Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information

Plasmonics of Au nanoparticles in a hot thermodynamic bath

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$S1$ SE spectra at temperatures between 25 °C and 350 °C: experimental and calculated (with uncorrected ε_{Au})

We report here the experimental and calculated SE spectra of the Au NPs arrays on LiF, at different temperatures between 25 °C and 350 °C (Figure S1). The calculated SE spectra shown here were obtained using the uncorrected dielectric function ε_{Au}, obtained from independent measurements on Au film. For increasing temperatures, we notice that the model reproduces the main variations observed in the experimental SE spectra: in ψ, the decrease in dip intensity around 550 nm; in Δ, the sharp transition at 75 °C and the progressive smoothing of the wiggle. However, the model with uncorrected ε_{Au} greatly underestimates the magnitude of variations observed both in ψ and Δ.

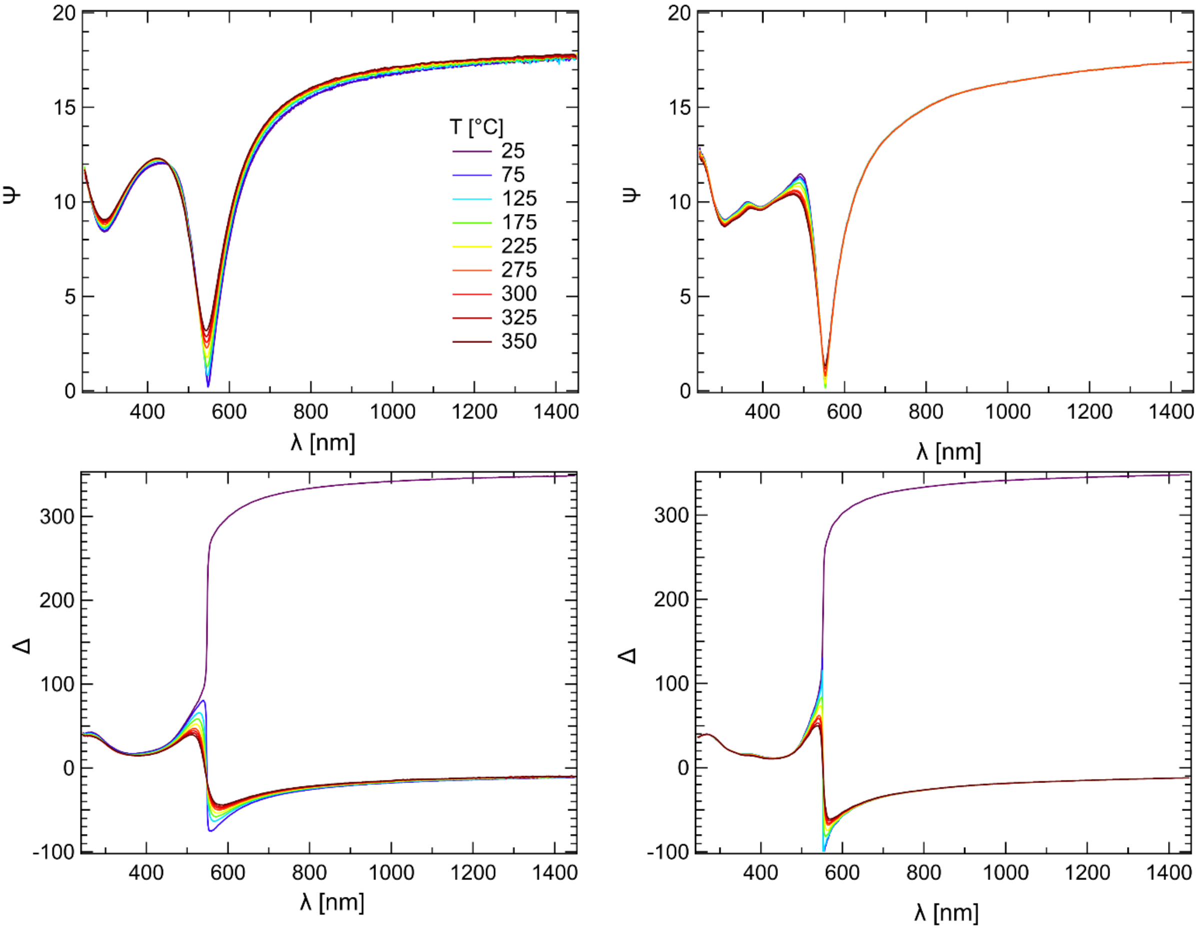

Figure S1: Experimental (*left, top and bottom*) and calculated (*right, top and bottom*) SE spectra of the Au NPs arrays on LiF.

S2 SE spectra at T between 25 °C and 350 °C: experimental and calculated (with effective dielectric correction to ε_{Au})

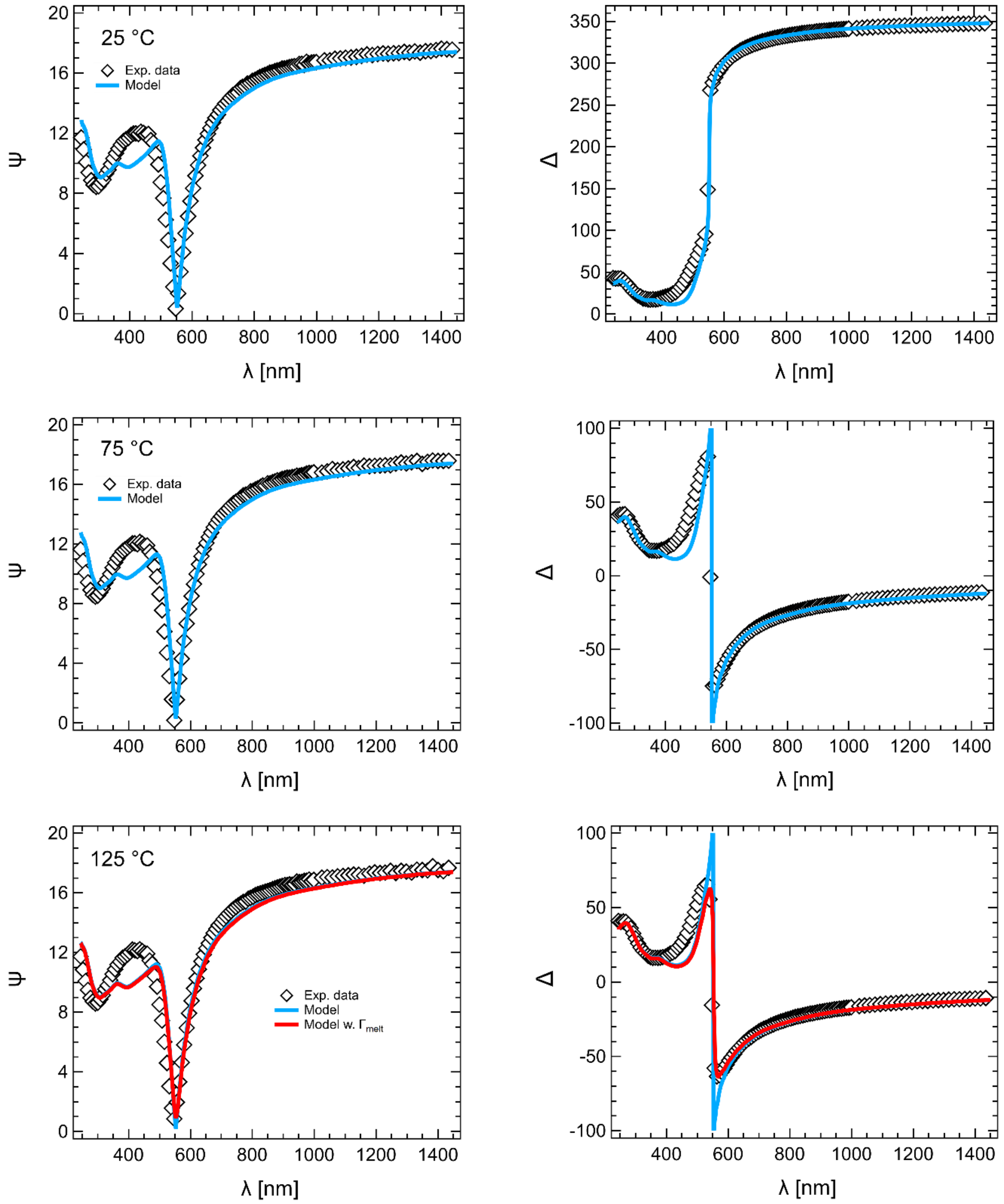

Figure S2-1: Ψ (*left*) and Δ (*right*); blue markers: experimental data; light blue line: calculated, without the effective dielectric correction; red line: calculated, with the effective dielectric correction Γ_{melt}. Temperature ranges from 25 °C to 125 °C (*top to bottom*).

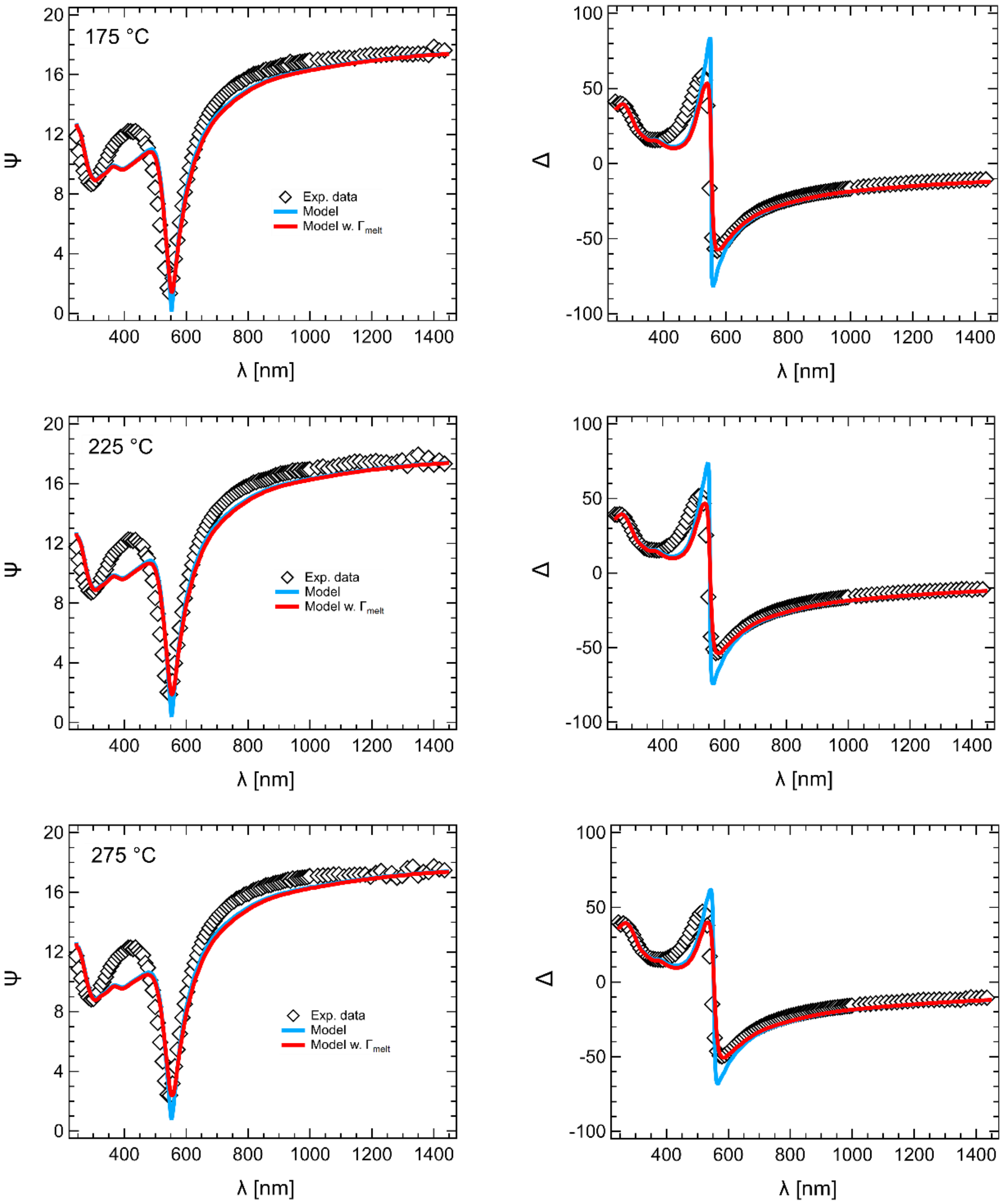

Figure S2-2: Ψ (*left*) and Δ (*right*); blue markers: experimental data; light blue line: calculated, without the effective dielectric correction; red line: calculated, with the effective dielectric correction Γ_{melt}. Temperature ranges from 175 °C to 275 °C (*top to bottom*).

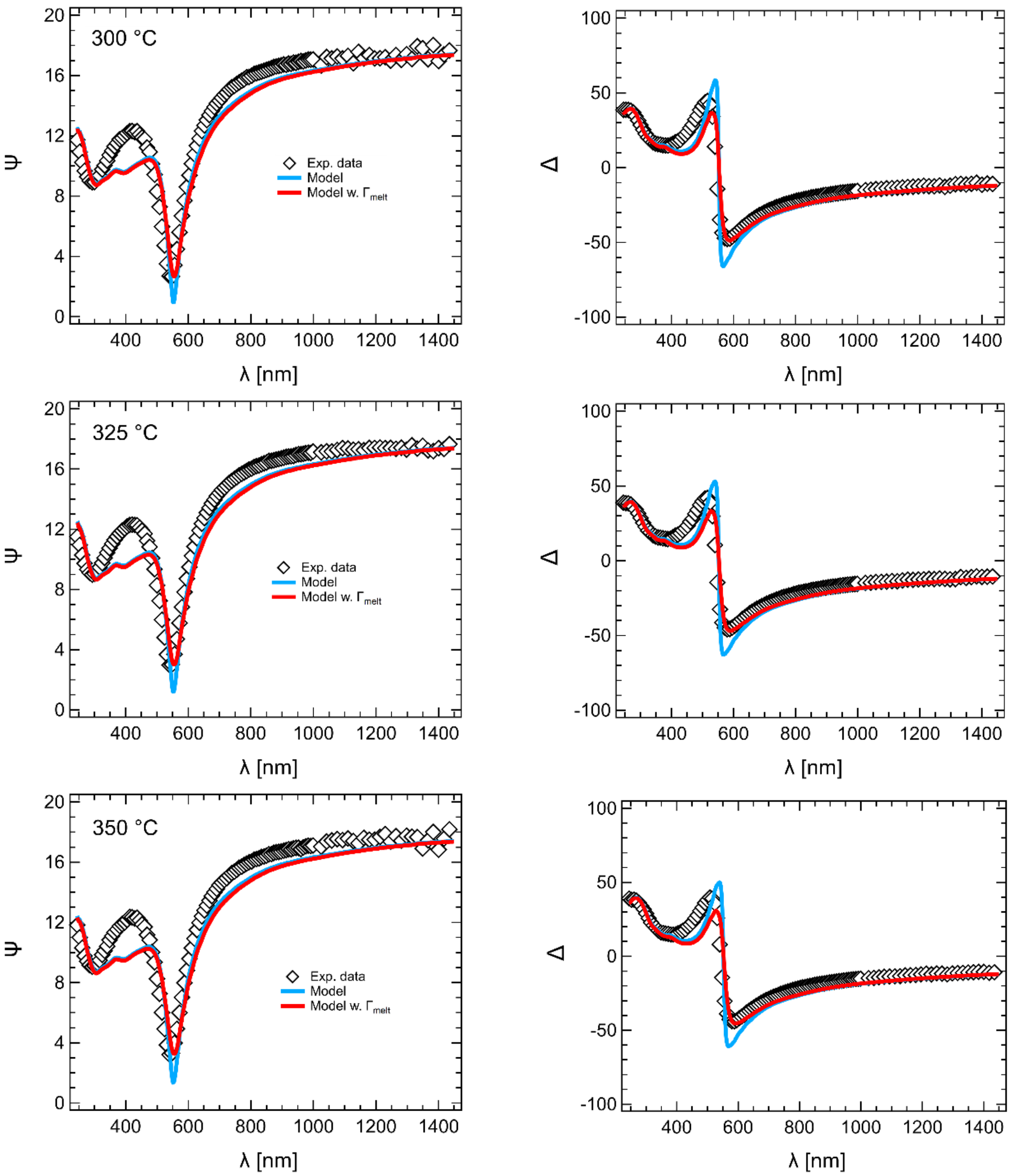

Figure S2-3: Ψ (*left*) and Δ (*right*); blue markers: experimental data; light blue line: calculated, without the effective dielectric correction; red line: calculated, with the effective dielectric correction Γ_{melt}. Temperature ranges from 300 °C to 350 °C (*top to bottom*).

S3 Effective dielectric function of the Au NPs layer

The model considers Au NPs embedded within a host material with is composed of air and LiF. The resulting effective layer has effective optical properties, that are simulated by the model through the effective dielectric tensor ε_{eff}^{ii}, where $i = x, y, z$. Here we present the effective dielectic tensor in *s*, *p* coordinates (i.e., perpendicular and parallel to the plane of incidence). The relations between the two coordinates systems are:

$$n_{eff}^{s} = \sqrt{\varepsilon_{eff}^{yy}}$$

$$n_{eff}^{p}(\theta) = \sqrt{\frac{\varepsilon_{eff}^{xx}\varepsilon_{eff}^{zz} + \left(\varepsilon_{eff}^{zz} - \varepsilon_{eff}^{xx}\right)\sin^{2}\theta}{\varepsilon_{eff}^{zz}}}$$

where both n and ε are complex.

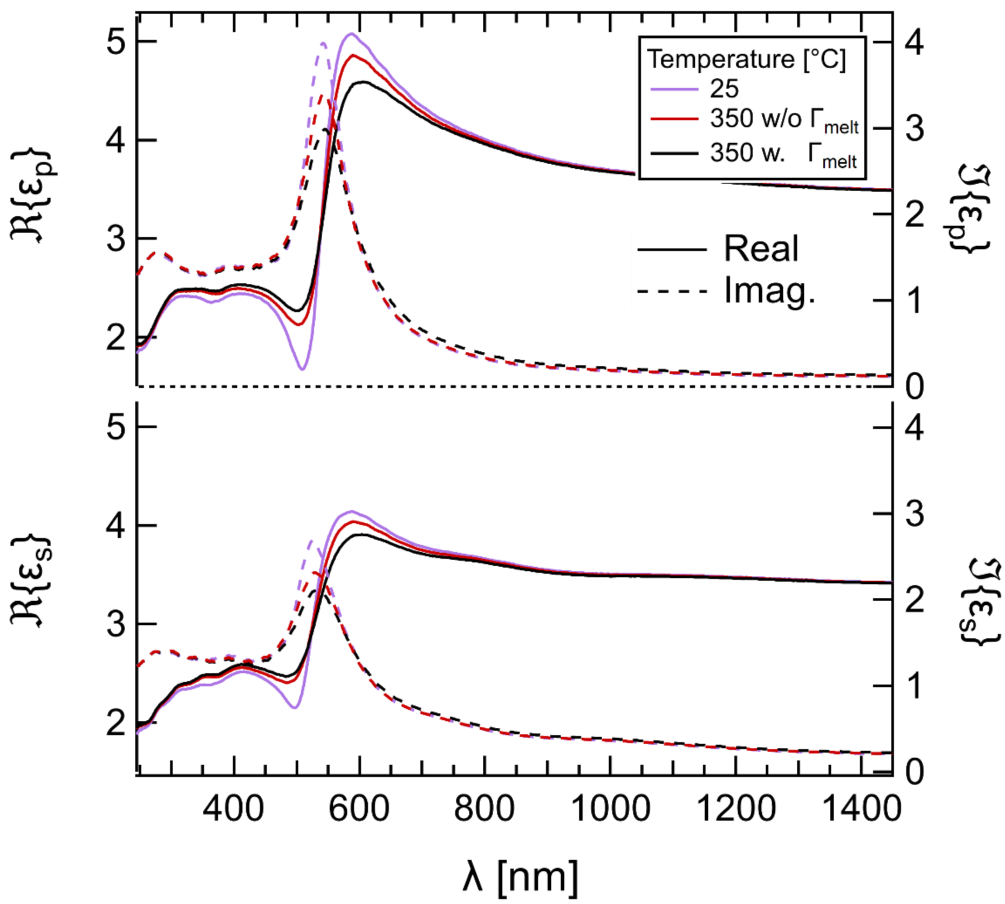

Figure S3. Calculated effective dielectric tensor for the layer of Au NPs. *Top*: *p*-components; *bottom*: *s*-components. The real parts are reported with continuous lines, while the imaginary parts are indicated with dashed lines. We report the effective dielectric tensor for the lowest and highest temperatures (25 and 350 °C), and the effective dielectric correction required at 350 °C.