (polar-dielectric) material, such that diverse microstructures are obtained in large surfaces. Moreover, the dielectric or polaritonic material does not only fill the holes, but can also tower over the metallic surface and participate in the coupling of the external electromagnetic (EM) waves with the photonic structure. Not less important is the fact that the operating wavelength of the structures can be tailored by design, either through the microstructural size or by the selection of the phonon-polariton resonance of the hole-filling material. Some examples with rods or ribbons with transverse optical modes between 26 μm and 41 μm are reported in [16], heavier halides shift them to longer wavelengths and eutectics of other compounds are still to be explored from this point of view. The obtained holey metal films with a polaritonic dielectric filling the holes can be exploited either in the form of a surface layer onto a rigid substrate (the eutectic ceramic) or as a flexible metal-dielectric structure.

Capabilities of these structures as EM, subwavelength radiation filters will be shown in the spectral range from NIR to THz. They are a consequence of enhanced optical transmission (EOT) related phenomena through the subwavelength apertures created [23], also assisted by the particle-like EM resonances excited in the pillars. The EOT phenomenon may involve electromagnetic resonances localized in subwavelength apertures drilled on holey flat metal films and EM modes bound to the metal surface [24, 25]. The first ones play the leading role in these structures. To be more precise, two optical effects belonging to the class of EOT phenomena will be shown to take place: localized EOT (LEOT) [26] and absorption-induced transparency (AIT) [27, 28]. The spectral location of LEOT appears close to the cutoff wavelength of holes for optically thick metal films [24], so it depends on the hole shape, size and dielectric filling. In thin films the location is very sensitive to the dielectric environment [26]. AIT consist in the appearance of peaks in transmission and dips in reflectance in the optical spectra of holey metal films in contact or filled with substances with sharp absorption bands at the same wavelengths were the bare filler absorbs [27, 29]. The AIT phenomenon was observed in the VIS regime [27], and it was subsequently predicted to operate also at lower energies [28], e.g., in the THz. Even an AIT-based molecular detection method has been recently proposed [30]. It is important to remark that in this communication AIT is experimentally demonstrated in the THz regime for the first time.

We have chosen as templates halide eutectics that form microstructures consisting of eutectic grains with almost perfect triangular arrangements of LiF fibers in a chloride matrix, which can be easily etched with water. The typical microstructure after etching is shown in figure 1a. Several microns tall LiF pillars, around 1 μm diameter, tower over the etched surface of a KCl-LiF directionally solidified eutectic. Diameter/pitch ratio are determined by the eutectic composition [14, 31], being 0.29 for KCl-LiF and 0.55 for NaCl-LiF eutectics. Pulling rates from 1 mm/h to 20 mm/h are feasible and generate homogeneous and large eutectic crystals (cm^2 -size cross-sections [16, 21]). Resultant pitch values in both eutectics are similar, going approximately from 5 to 23 μm [32, 33]. Then, rod diameters can span from 1.6 μm (solidifying KCl-LiF at 20 mm/h) to 12 microns (with NaCl-LiF at 1 mm/h). Standard deviations of measured values of pitch and LiF rod diameter amount to 5 to 10 % of the corresponding value. Etching depths from 2 μm to 12 μm have been achieved on the samples. Once the etched surface of the eutectic is prepared (steps I and II, first row in figure 2), three different procedures were followed (sketched in 2nd to 4rd rows in figure 2) that resulted in three different configurations of metal-dielectric structures.

The first procedure (A, row 2 in figure 2) deposits gold by sputtering on all the exposed surface of the etched material (III), then the empty space is filled with embedding resin and cured. After polishing until the gold layer on top of the pillars has been eliminated, a corrugated, holey gold metal layer results, with the cylindrical holes filled with LiF. A SEM micrograph of this polished surface is shown in figure 1b. The bright annular phase in the image is gold, inside there is LiF and the rest, darker grey color corresponds to the embedding resin.

Figure 1. Microstructure of the etched and metal coated samples. The first row (a) and b)) are prepared out of KCl-LiF eutectic; figures c) to f) correspond to samples prepared with NaCl-LiF eutectics. The different filling ratio between them is evident. (a) SEM micrograph of an etched surface of a KCl (matrix)-LiF (rods) directionally solidified eutectic polished slice. The sample had been grown at 10 mm/h by the Bridgman method. (b) to (f) SEM of surface etched and metallized surfaces. (b) SEM micrograph of the surface of a sample prepared by procedure A. LiF pillars (dark grey circles) are surrounded by a thin layer of Au (bright). The matrix here is resin. (c) SEM picture of pillared structures covered with Au prepared by procedure B. The dark colored dots are LiF pillars, the bright sparse dots are pillars where lift-off did not succeed, so there is still Au on top, and the matrix background is NaCl covered with Au. (d) One LiF pillar covered with 235 nm Au layer deposited by directional evaporation. There is Au on the top surface and over the NaCl back laying matrix, while the side walls of the LiF micropillar stays unmetallized. (e) and (f) correspond to a sample prepared by porcedure C. LiF tall cylinders (large shape-factor) emerge from the several microns thick aluminum layer. Picture (f) shows a concave curved surface, showing that the final structure is flexible.

Figure 2. Diagram showing the different procedures used to prepare the holey metallic films perforated with LiF micropillars. The first row is common to all of them. A, B and C rows correspond to the respective procedure, as described in the text.

The second procedure (B) consists of wetting with a lift-off resist the top surface of the pillars, followed by vertical electron-beam evaporation of a 235 nm thick gold layer. A short time immersion in acetone eliminates the resist and gold on top of the micropillars and the microstructure shown in the SEM micrographs of figure 1c is obtained. Figure 1d proves the directional deposition of gold, where a single gold-covered pillar, is shown. Gold covers the background NaCl substrate and the top of the pillars, but not the sides. Note that with appropriate angle-cut surfaces and etched depths, different configurations of metal-pillar-substrate can be prepared. Both metal-dielectric layers prepared by procedures A and B lay on top of an around 1 mm thick NaCl-LiF or KCl-LiF substrates, which are rather transparent only from 0.4 μm to 4 μm approximately.

Figure 3. (a) Refractive index ($n+ik$) of LiF [34]. Reflectance (panel b) and transmittance spectra (dotted lines in panels c and d, with right hand side scale axes) measured in samples prepared by procedure C using NaCl-LiF as template. The insets in (b) and (c) show the configuration of the reflectance and transmittance measurements respectively. Microstructural feature sizes are: LiF cylinder radius $r = 2.8 \mu\text{m}$ (in (c) and black curve in (b)) and $r = 6.2 \mu\text{m}$ (in (d) and red line in (b)). The LiF rods are $t = 27 \mu\text{m}$ high (c), and around $70 \mu\text{m}$ high (d); and the LDPE layer is around $200 \mu\text{m}$ thick, w_{Al} = thickness of the Aluminum metal layer is $3 \mu\text{m}$. The continuous lines on graphs plotted in panels (c) and (d) (and corresponding left hand side scale axes) are FDTD calculations done varying the height of the LiF rods (t), considering a square lattice periodic arrangement of LiF circular rods, P = periodicity of the triangular LiF rod lattice ((c) $P = 10.5 \mu\text{m}$; (d) $P = 20.3 \mu\text{m}$), PEC layer and infinite thickness LDPE substrate (non-absorbing and $n=1.5$).

In procedure C, sketched in the last row of figure 2, the LiF pillared sample was covered by a $3 \mu\text{m}$ thick layer of aluminum by magnetron sputtering. This completely filled the volume between the LiF pillars and allows front-side polishing. In step IV of procedure C we recover the same kind of microstructure than in procedure B, except for the thickness of the metallic layer (200 nm in B vs. $3 \mu\text{m}$ in C), and the fact that the pillars do not tower over the surface in procedure C. This polished layer is then fixed to a rigid substrate by means of molten and resolidified layer of low density polyethylene (LDPE). The polymer acts now as substrate, and the bulk of the initial NaCl-LiF substrate is lapped down to around $27 \mu\text{m}$ thick and afterwards etched with water to eliminate all the NaCl which blocks FIR radiation. Towering LiF pillars emerge now on this side. SEM micrographs of tilted samples are shown in figure 1e. The LiF pillars are no longer embedded in any matrix, but remain attached to the substrate by the

metal and LDPE. To end the process, the LDPE-metal-LiF pillared structure is peeled off the rigid substrate. Once peeled-off, the LDPE and the thin Al layer are flexible, thus it can be bent to take convex or concave shapes, as shown in figure 1f. We did not attempt to determine maximum curvature before fracture.

The Reflectance spectra measured at quasi-normal incidence on the LiF filled holey aluminum layers after front-side polishing (step IV, Procedure C) are given in figure 3b for samples with LiF rod diameter of 5.6 μm (black line) and 12.4 μm (red line). Sharp reflectance minima are observed in the MIR range at around 10 and 14 μm , respectively. The sharp minima are near to the cut-off wavelength (λ_c) for LiF-filled Al circular apertures, $\lambda_c = 3.4\pi r$ [35]. For the given hole radii (r) and LiF refractive index (n , Figure 3 a) these are $\lambda_c = 10.4 \mu\text{m}$ and $\lambda_c = 13.9 \mu\text{m}$ respectively. Consequently, those are associated to LEOT peaks, as discussed above. [24, 26] In fact, transmittance peaks have been observed in samples prepared by procedures A and B with LiF rods (metal holes) of diameters = 2.1 μm ($\lambda_{\text{max}} = 4 \mu\text{m}$) and 7.1 μm ($\lambda_{\text{max}} = 9.7 \mu\text{m}$) on KCl-LiF or NaCl-LiF substrates respectively (see figure S1 in supplementary information).

In the FIR range of the spectrum, wavelength dependence of the refractive index of polaritonic LiF and NaCl-LiF substrate prevents such a simple analysis of the reflectance spectra. Instead, the transmittance (T) measured after step VI (LiF filled holey aluminum supported on FIR transparent LDPE), is given in figures 3c and 3d. The dotted lines are the measured spectra, the continuous lines are finite-difference time-domain (FDTD) calculations. These spectra show enhanced transmittance in the THz range. A 2 % transmittance peaking at 40 μm is observed on a 3 μm thick holey aluminum layer with LiF rods 27 μm high and 5.6 μm average rod diameter (the sample area was 8x8 mm^2), which fits very well with the calculations (figure 3c, cyan curve). The T band at around 40 μm , as it appears just on the low energy side of the strong phonon-polariton absorption of LiF, can be associated to AIT. This is the first experimental demonstration of AIT operating in spectral regimes different than VIS, the absorbing medium being the polaritonic LiF. Shifts and intensity changes of the transmittance peak with microstructural parameter variations within the standard deviation of the composite cause broadening of the band (Figure S3, supplementary information). As the hole diameter ($\emptyset$) increases, the maximum in transmittance moves to longer wavelengths.

At much larger rod diameters (as in figure 3d), longer wavelength modes propagate along the hole, for which the LiF filling material is much less absorbing and has large refractive index. This transmission band is better understood as the related phenomenon of subwavelength LEOT at THz frequencies. The much smaller transmission intensity measured in Figure 3d, sample with 70 μm high LiF pillars, when compared to calculations is to be associated to the poor mechanical stability of this sample, where excessively tall (70 μm) LiF rods are to be kept vertically in place by collars of 3 μm maximum thickness. LiF pillars tended to tilt and some dropped flat onto the surface in step VI of procedure C. These defects can diffuse transmitted light to other directions not reaching the spectrometer detector. In both cases, the total calculated transmittance increases when the LiF micropillars tower over the metallic film, strongly in the $r = 2.8 \mu\text{m}$ sample. The micropillars couple with the incident plane wave, and harvest radiation that is then injected through the LiF filled metallic holes. An optimum height of the LiF rods exists, as the propagation along the LiF rod also involves absorption. In both calculated cases, this height is around 10 μm .

To conclude, a new facile procedure, using salts of directionally solidified eutectics, has been designed and used to fabricate diverse metal-polaritonic (or dielectric) microstructures on several mm² surfaces. In the particular example shown here they consist of holey metal films with the holes filled with LiF micropillars. MIR and THz Reflectance and THz Transmittance has been measured, associated either to LEOT or demonstrating experimentally AIT in the THz range for the first time. Moreover, the towering LiF micropillars that fill the holes act as light harvesters for THz radiation, which is then successfully injected into the subwavelength holes and transmitted. We have also achieved flexible structures that combine a polymeric film (LDPE) and a microstructured metallic layer pierced by a forest of LiF micropillars, that can eventually be used to coat different kind of devices for THz light injection or sensing. Other ways to use these templates can be envisaged. For example, the micropillared surfaces could as well be used as stamps to fabricate microstructures on different substrates or to create corrugated structures by deposition of suitable materials on the etched eutectic substrate.

Experimental Section

Manufacturing procedures: Ingots of 14 mm diameter and 50 mm length of the eutectics were prepared with starting compositions NaCl-LiF (71 wt %NaCl and 29 wt% LiF) and KCl-LiF (91 wt %KCl and 9 wt% LiF). Powders of 99.98 % pure LiF (Alfa Aesar), 99.5% pure KCl (Merk) and 99.99% pure NaCl (Alfa Aesar) were dried, weighted and mixed. Solidification was done in carbon-glass crucibles using the Bridgman method in an electrically heated furnace and under an Ar atmosphere. We used pulling rates from 1 to 10 mm/h. Slabs of transverse cross-sections around 1mm thick were dry-polished with abrasive grain size down to 0.25 μm . Then selective etching was performed by short (tens of seconds) immersion of the samples in agitated water-ethanol solutions at 25°C. Immediately afterwards a short cleaning procedure in water-free acetone plus ultrasonication removes any trace of salt that could remain adhered on the minority phase. In procedure A, a 200 nm of gold was sputtered in a Balzers SCD004 Sputter Coater. Then, a two component epoxy resin (KEM90, ATM GmbH, Mammelzen, Germany) was vacuum infiltrated onto the coated surface, cured overnight and subsequently lapped and polished until the metal from the top surface of the LiF micropillars was polished out. In procedure B, a 3.2 microns thick resist (Microchemicals, AZ6632) was spin coated on a silicon wafer. The sample is positioned face down in contact with the fresh coated wafer for 60 s with uniform pressure and then separated. A layer of 235 nm of gold was then evaporated in an Auto 500 Electron Beam Evaporation System (Edwards). Then, the resist was dissolved in acetone for lift-off. In procedure C, a thick layer (aprox. 3 μm) of aluminum was deposited onto the sample by magnetron sputtering (Leybold L560). LDPE (low density polyethylene) was used to fix the polished, metalized layer on a Silicon wafer. The opposite side could then be lapped and polished to reduce the sample thickness to around 25 μm . LDPE with sample can then be peeled off the Si wafer and immersed in water-ethanol mixture for complete removal of the NaCl. This flexible sample is suitable for transmission measurements.

Characterization: SEM micrographs were taken on a Merlin Field Emission Scanning Electron Microscope from Carl Zeiss (Germany) belonging to the *Servicio de Microscopía Electrónica* of the *University of Zaragoza*. MIR and FIR spectra in the range 3-100 μm (transmittance or back-reflectance) were measured with a vacuum IFS66v/S Bruker IR Spectrometer, using a CsI and Mylar beam splitters to cover the whole spectral range. Near normal reflectance

measurements were made by using a near normal incidence ($\theta=13^\circ$) specular reflectance attachment. We measured sample areas larger than 40 mm² for meaningful quantitative measurements.

Electromagnetic calculations: We used the Finite-Difference Time-Domain (FDTD) method to compute scattering coefficients [36]. Further details of our particular implementation can be found in [37]. The metal was considered a perfect conductor. The optical properties of LiF (real and imaginary refractive index) was taken from Palik [34]. When LDPE was present, it was considered non-absorbing with $n=1.5$, as well as the rest of the eutectic substrate. The systems are assumed to be periodic, with square lattice, and with LiF rod diameters appropriate to each sample. Lattice period was taken in each calculation to give a hole filling fraction near to the LiF filling fraction in the respective eutectics. No bands (reflectance or transmittance, THz or NIR regions) were observed experimentally that could be associated to the lattice symmetry, and neither one appeared in the calculated spectral range investigated. So, the square lattice was chosen for the sake of simplicity in numerical calculations.

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References

- ¹ N. Liu, M. Mesch, T. Weiss, M. Hentschel, H. Giessen, *Nano Lett.* **2010**, *10*, 2342-2348.
- ² B. Ng, J. Wu, S.M. Hanham, A.I. Fernández-Domínguez, N. Klein, Y.F. Liew, M.B.H. Breese, M. Hong, S.A. Maier, *Adv. Optical Mater* **2013**, *1*, 543-548.
- ³ M. Burrese, F. Pratesi, F. Riboli, D.S. Wiersma, *Adv. Optical Mater* **2015**, *3*, 722-743.
- ⁴ F.J. Bezares, J.P. Long, O. J. Glembocki, J. Guo, R.W. Rendell, R. Kasica, L. Shirey, J.C. Owrutsky, J. D. Caldwell, *Optics Express* **2013**, *21*, 27587-27601.
- ⁵ C.M. Watts, X. Liu, W.J. Padilla, *Adv. Mater* **2012**, *25*, OP98-OP120.
- ⁶ M. Tonouchi, *Nature Photonics* **2007**, *1*, 97-105.
- ⁷ S. Walia, C.M. Shah, P. Gutruf, H. Nili, D. R. Chowdhury, W. Withayachumnankul, M. Bhaskaran, S. Sriram, *Appl. Phys. Rev.* **2015**, *2*, 011303.
- ⁸ P.V. Braun, *Chem Mater* **2014**, *26*, 277-286.
- ⁹ K.A. Arpin, M.D. Losego, A.N. Cloud, H. Ningn, J. Mallek, N.P. Sergeant, L. Zhu, Z. Yu, B. Kalanyan, G.N. Parons, G. S. Girolami, J. R. Abelson, S. Fan, P.V. Braun, *Nat. Comm.* **2013**, *4*, 2630.
- ¹⁰ J. Dintinger, S. Mühlig, C. Rockstuhl, T. Scharf, *Opt. Mat. Express* **2012**, *2*, 269-278.
- ¹¹ D.A. Pawlak, K. Kolodziejak, S. Turczynski, J. Kisielewski, K. Rozniatowski, R. Diduszko, M. Kaczkan and M. Malinowski, *Chem. Mater.* **2006**, *18*, 2450-2457.
- ¹² D.A. Pawlak, S. Turczynski, M. Gajc, K. Kolodziejak, R. Diduszko, K. Rozniatowski, J. Smalc, I. Vendik, *Adv. Funct. Mat.* **2010**, *20*, 1116-1120.
- ¹³ V. Myroshnychenko, A. Stefanski, A. Manjavacas, M. Kafesaki, R.I. Merino, V.M. Orera, D.A. Pawlak and F.J. García de Abajo, *Optics Express* **2012**, *20*, 10879- 10887.

- ¹⁴ A. Reyes-Coronado, M. F. Acosta, R. I. Merino, V. M. Orera, G. Kenanakis, N. Katsarakis, M. Kafesaki, Ch. Mavidis, J. García de Abajo, E. N. Economou, C. M. Soukoulis, *Optics Express* **2012**, *20*, 14663.
- ¹⁵ M. Kafesaki, A.A.Basharin, E.N. Economou, C.M.Soukoulis, *Photonic Nanostruct.* **2014**, *12*, 376-386.
- ¹⁶ R.I. Merino, M.F. Acosta, V.M. Orera, *J. Eur. Ceram. Soc.* **2014**, *34*, 2061-2069.
- ¹⁷ K. Sadecka, M. Gajc, K. Orlinski, H.B.Surma, A. Klos, I. Jozwik-Biala, K. Sobczak, P. Dluzewski, J. Toudert, D.A. Pawlak, *Adv. Opt. Mater.* **2015**, *3*, 381-389.
- ¹⁸ J. Kim, L.K. Aagesen, J.H. Choi, J. Choi, H.S. Kim, J. Liu, C.R. Cho, J.G. Kang, A. Ramazani, K. Thornton, P.V. Braun, *Adv. Mater.* **2015**, *27*, 4551-4559 (doi:10.1002/adma.201502265).
- ¹⁹ N. Yasui, Y. Ohashi, T. Kobayashi and T. Den, *Adv. Mater.* **2012**, *24*, 5464-5469.
- ²⁰ J. Llorca and V.M. Orera, *Progr. Mater. Sci.* **2006**, *51*, 711-809.
- ²¹ V.M. Orera, J.I. Peña, "Directional Solidification", in "Ceramics and Composites Processing Methods" 1st Edition, pp 471-457. N.P. Bansan and A.R. Bocaccini Eds; The American Ceramic Society **2012**, by John Wiley and Sons Inc.
- ²² K. Bienkowski, S. Turczynski, R. Diduszko, M. Gajc, W. Gorecka and D.A. Pawlak. *Cryst. Growth Des.* **2011**, *11*, 3935-3940.
- ²³ T. W. Ebbesen, H. L. Lezec, H. F. Ghaemi, T. Thio, and P. A. Wolff, *Nature* **1998**, *391*, 667-669.
- ²⁴ F.J. García Vidal, L. Martín-Moreno, T.W. Ebbesen and K. Kuipers. *Rev. Mod. Phys.* **2010**, *82*, 729.
- ²⁵ S. G. Rodrigo, F. de León-Pérez and L. Martín-Moreno, in Proceedings of the IEEE (Eds: P. Berini, S. Bozhevolnyi and D. S. Kim) **2016**,
- ²⁶ S. Carretero-Palacios, F. J. García-Vidal, L. Martín-Moreno, and S. G. Rodrigo, *Phys. Rev. B* **2012**, *85*, 035417.
- ²⁷ J.A. Hutchison, D.M. O'Carroll, T. Schwartz, C. Genet, T. Ebbesen, *Angw. Chem. Int. Ed.* **2011**, *50*, 2085-2089.
- ²⁸ S. G. Rodrigo, F.J. García Vidal, L. Martín Moreno, *Phys. Rev. B* **2013**, *88*, 155126.
- ²⁹ X. Zhong, S.G. Rodrigo, L. Zhang, P. Samori, C. Genet, L. Martín-Moreno, J.A. Hutchison and T.W. Ebbesen. *ACS Nano* **2016**, *10*, 4570-4578.
- ³⁰ S.G. Rodrigo and L. Martín-Moreno, *Optics Letters* **2016**, *41*, 293-296
- ³¹ P Chartrand, A.C. Pelton, *Metall. and Mat. Trans. A*, **2001**, *32A*, 1417- 1430.
- ³² V.M. Orera and A. Larrea, *Opt. Mater.* **2005**, *27*, 1726 – 1729.
- ³³ M. Massaouti, A.A. Basharin, M. Kafesaki, M.F. Acosta, R.I. Merino, V.M. Orera, E.N. Economou, C.M. Soukoulis and S. Tzortzakis. *Opt. Lett.* **2013**, *38*, 1140-1142
- ³⁴ E.D. Palik. "Handbook of Optical Constants of Solids", vol 3, Academic Press, **1998**.
- ³⁵ A. Roberts. *J. Opt. Soc. Am.* **A19874**, 1970-1982.
- ³⁶ A. Taflove, S. Gahness, "Computational Electrodynamics: The Finite-Difference Time-Domain Method", Artech House, Boston, **2000**.
- ³⁷ S.G. Rodrigo, "Optical Properties of Nanostructures Metallic Systems Studied with the Finite-Difference Time-Domain Method"; Springer Theses, Springer, **2011**.

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Full information about the preparation procedures:

We have chosen as templates halide eutectics that form microstructures consisting of almost perfect triangular arrangements of LiF fibers on a chloride matrix, and where the NaCl (or KCl) matrix can be easily etched with water. The result of the etching is shown in figure 1a (main article), where several microns tall LiF pillars, around 1 μ m diameter, tower over the etched surface of a KCl-LiF directionally solidified eutectic. Diameter/pitch ratio are determined by the eutectic composition [⁵³⁸, ⁵³⁹], being 0.29 for KCl-LiF and 0.55 for NaCl-LiF eutectics. Etching depths from 2 μ m to 12 μ m have been achieved on samples with LiF rod diameters from 2 to 12 μ m. Once the etched surface of the eutectic is prepared (first row in figure 2 or the main article), three different procedures were followed (sketched in rows 2nd, to 4rd in figure 2, main article, respectively) that resulted in three different configurations of metal-dielectric structures, as described in the following.

The first procedure (A, row 2 in figure 2 in main article) deposits gold by sputtering on all the exposed surface of the etched material (III), then the empty space is filled with embedding resin and cured. Afterwards they are polished until the gold layer on top of the pillars has been eliminated. A corrugated, holey gold metal layer results, with the cylindrical holes filled with LiF. A SEM micrograph of this polished surface is shown in figure 1b. The bright annular phase in the image is gold, inside there is LiF and the rest, darker grey color corresponds to the embedding resin.

The second procedure (B) consists of wetting with a lift-off resist the top surface of the pillars, followed by vertical electron-beam evaporation of a 235 nm thick gold layer. A short time immersion in acetone eliminates the resist and gold on top of the micropillars and the microstructure shown in the SEM micrographs of figure 1c is obtained. The main drawback of this procedure is the use of solvents with a rather labile substrate (NaCl or KCl), for which even dry acetone can be deleterious. Optimized e-beam evaporation and lift-off temperatures and times are required. Figure 1d proves the directional deposition of gold, where a single gold-covered pillar, tilted for the observation, is shown. Gold covers the background NaCl substrate and the top of the pillars, but not the sides. Note that with appropriate angle-cut surfaces and etched depths, different configurations of metal-pillar-substrate can be prepared. Both metal-dielectric layers prepared by procedures A and B lay on top of an around 1 mm thick NaCl-LiF or KCl-LiF substrates, which is rather transparent only from 0.4 μm to 4 μm approximately, and are not suitable to study transmission in the FIR range.

Procedure C, sketched in the last row of figure 2, overcomes this limitation. The LiF pillared sample was covered by a 3 μm thick layer of Aluminum by magnetron sputtering. This filled completely the volume between the LiF pillars, and is thick enough to protect them from breaking by shear stresses during front-side polishing. In step IV of procedure C we recover the same kind of microstructure than in procedure B, except for the thickness of the metallic layer (200 nm in A vs. 3 μm in C), and the fact that the pillars do not tower over the surface in procedure C. This polished layer is then fixed to a rigid Silicon substrate by means of molten and resolidified layer of low density polyethylene (LDPE). This acts now as substrate, and the bulk of the initial NaCl-LiF substrate is lapped down to 27 μm thick and then etched with water to eliminate the FIR absorbing NaCl. Towering LiF pillars emerge now on this side. SEM micrographs of tilted samples (onto the Si substrate) are shown in figure 1e. The LiF pillars are no longer embedded in any matrix, but remain attached to the substrate by the metal and LDPE. To end the process, the LDPE-metal-LiF pillared structure is peeled off the Si substrate. Once peeled-off, the LDPE and the thin Al layer are flexible, thus they can be bent to take convex or concave shapes, as shown in figure 1f.

MIR (medium infrared) transmittance on structures prepared by procedures A and B described in the main article.

Figure S1. Transmission spectra in the MIR range, measured on metallized samples prepared on KCl-LiF substrate (black curve, sample shown in Figure 1b of the main article) and NaCl-LiF substrate (blue dotted curve, sample as shown in Figure 1c of the main article). A transmission peak maximum observed at around 4 μm with 0.15 % transmittance (LiF rod diameter = 2.1 μm , substrate KCl-LiF, sample prepared by procedure A) and at around 9.7 μm with 0.85 % transmittance (LiF rod diameter = 7.1 μm , substrate NaCl-LiF, procedure B). These transmission maxima appear near to the cut-off wavelength for a LiF single metallic hole of the respective diameters, located at 4.9 μm and 9.9 μm respectively ($\lambda_c = 3.4rn_{\text{LiF}}$), and therefore associated to LEOT as discussed in the main article.

Experimental: These MIR transmittance measurements were taken on a Spectrum 100 spectrometer from Bruker. In this case the measured area could be as small as 1 mm^2 .

Propagation constant of waves guided in cylindrical metallic waveguides filled with LiF.

Figure S2. Real and Imaginary part of the propagation constant of the dominant guided mode in a cylindrical metallic waveguide (TE_{11} mode) filled with LiF, k_z , for guides with the diameters indicated. This has been calculated as in^[540]

$$k_z = \sqrt{\epsilon_{LiF} \left(\frac{2\pi}{\lambda} \right)^2 - \left(\frac{1.84}{r} \right)^2}$$

where r is the waveguide radius.

The AIT arises when the propagation constant inside the hole has a positive real part (that is, below cut-off) and at the same time there is moderate absorption^[541]. Therefore, for $r = 2.79 \mu\text{m}$, the AIT peak appears at around $40 \mu\text{m}$ (figure 3c in the main article).

Farther from the LiF polaritonic filler phonon-polariton absorption, with large waveguide radii, the cut-off shifts to longer wavelengths, the attenuation decreases, and the transmittance increases and broadens. Several modes are now allowed, depending on the waveguide length, as shown by the calculations in Figure 3d of the main article.

Dependence of the AIT (absorption induced transparency) transmittance peak position and height with variations of the geometrical parameters (hole diameter and Al layer thickness).

A 2 % transmittance peaking at 40 μm is observed on a 3 μm thick Al holey metal layer with thickness around 3 μm and average LiF rod diameter 5.6 μm (the sample area was 8x8 mm^2), prepared by procedure C. The template material (eutectic) has LiF rods with average radius 2.8 μm and 0.16 μm standard deviation. This broadens the transmittance band as it shifts position and intensity, from rod to rod. The same is true for variations in Al layer thickness. The calculated dependence of the transmittance peak position and intensity on the small variation of microstructural parameters is shown in Figure S3. As the hole diameter ($\emptyset$) increases, the maximum in transmittance moves to longer wavelengths, as well as increases intensity ($\text{Im}(k_z)$ minimum decreases and shifts to longer wavelengths, SI figure S2).

Figure S3. FDTD calculated transmittance spectra of the sample sketched in the upper drawing, consisting of a square lattice of period 10.5 μm of LiF filling the holes of a perforated aluminum layer (considered as a perfect electric conducting layer PEC), on a low density polyethelene (LDPE) non-absorbing substrate. The graph on the left shows, with continuous lines, the calculations for different values of the LiF rod diameters; on the right graph, the thickness of the PEC layer has been varied. $w=t$ has been considered in these calculations. With pink discontinuous lines we show the experimental curve measured on a sample with $r=2.79 \mu\text{m}$, $w=3 \mu\text{m}$, $t=27 \mu\text{m}$.

References

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- ^{S38} A. Reyes-Coronado, M. F. Acosta, R. I. Merino, V. M. Orera, G. Kenanakis, N. Katsarakis, M. Kafesaki, Ch. Mavdis, J. García de Abajo, E. N. Economou, C. M. Soukoulis, *Optics Express* **2012**, 20, 14663.
- ^{S39} P Chartrand, A.C. Pelton, *Metall. and Mat. Trans. A*, **2001**, 32A, 1417- 1430.
- ^{S40} D.K. Cheng.*Field and Wave Electromagnetics*. Second Edition 1989.Addison Wesley Publishing Company, Reading Massachusetts.
- ^{S41} S. G. Rodrigo, F.J. García Vidal, L. Martín Moreno, *Phys. Rev. B* **2013**, 88, 155126.