Ultra-porous alumina for microwave planar antennas

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Abstract We report on the experimental study of ultra-porous alumina (UPA) of transition phases γ and θ, which we fabricate by oxidation of laminated metallic aluminum followed by chemical and thermal treatments. Its morphology of a nanostructured monolith with up to 99% porosity brings together several crucial advantages with respect to existing aluminum oxides: an ultra-low density, the potential of refractive index gradients, and a chemically tunable hydrophilic character. Its extremely low permittivity measured here for the first time, \( \varepsilon_r \approx 1.2 \) at 130–165 GHz, makes UPA a promising substrate material for planar electromagnetic components in this microwave spectral range of great interest for the cosmic microwave background observation. The dielectric loss \( \tan \delta \approx 10^{-3} \), although being relatively low, can be further reduced after a chemical treatment that conveys hydrophobic character to the UPA constituting nanofibers.

Keywords Ultra-porous alumina, Oxides, Planar antennas, Microwaves.

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Introduction

For the last few decades, compact microstrip antennas have drawn a great deal of attention because of miniaturization purposes related to portable communications, going from the market of consumer electronics to applications fields associated to satellite-born antennas. In particular, their use is becoming ubiquitous for the cosmic microwave background (CMB) observation in the 40–600 GHz range, where they are used to illuminate telescope optics, or as waveguide probes in horn structures. Planar antenna-coupled detectors are considered as crucial devices for future space missions, because they are naturally polarization-sensitive, they can feed microstrip filters, they can easily be fabricated with superconducting technologies, and they can be coupled to the most sensitive cryogenic direct detectors in use today. In this context, dielectric materials must be suitable for low-loss cryogenic operation, device miniaturization and frequency-independent beam forming with lenses, polarization diplexing, etc. Moreover, millimeter-wave devices are also relevant for satellite communications, where the Ka-band (26–40 GHz) is already in use for space missions. For such applications there is a demand for innovative low-loss substrates, which should either be micro-machined to reach the required specification of impedance matching with vacuum or have a very low refractive index. Planar antennas are one of the most interesting items that can benefit from this study on ultra-porous alumina (UPA). In fact, a key issue where low refractive index plays a role is the radiation efficiency. This fundamental parameter depends on the ratio \( P_{\text{rad}}/P_{\text{leak}} \) where \( P_{\text{rad}} \) is the power launched in free space, and \( P_{\text{leak}} \) is the power leaking into surface waves. Since this ratio must be as small as possible, we have to avoid the onset of surface wave modes, whose cut-off frequency scales as \( \left(4 \times t \times \sqrt{\varepsilon_r - 1}\right)^{-1} \), \( t \) being the substrate thickness. This effect is well known and potentially harmful, but we can see how a low permittivity is decisive to push to

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higher frequencies all the unwanted modes for a given t, in a
given frequency band. Another potentially interesting device
for the THz spectral range is the Luneburg lens, a tentative ver-
sion of which has been fabricated for radio communications
from 12 to 16 GHz, by assembling spherical shells of different
dielectric constants. The realization of Luneburg lens for the
THz spectral range would require advanced low-ε materials
with a smooth radial variation of the refractive index.

In this context, the aluminum oxide of transition γ and θ
polymorphs is a material of high technological value. The alu-
mminum oxide is presently produced via the Bayer method but
also by a sol–gel process developed by Sasol. Massive porous
units of typical ~3–5 mm size are commonly prepared by pow-
der compaction, for several applications as adsorbents, cata-
lysts, etc. A direct way to form massive aluminum oxides with
an inherent nanofibrous structure, through the oxidation of
liquid-metal alloys, was discovered in Al–Hg system over one
century ago. Since that time, different fabrication methods of
fibrous alumina have been developed and investigated. The
obtained raw material is aluminum oxyhydroxide (Al₂O₃·nH₂O),
which is transformed into the transition phases after thermal
annealing at a temperature range between 750 and 1200 °C.
This transformation can be delayed via the chemical vapor
impregnation of a silica layer1 reinforcing the mechanical sta-
bility of the monoliths. Both chemical and thermal treatments
remove the adsorbed and structural water from the fibrous
structure.

Alumina, which was used for microstrip antenna sub-
strates before being replaced by low-permittivity dielectrics
like Duroid®, is also employed as an insulator in microelec-
tronics, and for high-pressure resistant optical windows in
the 0.15–5 μm spectral range. Broadband dielectric proper-
ties of commercial aluminum oxide have been reported, with
a refractive index \( n \sim 3.1 \) (for a frequency \( f < 10 \text{ THz} \)) and a
dielectric loss \( 10^{-3} < \tan \delta < 10^{-2} \) (0.4 < \( f \) < 2 THz), the latter
decreasing to \( 3.1 \times 10^{-4} \) (\( f \sim 0.02 \text{ THz} \)) in higher purity 99.6%
alumina.\(^{13}\) Alumina photonic crystals with a photonic band
gap between 0.40 and 0.47 THz have been fabricated and their
guiding properties studied,\(^{14}\) in the perspective to control THz
waves. Although the principle feasibility of nanofibrous alu-
mina photonic structures has been demonstrated,\(^{9}\) and
the importance of measuring their dielectric and guiding prop-
erties in the THz range has been highlighted,\(^{10}\) no practical
realization of such systems has been published to date.

In the present communication, we report on the sample
preparation and the measurements of refractive index and
dielectric loss in the GHz–THz frequency range in nanofibrous
UPA.

Sample preparation and structural
caracterization

The nanofibrous UPA monoliths (Fig. 1) were grown according
to our original patented method.\(^{14}\) Since low-refractive index
media are required for applications in THz optics, a compro-
mise has to be found between UPA mass density and mechan-
ical strength. The crystallization of γ, θ, and α phases in UPA
takes place, respectively, at 870, 1100, and 1200 °C. Raw UPA
has a mass density of 0.03 g/cm³, porosity of 99%, specific
area of 300 m²/g, and thermal conductivity of 0.01–0.03 W/
mK. The characteristic size of alumina fibrils and specific area
of these polymorphs are: 7 nm and 150 m²/g (γ), 10 nm and
100 m²/g (θ), and 250 nm and 10 m²/g (α), respectively. At
the same time, the raw alumina mass density augments up
to 3 g/cm³ as the thermal treatment temperature is increased
up to 1700 °C. Along with the pure UPA materials, UPA treated
with the trimethylethoxysilane (TMES: (CH₃)₃-Si-C₂H₅O) vapor
at room temperature were used in the present work. The
monolayer of grafted TMES molecules on the alumina fibers
endows them with a hydrophobic character and gets trans-
formed into a molecular silica layer after the thermal treat-
ment. Moreover, partial hydrophobicity of the formed silica
layer can be expected.\(^{15,16}\) The THz absorption of UPA samples
is related to a water content, which is expected to be high in
such open structure nanofibrous materials. In fact, the raw
UPA is aluminum oxyhydroxide that contains structural and
adsorbed water. According to Khodan et al.,\(^{10}\) the adsorbed
water amounts to 0.5–0.7 molecules per Al₂O₃ regardless of

Figure 1  Cut part of UPA monolith
The mass density of disk samples varied between 0.2 and 1.2 g/cm³ for each monolith. As shown in Table 1, method A results in quasi-perfect defect-free disks that conserve high porosity and low density compared to silica-treated UPA samples. Method B, where the intermediate thermal treatment was introduced at temperature 870 °C, produced disks that were easily compacted by method A. In contrast, silica-treated UPA samples, as shown in Fig. 3, can be rolled into high quality disks of 800–850 mm in length and ≤ 1000 bar pressure.

For electromagnetic measurements, the produced UPA samples were compacted using 32-mm diameter and different thicknesses as indicated in Table 1. The appearance of the crystalline phases was checked by XRD diffraction method in UPA samples.

The transition aluminas were obtained by adequately tuning the temperature: 870 °C ($\gamma$) and 1050 °C ($\theta$) in pure UPA and 1100 °C ($\gamma$) in UPA with silica-covered fibers, as indicated in Table 1. The appearance of the crystalline phases was checked by XRD diffraction method.

For electromagnetic measurements, the produced UPA samples were compacted in disks of 32-mm diameter and different thicknesses as indicated in Table 1. Since the applied pressure tends to increase the material mass density and consequently its refractive index, moderate static pressures ($P \leq 1000$ bar) were used. Two compaction methods (A and B) were applied as indicated in Fig. 2. The simplest one-stage method A, used for samples 2, 4, 8, and 10, consisted in UPA growth followed by a thermal treatment (4 h) and compaction of disks at a static pressure. The mass density of these samples is close to 1 g/cm³. A slight modification of method A, consisting in the introduction of chemical impregnation with TMES vapor at room temperature overnight before thermal treatment and compaction, was used for samples 1, 3, 7, and 9. Finally, samples 5 and 6 were prepared according to a two-stage method B, where the intermediate thermal treatment was introduced at temperature 600 °C below the crystallization threshold of $\gamma$ phase (870 °C). Samples prepared according to methods A and B are shown in Fig. 3. UPA samples non-treated with silica can be easily compacted by method A. In contrast, silica-treated UPA disks produced by this method contain shape failures. Method B results in quasi-perfect defect-free disks that conserve high porosity of UPA monoliths.

To estimate the complex permittivity of such ad hoc UPA samples, we have resorted to the experimental measurement of their scattering-matrix parameters (Fig. 4). Our setup is based on a Vector Network Analyser MVNA-8-350, endowed with a set of multipliers that allow to cover W-band (75–110 GHz), D-band (110–170 GHz), and the 170–240 GHz band. For the present work, only the D-band millimetric extension has been used, for which quasi-optical components were readily available in our lab. From an optical point of view, our setup is composed by two identical horn antennas, and by two identical off-axis ellipsoidal mirrors (bulk aluminum, machined in-house). The two horns launch a Gaussian beam (98% of the power in the fundamental mode) with FWHM = 10° and waist radius $w_0 \approx 5.0$ mm, located 7.9 mm behind the aperture. Each ellipsoidal mirror bends the beam by 90°, and images the horn waist radius at the common focal point with magnification $M = 1$ (see Fig. 4). As a result, the waist of the first horn (Port 1) is imaged on the waist of the second horn (Port 2) with overall unitary magnification. In the region between the two mirrors we have a focal point where the beam has a radius comparable with $w_0$, so that a sample with a clear aperture of 20 mm collects ~100% of the power launched in the fundamental mode, and it is collimated. Here, we put the sample holder. Material properties are inferred from the measurement of the scattering matrix of our dielectric slab. In particular, the signal launched from Port 1 is received in Port 1 ($S_1$, scattering matrix element) and Port 2 ($S_2$, scattering matrix element). The parameter $S_2$, gives the complex reflected signal, while $S_1$ provides the transmitted one. Both parameters are available in amplitude and phase vs. frequency. After calibrating the zero optical path length (equal to the path before the insertion of

### Table 1 Preparation conditions of UPA samples for THz measurements

| Sample | 1st thermal treatment, °C | TMES treatment | Pressure bar | 2nd thermal treatment, °C | Crystalline phase | Density, g/cm³ | Thickness, mm |
|--------|--------------------------|----------------|--------------|---------------------------|------------------|--------------|--------------|
| 1      | 600                      | Yes            | 340          | No                        | Amorphous        | 0.888        | 4.0          |
| 2      | 600                      | No             | 1000         | No                        | Amorphous        | 0.978        | 2.9          |
| 3      | 800                      | Yes            | 340          | No                        | Amorphous        | 0.728        | 4.2          |
| 4      | 870                      | No             | 340          | No                        | $\gamma$         | 0.846        | 3.6          |
| 5      | 600                      | Yes            | 340          | No                        | $\gamma$         | 0.726        | 4.4          |
| 6      | 800                      | Yes            | 340          | No                        | $\gamma$         | 0.648        | 4.4          |
| 7      | 1100                     | Yes            | 340          | No                        | $\gamma$         | 0.666        | 3.3          |
| 8a     | 870                      | No             | 1000         | No                        | $\gamma$         | 1.150        | 2.7          |
| 8b*    | *                        | *              | *            | *                         | $\gamma$         | 1.150        | 2.4          |
| 9a     | 1150                     | Yes            | 340          | No                        | $\gamma$         | 0.234        | 8.9          |
| 9b*    | *                        | *              | *            | *                         | $\gamma$         | 0.234        | 7.4          |
| 10a    | 1150                     | No             | 600          | No                        | $\theta$         | 0.824        | 3.5          |
| 10b*   | *                        | *              | *            | *                         | $\theta$         | 0.824        | 5.4          |

*Samples 8b, 9b, and 10b (similar respectively to 8a, 9a and 10a) received an additional hydrophobic chemical treatment after the preparation.
The measured refractive indices \( n \) and tangent losses \( \tan \delta \) of UPA samples in the frequency range 135–165 GHz are presented in Fig. 5 and Table 2. A quite broad scope of values \( 1 < n < 2 \) and \( 10^{-3} < \tan \delta < 10^{-2} \) have been obtained, depending on the preparation method. Hereafter, we discuss the observed correlations between these data.

1. The refractive index is found to correlate with the mass density of the samples, as suggested by Fig. 6. Some deviations are related to small variations of the sample composition due to the chemical treatments. The linear fit of these data results in \( n = 1 + 0.7 \rho \), whose extrapolation to the high-density solid Al\(_2\)O\(_3\) is in a good agreement with the direct measurements \( n \approx 3.1 \) performed by Rajab et al.\(^{11}\)

2. The dielectric loss of silica-treated samples is generally found smaller compared to non-treated samples. Moreover, the samples prepared with the two-stage method show smaller losses (~3 \( \times \) 10\(^{-3}\)) as compared
measurement of the higher frequency electromagnetic response in a THz FTIR shows a transparency window below 2.5 THz, which opens after the hydrophobic treatment. In particular, the transmittance of sample 9 at 1 THz increases from 0.025 to 0.25 after the treatment. By inserting in the formula

\[ T = \exp \left( -\alpha d \rho M_{H_2O}/\rho M_{Al_2O_3} \right) \]

the absorption coefficient of liquid water \((\alpha \approx 200 \text{ cm}^{-1} \text{ at 1 THz})\), the measurement of the higher frequency electromagnetic response in a THz FTIR shows a transparency window below 2.5 THz, which opens after the hydrophobic treatment. In particular, the transmittance of sample 9 at 1 THz increases from 0.025 to 0.25 after the treatment. By inserting in the formula

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with the one-stage one \((4 \times 10^{-3} \text{–} 6 \times 10^{-3})\), as shown in Fig. 7. The last values are comparable with those measured in solid \(\text{Al}_2\text{O}_3\).

(3) The additional hydrophobic treatment improves the sample transparency. Figure 8 shows that the dielectric loss decreases in the treated samples by an order of magnitude and reaches in the less dense sample \(~10^{-3}\) in the frequency range \(~150 \text{ GHz}\). The complementary

\[ n \quad \tan \delta \times 10^{-3} \]

\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline
Sample & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8a & 8b* & 9a & 9b* & 10a & 10b* \\
\hline
n & 1.469 & 1.541 & 1.476 & 1.563 & 1.445 & 1.406 & 1.485 & 1.687 & 1.927 & 1.121 & 1.081 & 1.513 & 1.421 \\
tan \(\delta\) \((\times 10^{-3})\) & 4.70 & 4.35 & 4.20 & 5.60 & 3.10 & 2.80 & 4.00 & 8.17 & 3.30 & 9.90 & 1.20 & 17.7 & 2.00 \\
\hline
\end{tabular}
0.74 cm), we estimate $T = 0.025$, which is in good agreement with our THz transmission measurements in untreated UPA sample (Fig. 9(b)). After the hydrophobic treatment, the transmission of sample (Fig. 9(a)) considerably improves, corresponding to the removal of about 60 mol.% water and $\psi = 0.26$. Since $\gamma$-UPA contains a very small amount of structural water (~1 mol.%), the main part of the residual water in our sample belongs to the adsorbed water. Its complete removal will decrease the absorbance by a factor of ~26, which would make nanofibrous UPA highly transparent material in the full THz spectral range and suitable for fabrication of refractive THz optics.

Our main result here is that we have singled out the fabrication parameters allowing for an ultra-low value of the refractive index $\sqrt{\varepsilon} \approx 1.1$ and a fairly encouraging value for the losses ($\tan \delta \approx 10^{-3}$). Such figures compare favorably with those of common alumina ($\sqrt{\varepsilon} \approx 3.2$ and $\tan \delta = 10^{-5}$) and Duroid® ($\sqrt{\varepsilon} \approx 1.4$ and $\tan \delta = 5 \times 10^{-5}$). If we compare our results to those presented in other works dedicated to microwave properties of UPA (e.g.19, 20), we can see that the refractive index we find in one of our samples (9b) is one of the closest to $n = 1$ ever reported in literature, nicely scaling to higher values with increasing density. More often, values of $n \geq 2$ are presented. On the other side, if we look at dielectric losses, our $\tan \delta$ is up to two orders of magnitude higher with respect to that found by Penn et al. This effect is likely ascribable to the combined action of humidity and porosity, as described in21, who find loss tangent values close to ours, of the order of some $10^{-3}$, in the range 12–18 GHz and in a moist environment. An improved hydrophobic treatment should allow us to solve this problem.

**Conclusion**

We have fabricated planar samples of UPA and characterized their morphological and electromagnetic properties while varying the fabrication parameters. The main results of our study, i.e. the extremely low value of the real part of the permittivity and the reasonably low value of its imaginary part, make this material a promising candidate for planar antenna substrates.
in the 150 GHz range of interest for the CMB. The UPA perfection is under way via the search of an optimal chemical treatment that should turn this material in a hydrophobic one.

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